DETERMINATION OF LANTHANIDES BY CONDUCTOMETRY USING SOME SEQUESTERING AGENTS

A
Thesis submitted in
fulfillment of the requirement of the degree of

Doctor of Philosophy

Submitted by

Komal Matharu
(Regd. No. 900909006)

School of Chemistry & Biochemistry
Thapar University
Patiala-147004
September, 2013

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Dedicated To My Parents

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No one walks alone on the journey of life. Just where you start to thank those that joined you, walked beside you, and helped you along the way. This is a "thanks" to all those who have helped make my life what it is today.

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To God the father of all, I am thankful for the strength that keeps me standing and for the hope that keeps me believing.

Declaration

I, hereby declare that the work presented in the thesis entitled "**DETERMINATION OF LANTHANIDES BY CONDUCTOMETRY USING SOME SEQUESTERING AGENTS**" in fulfillment of the requirement for the award of the Degree of Doctor of Philosophy, School of Chemistry and Biochemistry , Thapar University, Patiala, is an authentic record of my own work carried out under the joint supervision of Dr. Susheel Mittal, Senior Professor, School of Chemistry & Biochemistry, Thapar University, Patiala, India and Dr. Ashok Kumar SK, Assistant Professor (Senior), School of Advanced Sciences, VIT University, Vellore (TN), India. The matter embodied in this thesis has not been submitted in part or full to any other university or institute for the award of any degree in India or Abroad.

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This is to certify that the above statement made by the candidate is correct and true to the best of our knowledge.

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Certificate

Certified that the thesis entitled **"DETERMINATION OF LANTHANIDES BY CONDUCTOMETRY USING SOME SEQUESTERING AGENTS"** which is submitted by Ms. Komal Matharu (Roll No. 900909006) in fulfillment of the requirement for the award of Degree of Doctor of Philosophy in the School of Chemistry and Biochemsitry, Thapar University, Patiala, is a record of candidate's own independent and original research work carried out by her under our supervision and guidance. The material embodied in this thesis has not been submitted in part or full to any other University or Institute for the award of any degree.

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METHODOLOGY

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List of Abbreviations

Abbreviation	Description
Ln	Lanthanide/ Lanthanoide
REE	Rare-Earth Elements
CN	Coordination Number
PACA	Polyaminocarboyxlic acids
Na_4EDTA/EDTA/L1	Ethylenediaminetertracetic acid tetrasodium salt
Na_3EDTA/$L1_i$	Ethylenediaminetertracetic acid trisodium salt
Na_2EDTA/$L1_{ii}$	Ethylenediaminetertracetic acid disodium salt
DCTA/L2	*trans*-1,2-Diaminocyclohexane-N,N,N′,N′-tetraacetic acid
EGTA/L3	Ethylene glycol-bis(2-aminoethylether)-N,N,N′,N′-tetraacetic acid
EDTA-OH/L4	N-(2-hydroxyethyl) ethylenediamine-N,N´,N´-triacetic acid
TMDTA/L5	1,3-Diaminopropane-N,N,N′,N′-tetraacetic acid
HIBA	α-hydroxyisobutyric acid
CMC	Critical Micelle Concentration
AAS	Atomic Absorption Spectrometry
ICP	Inductively Coupled Plasma Spectroscopy
UV	Ultraviolet
XRF	X-ray Fluorescence
HPLC	High Performance Liquid Chromatography
IC	Ion Chromatography
CE	Capillary Electrophoresis
NAA	Neutron Activation Analysis
ppb	Parts per billion
E.P.	Equivalence Point
CA	Contrast Agent
MRI	Magnetic Resonance Imaging
cond.	Conductivity
AHA	Hydroxycarboxylic acid

DA	1,4-dioxane
ACN	Acetonitrile
DMSO	Dimethylsulphoxide
DMF	N,N´-dimethylformamide
THF	Tetrahydrofuran
MA	Methanol
v/v	volume/volume
NMR	Nuclear Magnetic Resonance

List of Symbols

Symbol	Description
log K	log of Stability Constant
μ	micro
K	Kelvin
°	Degree
C	Celsius
m	milli
M	Molar
L	liter
g	gram
V	Volts
S	Siemens
ΔG	Change in Gibbs free energy
ΔH	Change in enthanlpy
ΔS	Change in entropy
f	femto
n	nano
dm	decimeter
p	pico
cm	centimeter
Z	Interfering Ion
Y	EDTA/DCTA (anionic form)
AsIII	Arsenazo III

Abstract

The present work envisages establishing conductometry as an analytical technique for the determination of lanthanides by employing the use of different polyaminocarboxylic acids (PACA) as sequestering agents. The technique offers the advantage of eliminating the need of separation or pre-concentration of the sample under study. Five different polyaminocarboxylic acids viz., Ethylenediaminetetracetic acid (EDTA); trans-1,2-Diaminocyclohexane-N,N,N',N'-tetraacetic Acid (DCTA); Ethylene glycol-bis(2-aminoethylether)-N,N,N',N'-tetraacetic acid (EGTA); N-(2-hydroxyethyl) ethylenediamine-N,N′,N′-triacetic acid (EDTA-OH) and 1,3-Diaminopropane-N,N,N',N'-tetraacetic acid (TMDTA) have been used as sequestering agents for this work. Effect of different parameters has been studied to establish appropriate conditions for the conductometric study of lanthanide–PACA complexes which enabled precise lanthanide determinations. For this purpose, firstly, the appropriate cell constant was established by carrying out a number of conductometric titrations at four different cell constant values using two-pole and five ring conductivity cells. The latter was found suitable for the study due to its linearity over a wide concentration range and a quick and stable response. Secondly, the detection limit of the five ring conductivity cell has been determined as 10^{-5} M by direct as well as conductometric titration methods. Thirdly, the effect of pH on the reaction system has been studied over four different pH ranges. Lastly, the effect of temperature on the reaction system was also studied by carrying out conductometric titrations at four different temperatures. Following the standardization of these parameters all the polyaminocarboxylic acids have been tested for use as potential ligands for the determination of lanthanides in solution containing single lanthanide ion or a mixture of two lanthanide ions.

The use of polyaminocarboxylic acid (PACA), α-hydroxyisobutyric acid (HIBA) as a co-ligand has been established for simultaneous determinations of lanthanides in their binary mixtures. After circumstantiating their potential, the selectivity of ligand and co-ligand in the presence of different interfering ions was adjudged to establish the competence of conductometry as an analytical tool for lanthanide determination. The interfering ions chosen for the study included metal ions like barium, cobalt, nickel, thorium, etc. that are

present along with lanthanides in various matrices and metal ions like calcium that bear chemical properties similar to those of lanthanides. The established method did not suffer interference from any of the species under study. The results of all the titrations have been used to furnish the efficacy of ligands for lanthanide determination by conductometry. The variation in exactitude of different ligands used has been explained on the basis of stabilities of resulting complexes. The adequacy of the performance parameters of the proposed technique has been validated by conducting lanthanide determination in different real time samples. Tap water, river water, clinical waste water, Welsbach gas mantle and MRI contrast - Gadopentetate dimeglumine samples have been tested for the presence of lanthanides. The results obtained were found to be coherent with those obtained by spectrophotometry.

Spectroscopic studies have been conducted to inspect the effect of different polyaminocarboxylic acids on Arsenazo III–lanthanide (III) complexes. Different spectrophotometric titrations have been performed in order to predicate the behavior of polyaminocarboxylic acids as competing and substituting ligands with respect to Arsenazo III for lanthanide bonding. The complexation behavior observed for different polyaminocarboxylic acids with lanthanides by spectrophotometric technique has been found to be congruent to that observed by conductometric technique.

***Keywords**: Conductometric titration, lanthanide, polyaminocarboxylic acid, Ethylenediaminetertracetic acid, trans-1,2-Diaminocyclohexane-N,N,N',N'-tetraacetic Acid, Ethylene glycol-bis(2-aminoethylether)-N,N,N',N'-tetraacetic acid, N-(2-hydroxyethyl) ethylenediamine-N,N´,N´-triacetic acid, 1,3-Diaminopropane-N,N,N',N'-tetraacetic acid, co-ligand, α-hydroxyisobutyricacid, interfering ions, spectrophotometric titrations, Arsenazo III.*

Introduction

In the 20th century, scientists began to exploit phenomena other than those used for classical methods for solving analytical problems i.e., measurements of physical properties such as conductivity, electrode potential, light absorption or emission, mass-to-charge ratio, etc., used for quantitative analysis. Present day analytical chemistry has become very refined due to diverse number of analytical techniques available for analyzing a wide variety of analytes and the analytical chemist needs to have a good knowledge of these scientific techniques. A typical example includes trace level determination of lanthanides by Inductively Coupled Plasma Spectroscopy.[1] Lanthanide [Ln(III)] ions are of great interest because of their specific characteristics in several areas, such as material science,[2] heterogeneous and homogenous catalysis,[3] diagnosis and therapy in medicine,[4] and in nuclear fuel cycle[5]. As a result of their usage, more and more Ln(III) ions are getting into the environment, accumulating in organisms and entering into the food chain. Thus, determination of Ln(III) in various matrices becomes increasingly significant. The major problem is that no specific reagents for individual Ln(III) ions are known. However, under certain conditions the selectivity of group reagents can be improved by binding the interfering ions as stable complexes. Also, because of poor selectivity of various reagents employed in analytical chemistry of Ln(III) ions, separation methods based on differences in the properties of their compounds acquire special importance. Hence, the quick determination of lanthanides by simple methods is of great importance in analytical chemistry and in today's world, determination of Ln(III) ions without any preliminary separation has become a priority on the scientific agenda of world's industrialized nations.

1.1 Lanthanides – A Perspective

Lanthanide compounds have been extensively used in the last decades as luminescent chemosensors[6], for medical diagnostics and optical cell imaging[6-8], contrast reagents for magnetic resonance imaging[9], shift reagents for Nuclear Magnetic Resonance spectroscopy[10], as well as for applications in fundamental and applied science such as organic synthesis, bioorganic chemistry and catalysis[11]. They are used principally as iron and steel alloying agents, glass polishing compounds and glass additives, phosphors for

television and lighting, in petroleum cracking and permanent magnets. They are essential for a diverse and expanding array of hi-tech applications. These applications were favored by an increased knowledge of fundamental properties (electronic, spectroscopic, thermodynamic, magnetic, and structural) of the elements, achieved as a consequence of rapid development of academic studies on lanthanide coordination chemistry during the last three decades. Most of these studies are mainly concerned with compounds where the metal ions have common +3 oxidation state [Ln(III)] and behave as hard acids with a strong affinity for hard bases like O-donors (neutral or negatively charged) or N-donors with which they essentially form non-directional bonds of predominant ionic nature.[12]

As the series La–Lu is traversed, there is a decrease in both the atomic and ionic radii of Ln(III) ions, more markedly at the start of series. The 4f electrons are 'inside' the 5s and 5p electrons and are core-like in their behavior, being shielded from the ligands, thus taking no part in bonding. Because of their large ionic radii and relatively low oxidation states rare-earth elements (REE) generally form complexes which have high coordination numbers and weak metal–ligand bonds. Rare-earth elements, which in addition to the lanthanoides (Ln) cerium to lutetium (f-electron number 1–14), include scandium, yttrium, and lanthanum; in general realize large coordination numbers (CNs) in their complex chemistry because of their large ionic radii. Rare-earth metals have CNs > 6. They use bulky ligand groups with low charge that in addition to saturating the three charges of Ln(III) ion also provide a substantial steric shielding effect and the complexes, thus, formed have a highly stable configuration. The ionic radii of Ln(III) cations decrease with the increase of their atomic number (lanthanide contraction).[13] Their coordination number (CN) and strength of solvation vary in solution within different reaction media, thus strongly influencing the thermodynamic stability of complexes. This is the reason why several studies have been carried out aimed at interpreting the changes of thermodynamic properties of Ln^{3+} complexes in terms of changes of the CN along the series.[14-16] In addition; Ln(III) exhibit chemical properties very similar to those of actinides (III) [An(III)]. This chemical similitude is a challenging problem in the separation of An(III) from excess of Ln(III) in nuclear waste treatments[17] but it is also useful because the safer Ln(III) ions can be used as surrogates for much more hazardous An(III) ions in preparatory studies.

Lanthanides have similar physicochemical properties which change periodically with atomic number. Lns are usually divided into three groups: light Lns, from La to Pm, medium Lns, from Sm to Ho, and heavy Lns, from Er to Lu. Although lanthanides are termed rare-earth elements, they are not rare in nature. Their levels in earth's crust are often equal to or higher than some physiologically significant elements, such as iodine, cobalt, silver, gold, platinum and selenium. Lns are never found as free metals in the earth's crust. All their naturally occurring minerals consist of mixtures of various Lns : Bastnaesite [$(Ce,La)(CO_3)F$], monazite [$(Ce,La,Nd,Th)(PO_4)$] [$(REE)PO_4$] and xenotime [YPO_4] are the three most significant minerals of lanthanides.

A wide range of coordination numbers (6–12, but compounds with 2, 3 or 4 are more commonly known), coordination geometries determined by ligand steric factors rather than crystal field effects, formation of labile 'ionic' complexes that undergo facile exchange of ligand, 4f orbitals that do not participate directly in bonding (being well shielded by the $5s^2$ and $5p^6$ orbitals), preference of anionic ligands with donor atoms of high electronegativity (e.g. O, F) for bond formation, formation of hydrated complexes readily (on account of the high hydration energy of the small Ln(III) ion) which causes uncertainty in assigning coordination numbers and domination of one (3+) oxidation state in aqueous solution are some key features exhibited by lanthanide coordination chemistry.

1.2 Analytical Techniques for Monitoring Lanthanides

The determination of Ln(III) ions in various matrices becomes increasingly significant and several techniques have been used (Table 1.1).[8-32] Still, no specific reagents for the determination of individual lanthanide Ln(III) ions are available. However, under certain conditions, the selectivity of group reagents can be improved by binding interfering ions as stable complexes.[33] Because of poor selectivity of various reagents employed in the analytical chemistry of Ln(III) ions, separation methods based on differences in properties of their compounds acquire special importance.[29] Hence, quick determination of lanthanides by simple methods would always be of great importance in analytical chemistry, particularly when no preliminary separation is desirable.

Table 1.1: Different analytical methods for determination of Ln(III) ions and their comparative study with respect to sensitivity, selectivity, speed and cost

Method	Measuring Range (mol/L)	Selectivity	Speed	Cost	Limitations
Gravimetry[18]	$10^{-1} – 10^{-2}$	Poor - moderate	Slow	Low	Insufficient reagents available
Titrimetry[19]	$10^{-1} – 10^{-4}$	Poor - moderate	Moderate	Low	Insufficient reagents available
Potentiometry[20,21]	$10^{-1} – 10^{-6}$	Good	Fast	Low	Ion-selective reagent needed and life time of electrode is short
Voltammetry[22,23]	$10^{-3} – 10^{-6}$	Good	Moderate	Moderate	Only Ce, Sm & Eu ions can be determined
Spectrophotmetry[24-26]	$10^{-3} – 10^{-6}$	Good - moderate	Fast moderate	Low - moderate	Very few reagents available
Atomic spectroscopy[27]	$10^{-3} – 10^{-9}$	Good	Fast	High	Pre-concentration and separation required
Capillary Electrophoresis[28,29]	$10^{-3} – 10^{-9}$	Good	Fast moderate	High	Very high voltage requirement
Neutron Activation Analysis[30]	$10^{-3} – 10^{-10}$	Good	Very slow	High	Nuclear reactor required
Ion Chromatography[31,32]	$10^{-3} – 10^{-6}$	Good	Moderate	High	Reproducibility of separation

Although, conductivity measurements give a non-specific response but when they are combined with a separation technique, these methods provide extremely sensitive and versatile detectors for chemical composition. The best example of this is Ion Chromatography, which in recent years has shown to be an invaluable instrumentation technique for the identification and measurement of concentration of almost all types of ions, particularly at low levels in aqueous solution.[34]

1.3 Electrical Conductivity of Solution

Conductivity of a solution i.e. measure of its ability to conduct electric current depends on the concentration of ions in solution, temperature of solution and specific nature of the ions

in solution. Technique used to measure the progress of reaction based on its electrolytic conductivity is known as conductometry. In analytical chemistry conductometry is used as a synonym of conductometric titration. Conductometry has notable applications in analytical chemistry, where conductometric titration is a standard technique. Conductivity measurement is a classical electroanalytical technique that finds numerous applications in a wide variety of chemical and biochemical studies like assessing solvent purity, determining relative ionic strengths of solutions (including functioning as a detector for ion chromatography), monitoring dissolution kinetics and approach to equilibrium for partially soluble salts, determining critical micelle concentrations, following the course of some enzymatic reactions, as well as providing basic thermodynamic data for electrolyte solutions. The term conductimetry is used to define non titrative procedures. Determination of reaction rates by conductometry has been known for a long time.[35]

1.3.1 Five-ring conductivity sensor

In a five-ring conductivity sensor the electrodes are separated into current-conducting and voltage-measuring electrodes. This has an advantage that the voltage-measuring electrodes are not polarized and thus measure an undistorted potential. The fifth ring forms a second base electrode, which reduces the outward propagation of electric fields. It allows precise measurements irrespective of the submersion depth and measuring position of the electrode. In addition, another measurement with a potentiometric electrode can take place in the same vessel.

1.3.2 Conductometric titration

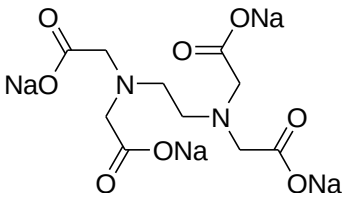
The conductance method can be employed to follow the course of a titration, provided that there is a significant difference in specific conductance between the original solution and the reagent or the product of reaction. Thus, conductometric titration is applicable to any titration in which there is a sharp change in the conductivity at the end point. This was introduced at the end of 19th century.[36] At that time it was difficult to espy the future application of this technique which is now comprehensively defined and has quantitative applications in chemical as well as industrial processes.[37] It is based on principle that one of the ions is replaced by other during the titration and these two ions consistently differ in their ionic conductivities. This results in variation of conductivity during the course of

titration which gives the equivalence point by graphically plotting the change in conductance as a function of volume of titrant added. The main advantages of conductometric titrations lie in the fact that they are applicable to very dilute and colored solutions and to system that involve relative incomplete reactions. Conductometric titrations offer a simple, easy and quick method for various types of determinations. One of the earliest quantitative interpretations of conductometric titration dates back to early 1960s when Kolthoff *et al*.,[38] derived an equation for the calculation of conductometric titration curves of intermediately strong acids with aliphatic amines in acetonitrile as a solvent. They also studied the effect of molecular acid-base dissociation of salts on the conductometric titration curves in acetonitrile and found the dissociation constant of 3,5-dinitrobenzoic acid in acetonitrile.[39] Conductometry has been extensively used for determination of physical and chemical constants like dissociation constant, formation constant, solvation, enthalpy and entropy change during a reaction, etc.[40-45] Instrumental assemblies with varying degrees of automation and sophistication are now becoming progressively available for titration purposes that they offer the possibility of increased selectivity.

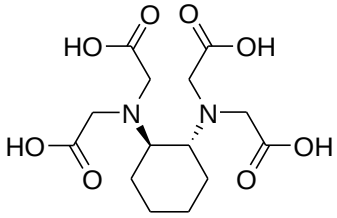
1.4 Polyaminocarboxylic Acids (PACA)

Tertiary amines contain carboxylic acid groups form remarkably stable chelates with many ions. G. Schwarzenbach first recognized their potential as analytical reagents in 1945.[46] Since this original work, investigators throughout the world have described applications of these compounds to volumetric analysis. Ethylenediaminetertracetic acid also called (ethylenedinitrilo)tertracetic acid which is commonly shortened to EDTA, is the most widely used complexometric titrant. EDTA molecule has six potential sites for bonding a metal ion: four-carboxyl groups and two amino groups, each of the latter with an unshared pair of electrons. Thus, EDTA is a hexdentate ligand. Schwarzenbach *et al*.,[47] first described *trans*-1,2-Diaminocyclohexane-N,N,N′,N′-tetraacetic acid (DCTA) as a new complexing agent for calcium and magnesium. In DCTA nitrogen atoms are connected by a cyclohexane ring in place of by two methylene groups in EDTA. It forms more stable complexes with the alkaline earth ions than EDTA. Thus, DCTA should be an excellent complexing agent for Ln(III) ions. The log K values for Ln(III) – DCTA complexes increase from 16.75 for La(III) complex to 20.91 for the Lu(III) complex. Ethylene glycol-bis(2-aminoethylether)-N,N,N′,N′-tetraacetic acid commonly abbreviated as EGTA is another polyamino carboxylic

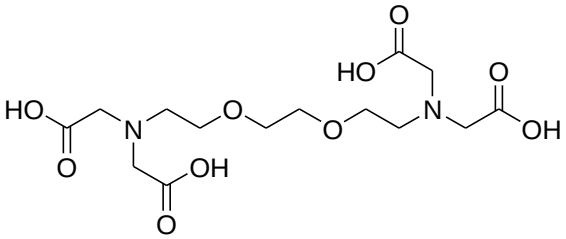
acid related to EDTA. It has much higher affinity for calcium than for magnesium ions and is used for continuous monitoring of the cerebral Mg(II)[48] and for the treatment of animals with cerium poisoning.[49] Another polyaminocarboxylic acid structurally similar to EDTA is EDTA-OH or N-(2-hydroxyethyl) ethylenediamine-N,N´,N´-triacetic acid. It contains a hydroxymethyl group instead of a carboxyl group in EDTA group i.e it has three carboxyl groups as against four in case of EDTA. 1,3-Diaminopropane-N,N,N′,N′-tetraacetic acid (TMDTA) is another hexadentate ligand with a trimethylene group in place of the ethylene group in EDTA. The structural formulae of these polyaminocarboxylates are given in Figure 1.1.



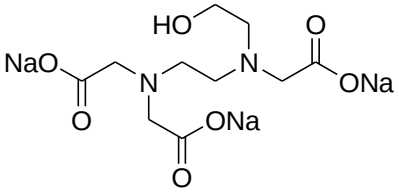
EDTA



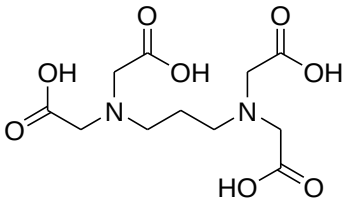
DCTA



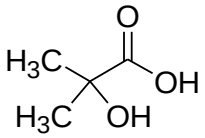
EGTA



EDTA-OH



TMDTA



HIBA

Figure 1.1: Structures of different PACA and α-hydroxyisobutyricacid (HIBA)

1.5 Theme of work done

Simple conductometric titrations can also be used to achieve quantitative information about an analyte provided some conditions are maintained. When a metal ion forms a complex, some changes in its ionic mobility occur, but these are normally too small to help detection of completion of reaction from the change in slope and hence do not permit a titration to be followed conductometrically. Moreover, the complexation is usually accompanied by the liberation of highly mobile hydrogen ion. Since changes in conductivity can be distinguished only when the background conductance of the solution is small, complexometric titrations can be followed conductometrically only if foreign electrolytes are absent or at a very low ionic strength of the matrix. To achieve this target, a series of conductometric titrations using polyaminocarboxylic acids as ligands in the presence of hydroxyl carboxylic acids (Figure 1.1) as co-ligands were carried out to determine lanthanides in binary mixtures and in presence of other interfering ions.

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Review of Literature

Electroanalytical chemistry has a long history of development for quantitative analytical methods that are based upon the electrical properties of solution of the analyte when it is made part of an electrochemical cell. Three types of Electroanalytical procedures are encountered. First involves establishing the relationship between analyte concentration and electrical quantities such as current, potential, conductance, capacitance or charge. Second one involves some electrical measurements used to establish the end point in titration of the analyte. In the third, an electrical current converts the analyte to a form that can be measured gravimetrically or volumetrically. Regardless of the type, the intelligent application of electroanalytical methods requires an understanding of the basic theory and practical aspects of operation of electrochemical cells. In order to establish the current state of knowledge, publications from technical journal articles since 1990 to 2013 are included in this chapter. In this review of literature, the articles related use of conductometric methods at academic level, research level and industry level are discussed. Also, different techniques involved for quantification of lanthanides are explained.

2.1 Performance of Conductometry at Different Levels of Study

The systematic study of the conductivity of electrolyte solutions owes much to the work of Friedrich Kohlrausch. He developed the basic techniques of the AC resistance bridge and recommended basic instrument designs and procedures to reduce the effects of electrode polarization. These empirical measures are still of value today. A number of review articles on various conductometric studies have been published.[1-3] Conductometric titration being a versatile technique finds a wide range of applications. It is a well-established analytical method for simple acid-base systems[4-5] and has recently been applied to analyze biological molecules for various purposes.[6-8] In pulp and paper industry conductometric measurements are conducted regularly to evaluate the mechanical performance of paper; or when stoichiometric neutralization of anionic trash is required.[9-11] The basic principles behind conductometric titration apparatus have been reported in literature.[12-17] Farris *et al.*,[18] reported the use of conductometric titration for determination of the charge density of two

biomacromolecules commonly used in food and biomaterials applications namely, pectin (a negatively charged polysaccharide) and chitosan (a positively charged biopolymer). Zaitsev *et al.,*[19] carried out conductometric titrations to study protolytically active groups using organosilica's functionalized with acid groups. Coelho *et al*.,[20] developed a chemometric method for the analysis of conductometric titration data for analysis of trace level acids and bases. Fras *et al*.,[21] have used conductometric titrations for determining the dissociation properties of natural and regenerated cellulose fibers. Titration method was concluded to be effective for monitoring the contents, strength, distribution of acidic groups, the total charge of natural and regenerated cellulose fibers.

2.1.1 Applications of Conductometry in Industry

Junsomboon *et al*.,[22] carried out the determination of Kjeldahl nitrogen in milk and chicken meat using flow injection conductometric system. The method furnished a detection limit of 1mg L^{-1}. An industrial use of conductometric method was demonstrated by Sereenonchai *et al.,*[23] with work on quantitation of calcium carbonate in cement using membraneless vaporization (MBL-VP) technique together with a contactless conductivity detection. No sample pretreatment was required for the analysis. Mitra *et al*.,[24] summarized the significance of conductometric studies during cane sugar manufacture. Martins *et al*.,[25] used conductometric titrations for the determination of Acetic Acid in Vinegar Adulterated Sample.

2.1.2 Conductometry for Medical Applications

Titrimetric procedures have even been accepted by many modern pharmacopoeias such as the United States Pharmacopeia[26] as an official method for various determinations in pharmaceutical products. Of these titrimetric methods, the most commonly used is conductometry. It has been abundantly used in determination of various chemicals in drugs[27-32]. Rossini *et al*.,[27] carried out the determination of an antihypertensive agent Losartan in pharmaceutical preparations using conductometric titration. The results obtained showed deviations between -1.2 and +4.0% from expected values and the average recovery of losartan ranged from 99 to 102.4% indicating no significant interference from the matrix effect. Conductometric titration of propranolol hydrochloride, a cardio-selective ß-

adrenergic receptor blocking agent, in pharmaceutical formulations using silver nitrate as titrant was reported by Sartori *et al*.[28] The method gave recoveries for four samples in the range of 96.8% to 105% and 95 % confidence level with those obtained using spectrophotometric method in several pharmaceutical formulations. Silva *et al*.,[29] carried out the determination of antibiotics trimethoprim and sulfamethoxazole using capillary electrophoresis with capacitively coupled contactless conductivity detection. Anis *et al*.,[30] developed and tested a conductometric titration procedure for determination of opioid analgesic Tramadol using cobalt thiocyanate solution as a reagent. The method exhibited a detection range of 1-15 mg mL^{-1}. Determination of Mebeverine hydrochloride (MVH), a widely used antispasmodic was carried out by Elazazy *et al.*,[31] using precipitating reagents: phosphomolybdic acid (PMA) and silver nitrate ($AgNO_3$). The procedures allowed the determination of MVH within the range of 2-15 mg using PMA and 1-20 mg using $AgNO_3$. MVH was shown to form 1:1 ion pair complexes with PMA and $AgNO_3$. Jarolimova *et al*.,[32] developed an analytical method based on capillary isotachophoresis with conductometric detection for determination of the composition of renal stones. The procedure was used for qualitative analysis and quantitative determination of Ca^{2+}, Mg^{2+}, Na^{+}, NH_4^{+}, $C_2O_4^{2-}$, PO_4^{3-}, urate and xanthate ions in renal stones with a detection limit of about 10 μML^{-1}.

2.1.3 Conductometry for Surfactant Analysis

Conductometry has been extensively used in surfactant chemistry to study micellar properties,[33] critical micelle concentrations (CMC),[34] interactions of polymers,[33,35] multivalent ions,[36] globular proteins,[37] etc. with surfactants and to calculate various thermodynamic properties of micelles.[33,38-39] Hnaien *et al*.,[40] were the first to propose a conductometric sensor for the detection of surfactants. They developed a conductometric sensor for the detection of cationic surfactant dodecyltrimethylammonium ions (DTA^{+}). It was based on interdigitated electrodes, working in differential mode and gave a detection limit of 3.2×10^{-11} M. Yan *et al*.,[41] studied anionic surfactant sodium dodecyl conductometrically and calculated the values of its critical micelle concentration (CMC) and counter ion binding constant (β) at five different temperatures showing that the micellization tendency of the surfactant increased in the presence of dipeptides. They calculated the

thermodynamic parameters (ΔG°_{m} , ΔH°_{m} and ΔS°_{m}) of micellization of $C_{12}SO_3Na$ in aqueous dipeptide solutions.[39] Azum *et al*.,[35] reported the effect of PEGs (polyethylene glycol) on dicationic dibromide gemini surfactants. Another group to study the affect of PEG on surfactants was Bayat *et al*.,[33] who calculated the Micellar and thermodynamic properties of sodium dodecyl sulfate in aqueous solutions of polyethylene glycol and polypropylene glycol. Specific interactions of surfactants with biomolecules such as proteins can lead either to their activation or to their denaturation.[42] Singh *et al*.,[37] reported the structural changes of a globular protein, bovine serum albumin, as a consequence of interaction with the surface active ionic liquids: 3-methyl-1-octylimidazolium chloride and 1-butyl-3-methylimidazolium octylsulfate.

2.1.4 Conductometric Sensors

2.1.4.1 Electrochemical Sensors

The use of electrochemical sensors for determination different cations, anions, organic molecules, etc. has become practically indispensable. Saiapina *et al*.,[43] applied natural zeolite clinoptilolite for electrochemical detection of ammonium by developing ammonium-selective sensor which was selective towards Na^{+}, K^{+}, Ca^{2+}, Mg^{2+} and Al^{3+}. The sensor displayed dynamic range and limit of detection of 0 - 8 mM and 1.0×10^{-8} M, respectively. Backer *et al*.,[44] presented a silicon-based modular solid-state sensor system for inline multi-parameter monitoring of cell-culture fermentation processes which was intended for continuous quantification of up to five (bio-)chemical and physical parameters, namely, glucose and glutamine concentration, pH value, electrolyte conductivity and temperature by applying different transducer principles.

2.1.4.2 Immunosensors

Various advantages of conductometric immunosensors like, high sensitivity, low cost, low power requirements, high compatibility with advanced micromachining technologies without the need of reference electrode, and suitability for sensor miniaturization and automated detection have led to their use as detectors of tumor markers.[45] Tang *et al*.,[46] designed a conductometric immunosensor for detection of plasma protein alpha-fetoprotein

(AFP) using carbon nanoparticles as labels. The immunosensor exhibited dynamic range of 0.1–500 ng/mL with a detection limit of 50 pg/mL and reproducibility and recovery were <10% and 83.9% – 112.3%, respectively.

2.1.4.3 Biosensors

Boisse *et al*.,[47] proposed the combining of two conductometric biosensors for the determination of total lactate in dairy products. A detection limit of 0.05μM was reported for both *l*- and *d*-lactate. Maniruzzaman *et al*.,[48] fabricated a titanium dioxide (TiO_2) cellulose hybrid nanocomposite to be used as a conductometric biosensor for glucose determination by immobilization of the enzyme, glucose oxidase into the hybrid nanocomposite by physical adsorption method. The glucose biosensor gave a linear response in the range of 1‑10 mM. Mahadeva *et al*.,[49] also reported a glucose biosensor using glucose oxidase immobilized cellulose-tin oxide (SnO_2). The biosensor displayed a linear response in the range of 0.5 ‑ 12 mM. Isildak *et al*.,[50] reported a conductometric biosensor based on solid-state contact ammonium-sensitive sensor for creatinine determination with a detection limit of 2×10^{-6} M displaying a response time less than 10 s in phosphate buffer solution at pH 7.20 and storage stability for at least 4 weeks kept in dry at 4-6°C. Soldatkin *et al*.,[51] used three-enzyme system (invertase, mutarotase, glucose oxidase), immobilized on the transducer surface for determination of heavy metal ions. The biosensor was reported to display the best sensitivity toward Hg^{2+} and Ag^{+} ions. Saiapina *et al*., developed a conductometric biosensor for l-arginine determination. The optimum features in terms of the sensitivity, the linear range, and the detection limit were listed to be 4.2 μS/mM, 0.01‑ 4 mM and 5.0×10^{-7} M, respectively. The biosensor showed high operational and storage stability.

2.1.5 Hyphenated Techniques of Conductometry

Conductometry has also been coupled with techniques like capillary electrophoresis[52] and ion chromatography[53] for determination after prior separation. Zhang *et al*.,[53] used capacitively coupled contactless conductivity detection for determination of inorganic ions after their separation by monolithic capillary column ion chromatography. The technique gave detection limits of 1.6, 0.28, 0.53, and 0.47 mg L^{-1} for F^{-}, Cl^{-}, NO_2^{-}, and NO_3^{-},

respectively. Wong *et al*.,[52] carried out separation of eleven underivatized fatty acids using capillary electrophoresis – capacitively coupled contactless conductivity detection. The method exhibited detection limits in the range of 0.9 – 1.9μg mL^{-1} for the ten fatty acids.

2.1.6 Conductometry for Physical Properties of Electrolytes

The electric conductivity is one of the most important properties of electrolyte solution.[54-55] From the results of conductivity experiment a series of fundamental parameters of electrolyte solutions such as ion association constants, limiting conductivities and solvation characteristics can be obtained. Ali *et al*.,[56] studied the interaction of β-cyclodextrin with amphiphilic drug amitriptyline hydrochloride via conductometry showing that apparent critical micelle concentration (CMC*) increased and ΔG_{mic} became less negative on increasing the β-cyclodextrin concentration.

2.1.7 Conductometry in Non-Aqueous Media

Solvent plays a crucial role in the binding selectivity. Hence, a number of studies have been conducted on interaction of various ions in non aqueous media by means of conductometry. Kalugin *et al*.,[57] studied the perchlorates of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+} and Ni^{2+} in acetonitrile and used their conductance data to obtain total limiting equivalent conductivities, the first step (primary) association constants, primary association constants and their temperature dependences. Single limiting equivalent conductivities and conventional transference number were also determined. Borun *et al*.,[58] reported studies on dilute solutions of the ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium tetrafluoroborate in N,N-dimethylformamide in a temperature range of 283.15 K to 318.15 K. The conductance data was used to calculate ionic association constant, limiting molar conductivities, distance parameters, activation enthalpy of charge transport and thermodynamic functions such as Gibbs free energy, entropy and enthalpy for the process of ion pair formation. Borun *et al*.,[59] also studied the conductances of sodium tetraphenylborate, tetrabutylammonium bromide, and sodium tetrafluoroborate in N,N-dimethylformamide over the same temperature range as their previous reports i.e., from 283.15 K to 318.15 K and calculated all the above parameters for these.

Rounaghi *et al*.,[60] published studies on reaction of dibenzo-18-crown-6 with ZrO^{2+} in binary solvent solutions of acetonitrile, 1,2 dichloroethane, nitromethane and ethylacetate with methanol. The stability constants of the resulting 1:1 complex were determined revealing that the complex was more stable in the EtOAc–MeOH solvents as compared with the other binary mixed solvent solutions. Ahmadzadeh *et al*.,[61] studied the complexation process between titanium (III) cation and meso-octamethylcalix[4]pyrrole conductometrically and determined the equilibrium constants and thermodynamic parameters (ΔH°_{c} and ΔS°_{c}) for complexation process. The stoichiometry of the complex in all binary mixed solvents was reported to be 1:1. Rezayi *et al*.,[62] conductometrically determined formation constants, the Gibbs standard free energies, the standard enthalpy changes and the standard entropy changes of 1:1 complex of tris(2-pyridyl)methylamine and Titanium (III) in Water-Acetonitryl Mixture.

2.2 Analytical Methods for Lanthanide Determination

The rare earth elements are the largest naturally occurring group in the periodic table. Starting with Cerium, electrons are added successively to the 4f shell to give the sequence of lanthanide elements. The 4f electrons are shielded by eight electrons, $5s^2$ and $5p^6$, so that their chemical significance is so slight as to allow the remarkable similarity of lanthanides. Although in fact they are not at all rare, the close similarity of their chemical and physical properties made the occurrence of several of them together in individual minerals almost inevitable and also accounted for the considerable difficulties in separating them from one another. Accurate determination of trace elements in important environmental studies is required as environmental protection becomes a higher priority on the scientific agenda of the world's industrialized nations leading to a rise in the demand for the development of methods providing quantitative determination of trace metals in a variety of environmental matrices.

Quantitative analytical techniques are required to determine REE accurately and rapidly with sufficient sensitivity for the determination in metallurgical, environmental, and geological samples. This requirement has led to major technological advances in the development of analytical instrumentation. On the other hand, the rapid studies made in

analytical techniques resulted in the increased sensitivity and quick analysis of individual REE than ever before. The availability of various powerful analytical techniques has led to a major impetus for the exploitation of REE in geological objects like rocks and minerals for elucidating petrogenesis and in the evaluation of the coefficients of partitioning of REE between various minerals and melts.[63-64] Various methods can be used to determine the content of a rare elements present in the sample in free form and as ionic compounds. These techniques involve determination of mass, volume, absorption and emission of IR, visible and UV radiation, X-RAY methods, light scattering measurements and electroanalytical techniques.

Different techniques developed for the determination of REE in metallurgical, environmental, and geological samples since 1980 is very appropriate. These procedures have been summarized below:

2.2.1 Classical Methods

As most of the lanthanide elements appear in solution as particularly stable three positive ions, few classical methods are available for the determination of individual elements.

2.2.1.1 Gravimetric methods

Not many reports of lanthanide determination are available in literature. Some of these are: Cerium can be determined gravimetrically by quantitatively precipitating cerium as ceric iodate, $Ce(IO_3)_4$, which is finally weighed as ceric oxide.[65] Oxalate precipitation is the best procedure available for the gravimetric isolation of the lanthanide elements.

Fitch *et al*.,[66] determined lanthanum gravimetrically by reacting it with oxalic acid and weighing the resultant as sesquioxide. Certain difficulties related to small irregular losses in the filtrate[67] faced in rare earth determination by gravimetery using oxalic acid were overcome by controlling the amount of oxalic acid and carefully cooling the solutions to about 0°C. Hassan *et al*.,[68] used gravimetric analysis for the determination of La(III), Ce(III), Pr(III), Nd(III), Sm(III), Eu(III) and Gd(III).

2.2.1.2 Volumetric methods

Volumetric determination of europium is carried out by quantitative reduction of Europium to the bipositive state by putting an acidified solution (pH 3-4) of its salt through a Jones redactor.[69] The europous ion is oxidized quantitatively to the 3+ state by a standard solution of either iodine (a) potassium dichromate. The original europium solution must be free from oxidizing agents and SO_4^{2-} ions.

2.2.2 Atomic Spectroscopy

2.2.2.1 Atomic Absorption Spectroscopic Method

Atomic absorption spectrometry (AAS) is a spectroanalytical procedure for the quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state. In determination of the lanthanides, atomic absorption spectroscopy lacks the precision that it leads to the determination of many other metals also.[70] AAS has been used to determine La[71], Yb[72] and Nd[73] giving detection limits as low as nanogram (ng). However, much greater sensitivity can be achieved with Inductively Coupled Plasma Spectroscopy (ICP).

2.2.2.2 Inductively Coupled Plasma Spectroscopic Method

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectroscopy (ICP-MS) are used to detect metals at trace levels. Analysis of lanthanides in rocks and minerals was one of the first milestones of ICP-MS.[74,75] Fission product solutions, particularly lanthanides are characterized by mass spectrometry techniques i.e., thermal ionization mass spectrometry (TIMS)[76] or multiple-collector inductively coupled plasma mass spectrometry (MCICP–MS)[77], in order to obtain precision and accuracy on isotope ratio of a few percent. ICP-AES can be applied in chromatographic lanthanide analysis, but the eluants used for HPLC separations of individual lanthanides can compromise the analysis.[78] Sawatari *et al*.,[79] described a system that combined HPLC separation and ICP-AES detection for lanthanide analysis. Under the reported conditions HIBA eluant did not compromise operation of the detection system. Campuzano *et al*.,[80] used a modular high-efficiency sample introduction–aerosol desolvating system (Apex–

Spiro) for the direct analysis of REE in calcium rich water samples taken from karstic environments. They reported that the sample allowed direct analysis of rare earth elements from 1-2 mL of natural water samples with detection limits ranging from 30–500 fg g^{-1}. The analysis was found to be severely affected by a complex mixture of Ba-based polyatomic species. Vio *et al*.,[81] carried out the mutual separation and analysis of 13 lanthanides by isotachophoresis coupled with ICP-MS for application in nuclear fuel analysis using 2-hydroxy-2-methylbutyric acid as a chelating agent. The ligand was reported to give maximum critical selectivity of 0.1 - 0.12 at pH=4.4 - 5.2 leading to an easier separation.

Kumar *et al*.,[82] used polyhydroxamic acid as a chelating agent for lanthanide preconcentration followed by their determination by ICP in seawater. The limit of detection as calculated was between 0.08 to 0.44 ng L^{-1}. The direct analysis by ICP-MS posed problem owing to salt deposition in the sample introduction parts, sampling interface and ion optics. Varga *et al*.,[83] developed a procedure for the trace-level determination of lanthanides in uranium-bearing materials by inductively coupled plasma sector-field mass spectrometry (ICP-SFMS). It involved a rapid chemical separation of lanthanides by TRUTM extraction chromatography resin followed by ICP-MS analysis. The method obtained lanthanide separation with chemical recovery of > 94%. The amount of chemicals consumed for the separation and thus the waste generated was only a few mL per sample. The method showed a potential for application in the field of nuclear forensics, where rare-earth element pattern can be used for the assessment of unknown samples.

2.2.2.2 X-ray Fluorescence Spectroscopy

Fluorescent X-rays are emitted, when samples are irradiated with sufficiently energetic X-rays. These permit the detection and quantitation of lanthanides. X-rays fluorescence spectrometry has the advantage of sample preparation and yielding relatively simple spectra. One of the disadvantages results from the several lines from different elements, leading to internal absorption and enhancement effects. Literature contains only a few reports on the analysis of lanthanides using X-ray fluorescence method (XRF). Kuang *et al.*,[84] determined the distributions of Au, Gd and Ba in the water phantom using reconstructed XRF computed tomography (XFCT) images created by a single scan. An increase in imaging performance

was predicted on using plane-polarized X-ray beams and quasi-monochromatic X-ray beam excitations and an XRF detector ring. Orescanin *et al.*,[85] developed a new analytical procedure for determination of lanthanides in environmental samples which utilized analyses of thin targets by energy dispersive X-ray fluorescence (EDXRF) method using ^{109}Cd as the source of excitation after chemical separation on DOWEX 50W-X8 resin and preconcentration with chelating agent ammonium pyrrolidine dithiocarbamate. Results showed that the selected lanthanides made stable complexes with APDC in the basic medium with the maximum recovery at pH = 8. The exception was La which reached maximum recovery at pH = 9. Vito *et al.*,[86] carried out determination of Sm(III), Eu(III) and Gd(III) by X-ray fluorescence (XRF) spectrometry using a chelating resin for its separation and preconcentration. The resin, prepared by adsorption of (*o*-[3,6-disulfo-2-hydroxy-1-naphthylazo]-benzenearsonic acid) (thorin) on a macroporous resin Amberlite XAD-7, helped in eliminating the interelemental effects in the sample, giving high enrichment factors and low detection limits of 13.8, 17 and 15.7 mg L^{-1} for Sm, Eu and Gd, respectively.

2.2.3 Molecular Spectroscopic Methods

2.2.3.1 UV-Visible Method

It is an analytical tool that measures the absorption of radiation, as a function of frequency or wavelength, due to its interaction with a sample. Spectrophotometry has been applied for the determination of lanthanides in various matrices. Post-column derivatization with the colorimetric indicator ligands PAR (4-(2-pyridylazo)resorcinol) or Arsenazo III [2,2_-(1,8-dihydroxy-3,6-disulfonapthalene-2,7-bisazo)bis(benzene arsonic acid)] is the most widely applied detection method for chromatographic analysis of lanthanides.[78] Saito *et al.*,[87] reported the precapillary complexing system with UV direct detection using 1-(4-aminobenzyl)ethylenediamine- *N,N,N',N'*-tetraacetic acid as a light-absorption ligand for Ln^{3+}. The reported limit of detection was 4.2×10^{-7} M dm^{-3}. Oztekin *et al.*,[88] carried out separation and detection of lanthanides by capillary zone electrophoresis in the presence of pyridine-2-carboxylic acid (picolinic acid) as UV-absorbing complexing agent. Complete separation of all 14 lanthanides with good peak shapes was achieved as a result of application of hydroxyisobutyric acid (HIBA) and formic acid as competing ligands giving

detection limits of 0.53–0.96 mg mL^{-1}. Previously, Timerbaev and co-workers had reported separation of a limited number of lanthanide ions using arsenazo III and 2,6-diacetylpyridine bis(N-methylenepyridinohydrazone)[89,90] and separation of 13 lanthanide ions using cyclohexane-1,2-diaminetetraacetic acid (DCTA) in a very basic medium, with the formation of mixed hydroxyl complexes.[91] Macka *et al.*,[92] had separated 10 lanthanide ions with arsenazo III using citrate as an auxiliary ligand to arsenazo III. Oztekin *et al.*,[93] achieved separation of 14 in 7 min by capillary zone electrophoresis in the presence of cupferron as UV absorbing complexing agent with a detection limit of 0.24 - 0.47 mg mL^{-1}.

2.2.4 Chromatographic Techniques

2.2.4.1 HPLC

High Performance Liquid Chromatography (HPLC) is the most common and useful of chromatographic methods used in lanthanide quantitation. These techniques were developed beginning in the 1960's and were first applied for lanthanide analysis by Sisson.[94] When column chromatography is conducted under pressure it substantially improves the resolution and efficiency of the separation process. HPLC separations use water-soluble chelating agents for lanthanide separation. These chelating agents form complexes of steadily varying strength across the lanthanide series and are applied using gradient elution i.e., the composition of the eluting solution is changed over the course of the analysis. Often, a linear ramping of the concentration of one or two complexants is used to accomplish the target separations.[75] The first HPLC and IC applications for detecting REEs in geological samples was performed by Cassidy and Elchuck[95] and Mazzucotelli[96] who were partially successful in measuring a few elements of the REE group by HPLC procedures based on spectrometric detection systems. The use of HPLC for lanthanide separation and quantification has been extensively reviewed by Verma *et al.*[97] Kumar *et al.*,[98] reported reversed phase HPLC method for the determination of lanthanides in high purity dysprosium oxide (Dy_2O_3) matrix using α-hydroxyisobutyric acid as an eluent and n-Octane as an ion interaction reagent. Santoyo *et al.*,[99,100] analyzed 13 lanthanides (La-Nd, Sm-Tb, and Ho-Lu) in different geochemical reference materials either isocratic or gradient elution programs together with an on-line spectrophotometric detection for achieving low detection limits.

2.2.4.2 Capillary Electrophoresis

Capillary electrophoresis (CE) is very attractive in the nuclear field because it offers minimal waste generation, high separation efficiency, low cost and fast analysis.[81] Application of capillary electrophoresis for lanthanide analysis is a recent development.[101,102] Capillary electrophoretic separations rely on differences in the electrophoretic mobility of analyte species in an electrolyte buffer while under the influence of an applied electric field. As compared to transition metals or alkali/alkaline earth metals, the mobilities of the aquo cations for lanthanide ions are not adequately differentiated for an effective mutual separation. An improved separation can be achieved by introduction of chelating agents that form complexes with the ions.[102] Vogt and Conradi[102] have described the relationship between complex formation and electrophoretic mobility. Robards *et al*.,[103] also described lanthanide separations by the related techniques of zone electrophoresis and isotachophoresis, both of which are based on the electrophoretic mobility of lanthanide complexes.[78] Under ideal conditions, CE can provide complete separation of the trivalent lanthanides in less than 10 min.[104] Clark *et al*.,[104] carried out separation of the trivalent lanthanides in the presence of two simple carboxylate ligands, a-hydroxyisobutyric acid (HIBA) and lactic acid (LA). The use of HIBA provided excellent separations for all lanthanides except lutetium. Saito *et al*.,[84] applied a newly synthesized aromatic polyaminocarboxylate as a chelating reagent for precapillary derivatizing capillary electrophoresis for lanthanide ions. Verma *et al*.,[105] reported the development of an improved capillary electrophoresis method for quantifying rare-earth elements in synthetic geochemical standards. The primary objective of study being the separation of REE total group (lanthanum to lutetium) with special emphasis on the solution of overlapping problem between Eu(III) and Gd(III). A significant reduction of the analysis time was achieved i.e., < 2 min.

2.2.5 Neutron Activation Analysis (NAA)

It is the most sensitive method available for the detection and measurement of lanthanides. It offers advantages such as low interference from other elements and requirement of minimal sample preparation. It suffers a drawback that it requires a nuclear reactor as a source of

neutrons with which to irradiate the sample. Neutron activation analysis for lanthanides is adversely affected by the presence of U, Th, transuranium elements, Fe, and Ta. The actinides undergo neutron-induced fission to produce some of the same lanthanide nuclides as fission products. The γ-ray energy for ^{59}Fe overlaps that for ^{141}Ce, while the γ-emission of ^{182}Ta overlaps ^{170}Tm. Quantitative separation of lanthanides from these elements is therefore of primary importance for application of neutron activation analysis.[78] Dybczynski *et al.*,[106] published a report comparing the performance of both variants of NAA: purely instrumental activation analysis (INAA) and radiochemical mode (RNAA) for lanthanide determination with pre- and post-irradiation group separation. This procedure was reported to remove most of potential spectral interferences. Danko *et al.*,[107] reported the use of radio-tracers for selective and quantitative isolation of the lanthanides as a group from biological materials. Ion exchange and extraction column chromatography were used for the isolation of elements of interest from matrix and the other trace elements prior to irradiation in a nuclear reactor. Gramatges *et al.*,[108] reported methods for the simultaneous preconcentration of lanthanides by cloud point extraction and their determination using neutron activation analysis. Detection limits between 0.3 and 3.0 ng g^{-1} were obtained. Danko *et al.*,[109] reported a method aimed at determining traces of lanthanides in the materials of biological origin by NAA. The chemical procedure involves both selective and quantitative pre-irradiation isolation of the elements based on classical column ion-exchange and extraction chromatography. Nayak *et al.*,[110] reported a powerful method to differentiate various geological belts of different origin. Ten rare-earth elements, such as La, Ce, Nd, Sm, Eu, Tb, Ho, Tm, Yb and Lu were qualitatively identified and quantitatively estimated in these samples.

2.2.6 Electroanalytical Methods

2.2.6.1 Potentiometric Method

The era of ISEs was initiated through the theoretical work of Nikolski and Schultz,[111] which was further expanded by Eisenman.[112] Indeed, the Eisenman-Nikolski equation is the basis of ISE theory and of the selectivity concept. Potentiometric sensors can offer an inexpensive and convenient analysis method of rare-earth ions in solution, provided that acceptable

sensitivity and selectivity are achieved. Literature contains a number of reports on determination of different lanthanides using diverse types of sensors.[113-117] Of all the lanthanides Ce(III) is one of the most commonly studied potentiometrically.[118-121] Bagheri *et al*.,[121] prepared Ce(III) carbon paste electrode based on a nanocomposite containing multi-walled carbon nanotubes, the sensor was reported to display excellent sensitivity for cerium with respect to a large number of alkali, alkaline earth, transition and heavy metal ions and gave a detection limit of 7.0×10^{-9} ML^{-1} in a pH range of 3.0 to 8.0. Afkhami *et al*.,[120] fabricated another cerium sensitive sensor that was able to furnish a detection limit of 6.45×10^{-9} ML^{-1}. Gupta *et al*.,[122] developed a membrane based on neutral carrier 2-(2-aminothiazol-4-yl)phenol and 2-(4-phenyl-1,3-thiazol-2-yliminomethyl)phenol as ionophores for sensing gadolinium ions. It was used as an indicator electrode for determination of end point in potentiometric titration of Gd(III) ion with EDTA and successfully applied for the determination of the concentration of gadolinium(III) ion in a mineral sample. Zamania *et al*.,[123] synthesized a compound, 3,4-diamino-N′-((pyridin-2-yl)methylene)benzohydrazide which exhibited high selectivity towards Dy(III) ion in a wide concentration range of 1.0×10^{-6} – 1.0×10^{-2} ML^{-1} with a detection limit of 5.5×10^{-7} ML^{-1}. They also reported a Nd (III) selective sensor based on N,N′-bis(quinoline-2-carboxamido)-4,5-dimethylbenzene as ionophore,[124] a Ho(III) -PVC membrane electrode with a detection limit of 5.0×10^{-7} ML^{-1} for Ho(III) ions[125] and a europium sensor based on N-pyridine-2-carboxamido-8-aminoquinoline (PCQ) as an ion carrier exhibiting a detection limit of 6.4×10^{-7} ML^{-1}.[126] Zamani *et al*.,[127] also reported Pr(III) poly vinyl chloride PVC membrane sensor.

2.2.6.2 Voltammetric Methods

Voltammetry is an electroanalytical technique based on measurement of current (I) as a function of applied potential (E). The use of voltammetric techniques has been stimulated by the advent of ultra-micro electrodes, due to their steady state currents, higher sensitivity, increased mass transport and their ability to be used in electroanalysis in solutions with high resistance.[128,129] Alizadeh *et al*.,[130] synthesized europium(III)-imprinted polymer nanoparticles which could be used for indirect voltammetric determination of Eu(III) based

on the decrease in Cu(II) signal in presence of Eu(III). The electrode demonstrated high selectivity for Eu(III), even in the presence of other lanthanide ions. Mirshafian *et al*.,[128] reported Er(III) nanocomposite carbon paste voltammetric ion selective sensor for erbium(III) based on the concept of ion transfer at the interface between two immiscible electrolyte solutions. The sensor displayed a detection limit of 5×10^{-7} ML^{-1}. Ma *et al*.,[132] reported the determination of europium(III) ion by differential pulse voltammetry (DPV) using a LaB_6 electrode with sodium dodecylbenzene sulfonate displaying a limit of detection = 6.0 nM. The benefits of the method included ease of fabrication, sensitivity, good reproducibility and stability. Pourjavid *et al*.,[133] reported separation of medium lanthanides (Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+} and Dy^{3+}) on Nucleosil 100-5-SA (an ion exchange column) in the presence of α-hydroxyisobutyric acid (HIBA) as an elution agent. The influence of HIBA concentration and pH of the eluent was studied. The best performance obtained was at pH 4.0, scan rate $30Vs^{-1}$, accumulation potential -300 mV and accumulation time 0.3 s. The proposed method displayed a linear dynamic range between 0.26 - 23 mg L^{-1}. The detection and identification of light lanthanides by fast Fourier transform continuous cyclic voltammetry (FFT-CCV) following their cation-exchange separations was also reported by Pourjavid *et al.,*[134] The method displayed a linear dynamic range between 250 and 21000 ppb and a detection limit of 90 ppb.

2.3 Conclusions

The comprehensive literature survey shows that conductometric method is used only for quantitative determination of acids/bases and some precipitation titrations. Conductometry is accepted as a simple, inexpensive and easy to operate technique and no research reports regarding conductometric analysis of Ln(III) ions using polyaminocarboxylic acids are available. This research theme has been systematically covered in this thesis.

2.4 References

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Materials and Methods

The materials and methods used for study have been discussed below.

3.1 Chemicals and Reagents

3.1.1 Lanthanides: Chloride salts of all 14 lanthanides used in their tripositive states with 99% purity were obtained from Chengdu Beyond Chemicals, China. These $LnCl_3$ salts were used to prepare stock solutions of Ln(III) ions which were standardized by volumetric titrations using EDTA as complexing agent and xylenol orange as an indicator. These stock solutions were further diluted to prepare Ln(III) solutions of required molarity for further studies.

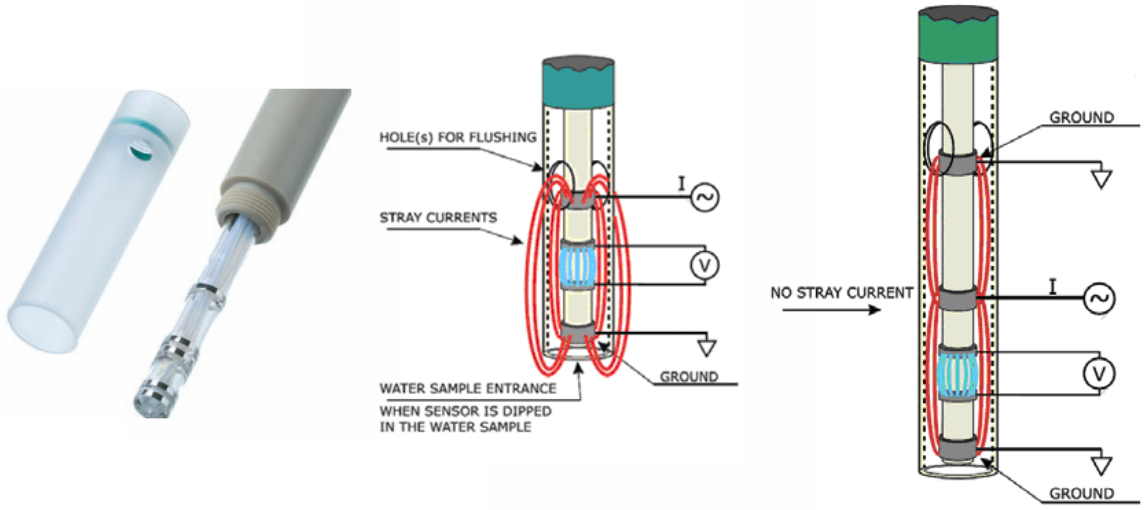
3.1.2 Interfering Ions: A total of 10 metal ions used to carry out interference studies were procured from Aldrich, India. These included chloride or nitrate salts of metals Mg(II), Ca(II), Ba(II), Mn(II), Co(II), Ni(II), Cu(II), Al(III), Pb(II) and Th(IV). Stock solutions of these salts were prepared and standardized, which were further used for preparation of metal solutions of required concentration (molarity) by dilution method.

3.1.3 Ligands and Chromophoric Agent: Ligands used for the study included polyaminocarboxylic acids Ethylenediaminetetraacetic acid (EDTA), *trans*-1,2-Diaminocyclohexane-*N,N,N′,N′*-tetraacetic acid (DCTA), Ethylene glycol-bis(2-aminoethyl-ether)-*N,N,N′,N′*-tetraacetic acid (EGTA), N-(2-Hydroxyethyl) ethylenediaminetriacetic acid (EDTA-OH) and 1,3-Diaminopropane-N,N,N′,N′-tetraacetic acid (TMDTA). All the three commercially available forms of EDTA i.e., Na_2EDTA, Na_3EDTA and Na_4EDTA were used for studies. All the above mentioned ligand salts were acquired from Aldrich, India and used as received. Arsenazo III, a chromophoric agent for UV studies, was acquired from Aldrich, India.

3.1.4 Solvents: Solvents used for studying the effect of co-solvent on conductometric determination of lanthanides included Acetonitrile (ACN), Tetrahydrofuran (THF), Dimethylformamide (DMF), Dimethylsulfoxide (DMSO), Methanol (MA) and 1,4-dioxane (DA) and were obtained from Merck, India.

3.2 Instrumentation

3.2.1 Conductivity Module: The instrument used for measuring conductivity consisted of 856-conductivity touch control module with a connected cell (Metrohm, Switzerland) as a standalone system. The conductivity module measures complex resistances using alternating voltages. The cell used was a 5-ring conductivity sensor which contains five rings that function as electrodes and are covered by a cuvette (Figure 3.1). They provide for a high linearity without plasticization of the cell. This guarantees highest precision, and the cell constant, once determined, remains stable over a wide measuring range. Of these five rings (electrodes) four are separated into current-conducting and voltage-measuring electrodes. This has the advantage that the voltage-measuring electrodes are not polarized and thus measure an undistorted potential. A current applied to the inner electrode generates a current toward the outer, grounded electrodes. This means that polarization effects and measuring errors are minimized. The fifth ring forms a second base electrode, which reduces the outward propagation of the electric fields. It allows precise measurements irrespective of the measuring position of the electrode. The cell has a cell constant of 0.7 cm^{-1} and a minimum



(a) (b) (c)

Figure 3.1: (a) five ring conductivity cell (b) Four rings: The electric fields are also detectable outside the boundary (c) Five rings: Better defined electrical fields *(figures reproduced in this thesis with written permission)*

immersion depth of 34 mm. The ideal measuring range of the cell is 0.005-20 mS cm^{-1}. It does not suffer any interference with potentiometric measurements. Conductivity and pH can be measured in the same vessel simultaneously. These properties, combined with the compact construction and a suitably large opening for fast mixing, are advantageous for manual use in the lab and especially in automation with Metrohm sample changers. The cuvette above the five rings is removable for cleaning the five-ring measuring cell. The cuvette is important for the definition of the current-conducting volume and was attached during measurement.[1]

3.2.2 Conductivity Meter: CM 180 conductivity meter (ELICO, India) digital display with accuracy and repeatability of ±1% was used for study. It contains a two-pole conductivity cells having facility for measurement of absolute cell constant and selection and adjustment of cell constant. Three cells with cell constants 0.1, 0.45, and 1.0 cm^{-1} were used. This two pole cell has two electrodes that face each other and are inert. Two-electrode cases are equipped with a pair of electrodes across which both the voltage and current can be measured. It provides manual temperature compensation from 0 to 50°C and capacitive correction for higher ranges. An AC voltage source is used to avoid polarization effects at the electrode/ electrolyte interface and due to electrolyte decomposition. It applies a constant AC EMF at 1000 Hz to a segment of solution between two parallel platinum electrodes and measures the electrical resistance and through it the conductance of the solution. A coating of platinum black is used to increase the surface area and to reduce the polarizing resistance. Conductance cells of appropriate cell constants were selected depending on the expected conductances of the solutions.

3.2.3 pH Meter: Complexation of metal ions with ligands is a pH dependent phenomenon. While 100% complexation between a metal ion and a ligand may be observed at a particular pH value, the same metal ion and ligand may not show any complexation at other pH values. For this purpose it is necessary to observe and maintain pH of the solution under study. For keeping a note of the pH of solutions digital pH meter Century (India) CP 901 was used. The pH meter has a range of pH 0 – 14 and accuracy of ±0.1 pH. The instrument is glass electrode based with Ag/ AgCl, KCl(saturated) as reference electrode.

3.2.4 Thermostat: An increase in temperature of the reaction system leads to a decrease in viscosity and hence, an increase in conductivity. This makes it necessary to maintain a constant temperature conditions. The instrument used to serve this purpose was a water thermostat, Julabo F12-ED (refrigerated/heating circulator) which has a working range of -20 to 100°C and a temperature stability of ±0.03°C. It is suitable for external temperature tasks and for temperature applications directly in the bath. Short heat-up and cool-down times are achieved due to powerful circulating pump systems and high heating and cooling capacities. Using this constant temperature conditions of 18± 0.1°C were maintained for all conductometric titrations.

3.2.5 Spectrophotometer: UV-VIS spectrophotometer (Analytik Jena, Switzerland, Specord 205) was used to record spectra of the solutions under study. Specord 205 is a computer-controlled double-beam spectrophotometer for the measurement of the transmission, absorbance, reflection as well as the energy of liquid and solid samples. It is designed for measurements in the spectral range 190-1100 nm. It provides a spectral resolution of 1.4 nm. It provides internal wavelength calibration with a holmium oxide filter as a result of which high wavelength accuracy and reproducibility can be achieved. The light sources used are a deuterium lamp for the UV region and a halogen lamp for the visible region of the spectrum. It provides self adjustment of photometric linearity and automatic correction of stray light. The software program WinASPECT allows the spectrometer and all its accessories to be controlled by PC. Quartz cuvettes having a path length of 1cm were used for all measurements.

3.3 Method and Evaluation of Experimental Data

Freshly prepared solutions of the $LnCl_3$ salt and ligand were used for every experiment. The lanthanide solutions were standardized by titration against EDTA using xylenol orange as indicator.

3.3.1 Conductometric Studies

3.3.1.1 For single ion determination: In a typical conductometric titration experiment, the reaction vessel was charged with 50 mL of the $LnCl_3$ salt solution (concentration range

from $1x10^{-5}$M to $1x10^{-3}$M) prepared in appropriate solvent system, sealed and left for an hour in a thermostatic bath at 291.15K to reach thermal equilibrium before each experiment. Subsequently, the ligand solution (having concentration 10 fold to the corresponding $LnCl_3$ salt being titrated) was added to the reaction vessel in increments of 0.5 mL using a burette. For each titration about 20-25 additions of the ligand solution were carried out such that the amount of ligand added was sufficiently larger than the 1 : 2 :: metal : ligand stoichiometry. The conductivity value of the reaction system was recorded after each addition and the conductometric titration curves were plotted for volume of ligand added versus conductivity of the solution.

3.3.1.2 For binary mixtures in the absence and presence of HIBA: For determination of lanthanides in their binary mixtures in the absence of HIBA 25 mL of each $LnCl_3$ salt solution ($1x10^{-3}$M) was added to the reaction vessel. After which the reaction vessel was sealed and left for an hour in a thermostatic bath at 291.15K to reach thermal equilibrium. Subsequently, the ligand solution (having concentration 10 fold to the corresponding $LnCl_3$ salt being titrated) was added to the reaction vessel in increments of 0.5 mL using a burette. For each titration about 20-25 additions of the ligand solution were carried out such that the amount of ligand added was sufficiently larger than the 1 : 2 :: metal : ligand stoichiometry. The conductivity value of the reaction system was recorded after each addition and conductometric titration curves for volume of ligand added versus conductivity of the solution were plotted.

For determination of lanthanides in their binary mixtures in the presence of HIBA the procedure was exactly the same as that described above except that the reaction vessel was charged with 1 equivalent of HIBA (with respect to the total lanthanides present in the system) along with the $LnCl_3$ of interest.

3.3.1.3 For interfering ion studies: Determination of lanthanides in the presence of interfering ions was carried out by taking 25mL of $1x10^{-3}$M each of the $LnCl_3$ solution and interfering ion solution and sealing the vessel for an hour in a thermostatic bath at 291.15K to reach thermal equilibrium. Later the ligand solution of 10 fold concentration was added to the vessel in 0.5mL increments and noted conductivity after each addition. Conductometric

titration curves were plotted from these readings. The procedure followed for the determination of lanthanides in presence of interfering ions in the presence of HIBA was the same as above with the addition that 1 equivalent of HIBA (with respect to the total metal ions present in the system) to the reaction vessel along with the $LnCl_3$ and interfering ion of interest.

3.3.1.4 Effect of nature and concentration of co-solvent: The effect of nature and concentration of co-solvents was determined by carrying out conductometric titration in the presence of various co-solvents at different concentrations of 10-80% (v/v). The procedures followed for different titrations were the same as given above with the difference that the solutions were prepared in co-solvent/solvent media of varying concentrations.

Figure 3.2: Experimental setup used for conductometric titrations

3.3.1.5 Evaluation of experimental data: Tangents were fitted on the two branches of the curve and the point of intersection of the tangents defined the endpoint/ equivalence point of the titration.

3.3.1.6 Real time samples analysis: Aforementioned procedure was followed for single ion and binary mixture determination of lanthanides after spiking the samples with the Ln(III) ions of interest (due to their low concentrations in the matrix). Spiking is the process of adding a known amount of metal solution to the sample under study in order to amplify its signal strength. Spike method was used for testing lanthanides in tap water, river water,

clinical waste samples and welsbach mantle. Analysis of lanthanides was also carried out in MRI contrast gadopentetate dimeglumine. The procedure mentioned for sample preparation is detailed below:

(i) Tap water and river water samples were spiked with 100 mg L^{-1} of Ln(III) ion mixtures containing La(III) + Ce(III) + Dy(III) + Eu(III) for their simultaneous determination. Ln(III) determination in these spiked samples was carried out using the proposed conductometric titration method

(ii) Another sample chosen for real time sample analysis was clinical waste sample collected from Christian Medical College, Vellore. This sample was tested for Gd(III) and spiked with 100mg L^{-1} of Gd(III)

(iii) Welsbach mantle which is used for generating light in gas stoves was also taken for real time analysis using the proposed conductometric titration method. The sample was digested (under exhaust conditions of fume hood) by dissolving in nitric acid followed by evaporation to give precipitates which were dissolved in water to produce aqueous samples.

(iv) Contrast Gadopentetate dimeglumine: The commercially available solution of 0.5M concentration was diluted to prepare a 10^{-3}M solution which was titrated against EDTA.

3.3.1.6.1 Arsenazo method[2]: This method was used to corroborate and check the reliability of the results obtained by conductometry in real time sample analysis. Solutions of varying concentrations of metal ions under study were prepared and their UV-Vis scans were run in presence of chromophore arsenazo III. Different concentrations of AsIII–Ln(III) complexes were plotted against their respective absorbance values to get a calibration curve which was used for measuring concentrations of real time samples. The results obtained were tallied with those obtained by conductometry.

3.3.2 Spectrophotometric Studies

All spectrophotometric studies were conducted in the presence of buffer pH =3.5

3.3.2.1 Spectrophtometric behaviour of AsIII in the presence of Na_4EDTA: AsIII ($5x\ 10^{-5}$M, 1 mL) solution and buffer of pH =3.5 (1 mL) were taken in seven different test

tubes. To each of these test tubes Na_4EDTA (1 mL) solution of different concentration ($5x10^{-5}M$ – $10^{-7}M$) was added. UV-Vis scan of each of these solutions was carried out to study the effect of Na_4EDTA on AsIII.

3.3.2.2 Spectrophotmetric behaviour AsIII–Ln(III) complex: Test tubes each containing AsIII solution ($5x10^{-5}M$, 1 mL) and buffer of pH =3.5 (1 mL) were taken. To each test tube was added La(III) solution of different concentrations ($10^{-4}M$ - $10^{-9}M$) and UV-Vis scans were taken for each solution. Concentration *vs*. absorbance curve was plotted for absorbance at λ_{max}= 538 nm.

3.3.2.3 Spectrophotmetric behaviour arsnazoIII–Ln(III) complex in presence of PACA: The effect of PACA on Ln(III)–AsIII bonding was investigated by using spectrophotometric titrations of lanthanide–arsenazo solutions with PACA solution. A number of experiments were conducted on five lanthanides viz. Ce(III), Nd(III), Dy(III), Tm(III) and Lu(III), and the titration spectra were recorded to study the complexation behavior of PACA with Ln(III) ions in the complexed form with AsIII [i.e AsIII–Ln(III) complexes]. Molarities of all the solutions i.e., AsIII, Ln(III) and PACA were kept same i.e., $5\times10^{-5}M$ for clear comparison. AsIII solution (1 mL) was taken for each titration. To each analyte solution of buffer of pH 3.5 (1 mL) was added. The experiments were divided into two categories as follows:

3.3.2.3.1 Spectrophotometric titrations of Ln(III)-AsIII complexes with different ligands: To start with, a solution containing AsIII solution (1 mL), buffer of pH =3.5 (1 mL) and Ln(III) [Ce(III) / Nd(III) / Dy(III) / Tm(III) / Lu(III)] (6 mL) was taken. The titrations started with successive additions of the ligand solution (1 mL EDTA/ DCTA/ EGTA/ EDTA-OH) to the above solution and continued till ligand added was equal to 1:1 :: Ln(III)–L stoichiometry. After each addition, the solution was subjected to UV-Vis scan in the spectrophotometer. The curves obtained were overlaid and the absorbance at the peak of the complex was followed to anticipate the effect of PACA on AsIII–Ln(III) complexes.

3.3.2.3.2 Spectrophotometric titrations of mixture of AsIII and different ligands with Ln(III): A mixture solution of AsIII (1 mL), buffer of pH =3.5 (1 mL) and ligand solution

[EDTA/ DCTA/ EGTA/ EDTA-OH (6 mL)] was taken. To this solution Ln(III) ion of interest [Ce(III) / Nd (III)/ Dy(III) / Tm(III) / Lu(III)] was added in increments of 1 mL each until the Ln(III)–L stoichiometry became equal to 1:1 i.e up to 6 mL. The results were obtained by superimposing the curves obtained for each scan.

3.4 References

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Polyaminocarboxylic Acid-Lanthanide (III) Complexation Studies by Conductometric Titrations and Quantitative Ion Recognition

All ions in a solution contribute to electrical conductance of the solution. However, contributions of different types of ions to electrical conductance differ and transport number of ion measures the extent to which it contributes to the electrical conductance. Different ions have different transport numbers. Relating conductance of a solution to the contributions from different types of ions is not easy. Hence, conductance measurements is not a specific analytical method for the quantitative analysis of a given ion despite the fact that conductance can be measured with high sensitivity (even the conductance of pure water which is very low, can be measured precisely). Conductometry can, however be used selectively to determine the amount of an analyte by following a titration in which the analyte participates. If the titration reaction involves a change of either the nature or the amount of ions, then there will be a change of electrical conductance during titration. In such cases, the titration may be followed conveniently, using conductometry. Such titration carried out with the use of conductometry is known as a conductometric titration. It has been used for determining water hardness.[1] The use of conductometric technique for determining metal ions and studying their complexation behavior with various ligands is quite common. Copper,[2,4,5] iron,[2] aluminium,[2] chromium,[2] gold,[2] platinum,[2] vanadyl,[2] zirconyl,[2] uranyl,[2] silver,[3] mercury,[3,5] cadmium,[5,6] lead,[5,6] cobalt,[6] nickel,[6] zinc[6] are some of the ionic species that have been determined using conductometric technique.

Scientists have been actively exploring the complexation chemistry of polyaminopolycarboxylic acids (PACA) with f-element cations for over the last five decades. In their coordination complexes lanthanides preferentially exist in trivalent state. This is due to the fact that on ionization the neutral lanthanide metal ions experience different degrees of stabilization in the 4f, 5d and 6s orbitals.[7,8] Their dative bonds are mostly ionic and covalency plays a minor role, except in some arene complexes that contain bulky substituted benzene, or cyclooctatetrenes, the nature of coordination sphere being controlled by a subtle interplay between electrostatic interaction and interligand steric constraints.[7,8] Lanthanides display a range of coordination numbers varying from 6-12, in

their complexes in crystalline as well as solution state, with coordination number 9 being predominant and demonstrating several geometries. Lanthanide ions resemble the alkaline earth ions i.e., they are type A or 'hard' acids which have a strong preference for oxygen donor ligands. In solids it is possible to have coordination via nitrogen, sulphur etc. but in aqueous solution complexation almost always involves substitution of the metal-oxygen bond of solvate waters by a ligand which forms another metal-oxygen bond.

PACA such as Ethylenediaminetertracetic acid and N-(2-hydroxyethyl) ethylenediamine-N,N′,N′-triacetic acid were first used in ion exchange separations of actinides from lanthanides.[9,10] An important characteristic of the f-element cations in aqueous solution is the strong ionic nature of their bonding with ligands, including the PACA. Various reports have confirmed the existence of ionic bonds in Ln(III)–PACA complexes based on data such as small ligand-to-cation charge transfer value.[11,12] This is explained by the fact that vacant 4*f* or 5*f* orbitals of these elements are largely shielded by the higher lying electrons at *s*2 and *p*6 sublevels, which prevent the ligand electron pairs from filling the vacant *f* orbitals.[13] Ln(III) ions interact with PACA by bonding to one or more oxygen atoms as well as nitrogen atoms in the ligand such that it forms a chelate, therefore, rendering the complex greater stability. Thus, PACA form multidentate complexes with lanthanides. The chemistry of lanthanide complexation in solution has been extensively studied and the results of earlier research have been reviewed often.[14-16] Critically selected data for lanthanide complexation with these ligands under study have been used for result interpretation. Figure 4.1 shows the stability constant (log K) values of lanthanides with various PACA.[17] High thermodynamic stability and extreme kinetic inertness of these complexes are due to augmenting effect of basic amino groups, high negative charge of several carboxylate groups and formation of numerous stable five-membered chelate rings with metal ions. This results in high values of stability constants for these complexes. These trivalent cations generally form 1:1 complexes with PACA. These ligands may be tailored to fine-tune the kinetic and thermodynamic stabilities of the resulting complexes according to the application in which they are to be used, e.g., as sequestering agents or as diagnostic tools in medicine. Among the latter applications, the use as contrast agents (CA) for magnetic resonance imaging (MRI) has attracted much attention in recent years.[18]

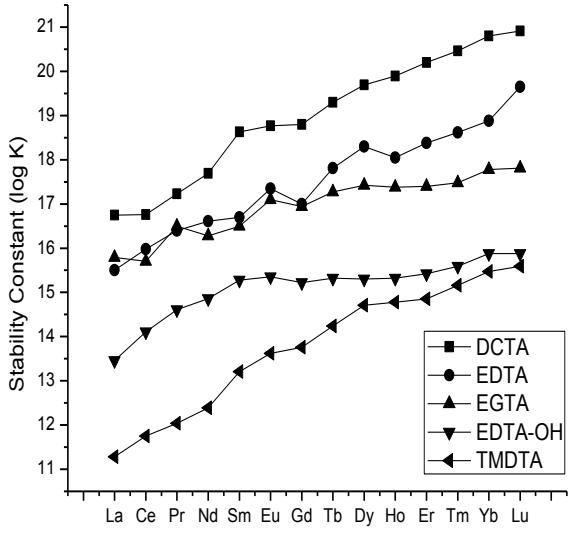


Figure 4.1: Stability constant values of lanthanides with different PACA[17]

4.1 Reagents and Experimental set up

The detailed discussion regarding reagents and experimental set up is given in Chapter-3, research methodology.

4.2 Results and Discussion

4.2.1 Standardization of Parameters for Conductometric Titrations

4.2.1.1 Criteria for Selection of Cell Constant

A two-pole conductometric cell consists of (i) two electrodes, including an anode (positively charged) and a cathode (negatively charged); (ii) an electrolyte solution; and (iii) a battery (current reading detection unit). The amount of current generated is determined by number of ions which in turn indicates the concentration of electrolytes. Due to the polarization effect at the electrode/ electrolyte interface and electrolyte decomposition the electric field over the cross section of a real cell is never homogeneous as a result of which calculating the actual conductivity of the cell is not possible. For this reason, the cell constant is constant only over a limited range of conductivity values.[19] The appropriate value of cell constant for

titration depends on the anticipated level of conductivity of the titration system. In general, a cell constant of 1.0 cm^{-1} was useful for monitoring lanthanide solutions having a concentration range of 1×10^{-2} M or greater, whereas cells with a cell constant of 0.45 cm^{-1} could be used for the titration of 10^{-3} and 10^{-4} M Ln(III) solutions against L1 or L2 with high accuracy and a cell constant of 0.1 cm^{-1} is suitable for 1×10^{-5} M Ln(III) solutions. Table 4.1 shows results obtained for determination of lanthanides using five-ring conductivity probe and two-pole conductivity cell. From the results we can conclude that five-ring conductivity probe is more useful as it displayed wide linearity and a quick as well as stable response.

Table 4.1: Conductometric titration of La (III) *vs.* L1 and L2 using 2-pole and 5-ring conductivity cell

Composition of Titration	**Expected E.P(mL)**	**Observed E.P (mL)**			
		2-pole cond. cell with cell constants			**5-ring cond. cell with cell constant**
		$1.0cm^{-1}$	$0.45cm^{-1}$	$0.1cm^{-1}$	$0.774cm^{-1}$
1×10^{-2} M La(III) *vs.* 1×10^{-1} M L1/L2	5.0	5.0	4.9	4.4	5.0
1×10^{-3} M La(III) *vs.* 1×10^{-2} M L1/L2	5.0	5.0	5.0	5.0	5.0
1×10^{-4} M La(III) *vs.* 1×10^{-3} M L1/L2	5.0	4.8	5.0	5.2	5.0
1×10^{-5} M La(III) *vs.* 1×10^{-4} M L1/L2	5.0	4.5	4.8	5.2	5.0
1×10^{-6} M La(III) *vs.* 1×10^{-5} M L1/L2	5.0	No change in conductivity			

Two-pole conductivity cell suffered from some drawbacks, such as polarization effects at higher conductivities, wall effect caused by stray current, and the effect of varying position of cell in the measuring vessel, which were absent in a five-electrode cell.[20,21] Hence, for different concentrations of solution (1×10^{-1}–1×10^{-7} M), cells of different cell constant values are required to obtain the actual conductance of the solution with accuracy. To study the performance of two-pole and five-ring conductivity probes, conductometric titrations of

various lanthanides were carried out using EDTA(L1) and DCTA(L2) as ligands, the results for which are given in Figures 4.2(a and b) and 4.3(a and b). The study shows that conductivity changes on complexation with L1 and L2 are sufficient for quantitative analysis of Ln(III) ions. Conductometric titrations with ligands (L1/L2) exhibited a special property; i.e., during complexation, very small incremental variation in the conductivity of the solution was seen until the equivalence point (E.P), after which the value of conductivity of the solution increases sharply, as the ligand (L1/L2) added to the solution remain unreacted, thereby increasing the number of current carrying species in the solution. The small incremental variation observed up to the equivalence point is due to the formation of $[Ln(III) - L1]^-$ or $[Ln(III) - L2]^-$ complex and the replacement of H^+ ions with less mobile Na^+ ions in the solution. In Figure 4.2a, for five-ring electrode, we observe that, during the titration of Ln(III) ions with L1/L2, the conductivity trend remains same throughout the titration, however, during the titration of Ln(III) with L1/L2, a dip in the conductivity is observed just after the equivalence point when a two-electrode cell is used [Figure 4.2(b)]. This sudden change in conductivity is not observed with a five-ring electrode, which may be due to polarization of the electrodes in the two-electrode cell. Therefore, further work was carried out using five-ring electrode.

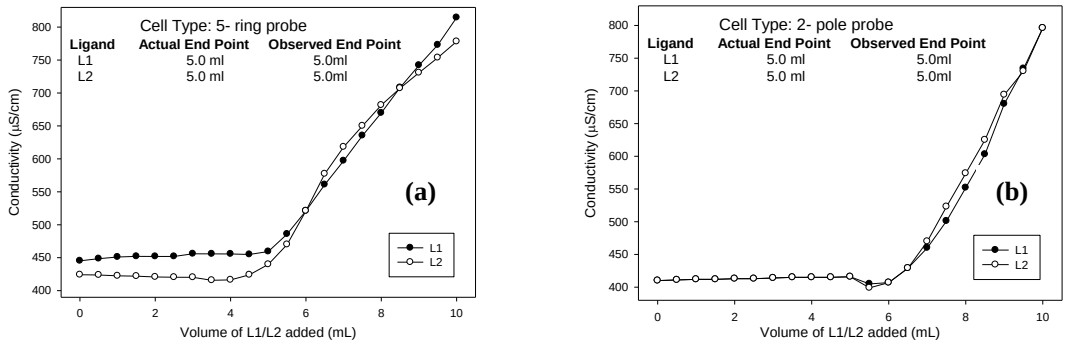


Figure 4.2 (a & b): Conductometric titration curves for 50 mL of Ce(III) (1×10^{-3} M) with L1 and L2 (1×10^{-2} M) in the absence of coligand HIBA using five-ring and two-pole conductivity cells

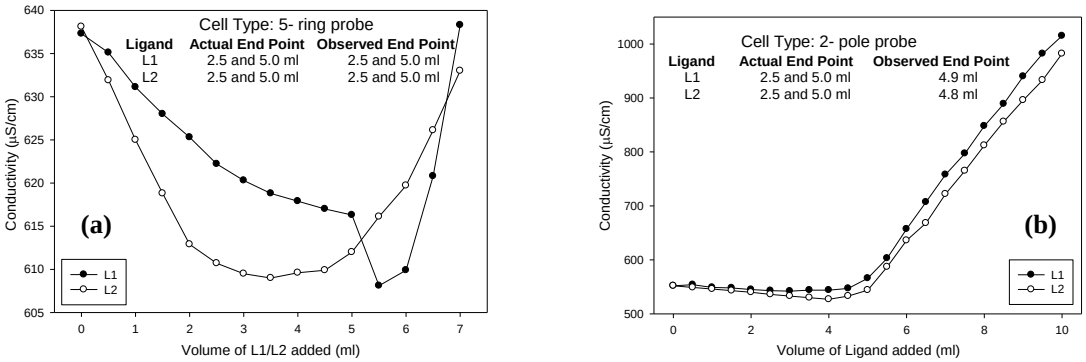


Figure 4.3 (a & b): Conductometric titrations of binary mixtures of lanthanides (25 mL of 1×10^{-3} M Ce(III) + 25 mL of 1×10^{-3} M La(III)) *vs*. 1×10^{-2} M L1 and L2 in the presence of coligand HIBA using five-ring probe and two-pole cell

4.2.1.2 Detection Limit

By direct method: Solutions in the concentration range of 1×10^{-10} M to 1×10^{-1} M were prepared for all lanthanide ions and their conductivity values were recorded as shown in Figure 4.4. The values of conductivity of these solutions ranged from 10 to 16000 mS cm^{-1}, which were plotted against square root of concentration to confirm Kohlrausch's Law and Onsager equation for strong electrolytes.[22] The plots between conductivity and concentration show that the law is applicable over a wide concentration range of 1×10^{-5} M to 1×10^{-1} M. In order to plot these wide ranges we used log/log plots. Curves were drawn between log conductivity and log concentration to find the detection limit of proposed analytical method. The point of intersection of two straight-line portions of the calibration curve was taken as the detection limit and it was found to be 1×10^{-5} M for Ln(III) ions.

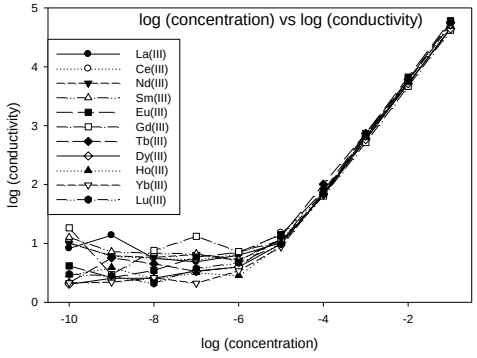


Figure 4.4: Plot of log (concentration) *vs*. log (conductivity) for lanthanides

By conductometric titration method: Conductometric titration method was also used for determination of detection limit. For this Ce(III) ions were conductometrically titrated against ligands L1, L2, L3 and L4. For all the titrations the concentration of ligand taken was about 10-fold to Ce(III) ions. The plots between conductivity *vs*. volume of titration were half sigmoid upto a concentration of 1×10^{-5} M, after which they became parallel to the volume axis [Figure 4.5(a-c)]. From this the detection limit was concluded to be 1×10^{-5} M with respect to the cell constant 0.774 cm^{-1}.

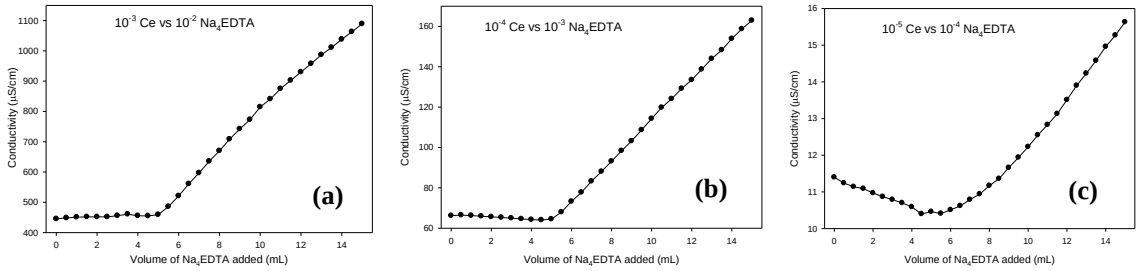


Figure 4.5(a-c): Conductometric titration curves for 50 mL of Ce(III) (1×10^{-3}M – 1×10^{-5}M) with L1 (1×10^{-2}M – 1×10^{-4}M)*

**Similar results were obtained for other ligands*

4.2.1.3 Effect of pH

The apparent stability constants of metal ligand complexes vary with pH of the solution. For each metal ion there exists an optimum pH which gives rise to a maximum value for the apparent stability constant i.e at which the metal-ligand complex is most stable. To study the affect of pH on reaction system conductometric titrations of Ce(III) with EDTA were performed in the presence of buffer at different pH values (Figure 4.6). Results obtained were found to coincide with previous studies and the equivalence point for Ce(III)–EDTA complex was correctly obtained at pH=4. However, it was also observed that the presence of buffer did not affect the equivalence point. This is due to the fact that the initial pH of the solution, which was 3.6, was the optimum for stable complex formation of EDTA with lanthanides. As the titration progresses, up to the equivalence point, the pH of the solution changes only up to 4.0 due to the release of H^+ ions on complex formation with EDTA. However, there was a change in the magnitude of conductivity values that did not cause any significant difference in the equivalence point. Hence, buffer solution was not used in subsequent studies.

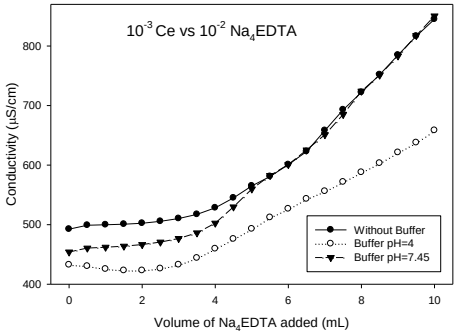


Figure 4.6: Conductometric titration curves for 25mL Ce(III) (1×10^{-3}M – 1×10^{-5}M) with L1 in the presence of various buffers

4.2.1.4 Effect of Temperature

Temperature is one of the most important factors that affect the mobility and, hence, the conductivity of various ions present in the system. An increase in temperature leads to increase in ionic mobility of the ions present in the system. To determine the affect of temperature on the titration system, titration of Ce(III) ion with ligand DCTA (L2) was carried out at four different temperatures i.e. 10, 18, 25 and 30°C. The results obtained for these titrations are given in Figure 4.7. It was observed that an increase in temperature of the reaction system affected neither the complexation of Ce(III) ion with L2 nor the shape of the conductometric titration curve. An increase in temperature merely led to an increase in conductivity of the system. This change in the magnitude of conductivity, however, affected the value of equivalence point to some extent but within tolerance limits. The observed equivalence point coincided with the actual equivalence point at a temperature of 18°C. Hence, for further titrations 18°C was fixed as the reaction temperature and all titrations were performed at 18±0.1°C.

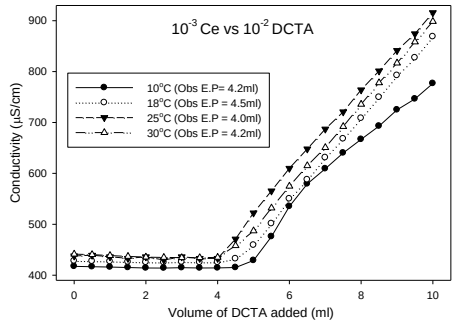


Figure 4.7: Conductometric titration curves for 45mL Ce(III) (1×10^{-3}M) with L2 at different temperatures

4.2.2 Complexation with various Polyaminocarboxylic acids (PACA)

4.2.2.1 Conductometric Titrations Using Ethylenediaminetetraacetic Acid (EDTA) As Complexing Ligand for Lanthanides

Various applications of polyaminocarboxylic acids to volumetric analysis have been described since Schwarzenbach first recognized the potential of EDTA (L1) as an analytical reagent in 1955.[23] Its powerful complexing action and commercial availability make it one of the most widely used ligands for chemical as well as biological applications. Having been used for the determination of more than forty-five elements, it is one of the most important classic reagents for complexometric determination of metal ions in solution, using direct and back-titration procedures. The EDTA complexes of common metal ions can be divided into four groups on the basis of their stability:

a) log K > 20: di, tri- and tetrapositive cations, including Fe^{3+}, In^{3+}, Bi^{3+}, Ga^{3+}, Tl^{3+}, Th^{4+}, Zr^{4+} and Hg^{2+}
b) log K = 12–20: dipositive transition metals, lanthanides (Figure 4.1) and Al^{3+}
c) log K = 7.5–12: alkaline earths and
d) log K < 7.5: alkali metals, Ag^{+} and Tl^{+}.

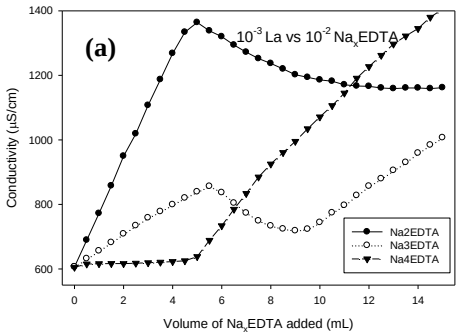
Studies show that cations in the first group can be titrated with EDTA at pH 1- 3 without any interference from cations of the third and fourth groups with no or only slight interference from those of the second group. Cations of the second group can be titrated at pH 4-6 with EDTA without interference from the alkaline earths. Also, the physical chemistry of metal-EDTA equilibria has been examined by several workers and methods for calculating the concentrations of free metal ion at the equilibrium outlined.[24-26]

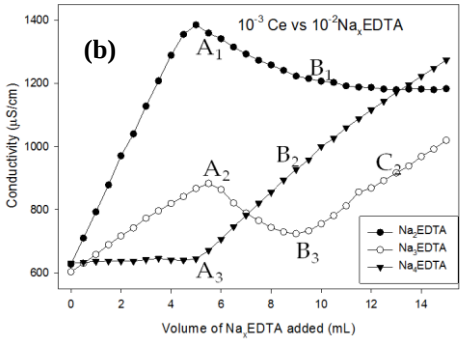
The study of complexation behavior of lanthanides with EDTA was carried out using different forms of EDTA i.e., Na_4EDTA (L1), Na_3EDTA ($L1_i$) and Na_2EDTA ($L1_{ii}$). Although chemical properties of all these forms of EDTA remain the same, however, there conductivity behavior varies markedly due to a difference in the number and nature of current carrying species. Figure 4.8 (a-j) shows the trends observed in the conductometric titration curves of these ligands with 14 lanthanides. From these titration curves we observe:

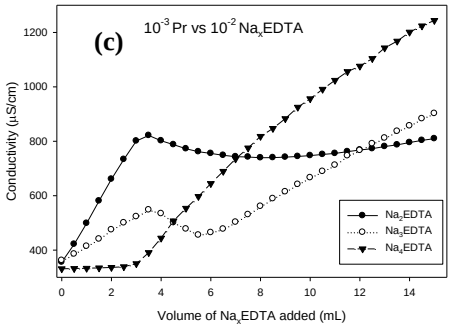
a) Curves for titration with L1 show two distinct features: Conductivity of the solution remains almost constant up to the equivalence point after which the conductivity increases regularly.
b) Titration curves for $L1_i$ exhibits three distinct features: Up to the equivalence point a regular increase in conductivity was observed, followed by a decrease in conductivity to give another equivalence point and then a gradual increase.
c) In case of titration with $L1_{ii}$ two distinct features were observed: In this case, unlike L1, the conductivity of the solution initially increases constantly up to the equivalence point and subsequently decreases slowly.

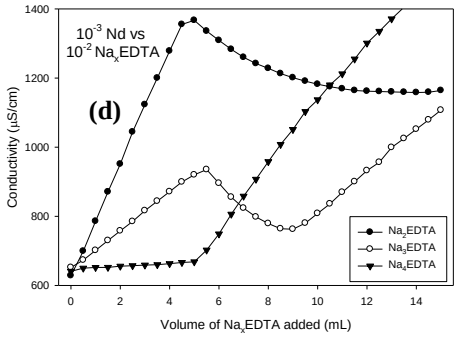
Factors such as the type of species present during the titration, viscosity, dielectric constant, solvation, ion-pair association and proton transfer affect the shape of the titration curve.[27]

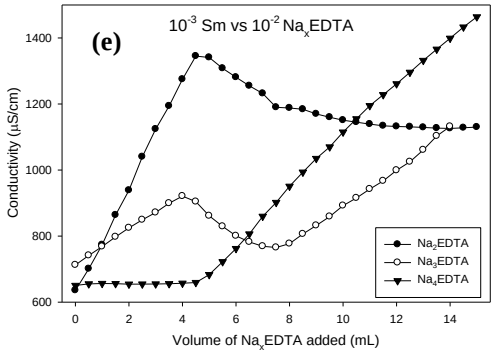
As seen in Figure 4.8(a-j), during titrations the conductivity increases with an increase in EDTA – Ln(III) ratio, involving $L1_i$ and $L1_{ii}$ with Ln(III) metal ions. Trivalent metal ions have a high charge to radius ratio; hence, they are highly solvated.[28] During complexation of $L1_i$ and $L1_{ii}$ with Ln(III), there is a release of H^+ ions at each step till a 1**:**1 stoichiometry of metal – EDTA complex is achieved. After the equivalence point conductivity of the solution starts decreasing resulting in a sharp change in slope of the titration curve at the equivalence point. The decrease in conductivity after equivalence point in case of $L1_{ii}$ is due to the formation of H_2Y from Na_2Y ($L1_{ii}$) added from the burette which results in replacement of $2H^+$ ions with $2Na^+$ ions in solution of very high K_f for the formation of H_4Y. Also, on complexation, EDTA replaces the solvent sheath around the metal ion and as a result, the moving entity becomes less bulky and more mobile. During titration with L1, on the other hand, we observe very small incremental variation in conductivity during complexation i.e till the equivalence point is reached from where on in rises steeply because of the increase in number of current carrying species due to presence of unreacted L1.

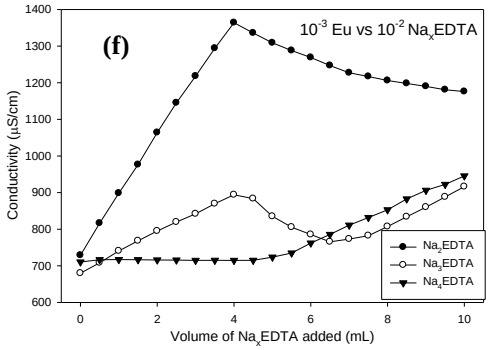

(a)
10^{-3} La vs 10^{-2} Na_xEDTA
Conductivity (µS/cm)
Volume of Na_xEDTA added (mL)
Na2EDTA
Na3EDTA
Na4EDTA

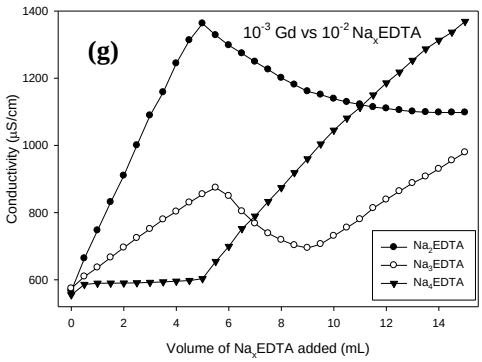

(b)
10^{-3} Ce vs 10^{-2} Na_xEDTA
A_1
B_1
A_2
B_2
C_2
B_3
A_3
Conductivity (µS/cm)
Volume of Na_xEDTA added (mL)
Na_2EDTA
Na_3EDTA
Na_4EDTA

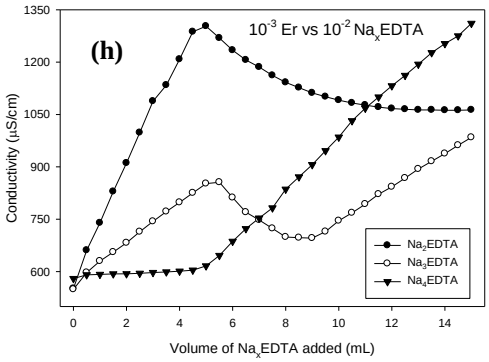

(c)
10^{-3} Pr vs 10^{-2} Na_xEDTA
Conductivity (µS/cm)
Volume of Na_xEDTA added (mL)
Na_2EDTA
Na_3EDTA
Na_4EDTA


10^{-3} Nd vs
10^{-2} Na_xEDTA
(d)
Conductivity (µS/cm)
Volume of Na_xEDTA added (mL)
Na_2EDTA
Na_3EDTA
Na_4EDTA


(e)
10^{-3} Sm vs 10^{-2} Na_xEDTA
Conductivity (µS/cm)
Volume of Na_xEDTA added (mL)
Na_2EDTA
Na_3EDTA
Na_4EDTA


(f)
10^{-3} Eu vs 10^{-2} Na_xEDTA
Conductivity (µS/cm)
Volume of Na_xEDTA added (mL)
Na_2EDTA
Na_3EDTA
Na_4EDTA


(g)
10^{-3} Gd vs 10^{-2} Na_xEDTA
Conductivity (µS/cm)
Volume of Na_xEDTA added (mL)
Na_2EDTA
Na_3EDTA
Na_4EDTA


(h)
10^{-3} Er vs 10^{-2} Na_xEDTA
Conductivity (µS/cm)
Volume of Na_xEDTA added (mL)
Na_2EDTA
Na_3EDTA
Na_4EDTA

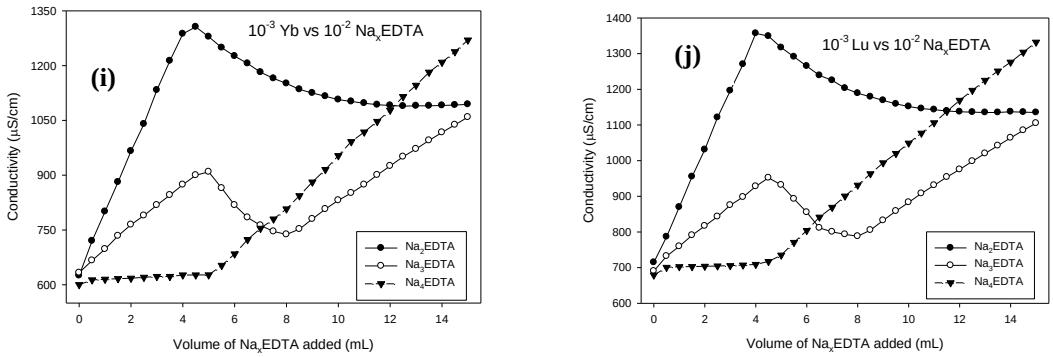


Figure 4.8(a-j): Conductometric titration curves for 50 mL of Ln(III) (1×10^{-3}M) with L1, $L1_i$ and $L1_{ii}$

In some cases, up to the equivalence point, a negligible change in conductance was observed in spite of an increase in $[Ln–EDTA]^-$ complex concentration. This might be due to the fact that the mobilities of $[Ln–EDTA]^-$ complex and the hydrated Ln(III) ion remain same at same concentration. The small incremental variation observed in some cases, before the equivalence point might be due to release of free sodium ions. Various species present in the reaction system at different stages of the titration are shown as a step wise process in Scheme 4.1(a-c). H^+ ions have a marked influence on the conductivity of the system. So, L1 was used for further work as its curve displayed less variation, due to change of H^+ ions in the system, during the course of titration.

Scheme 4.1(a-c): Various species present in the reaction system at different stages for titration of Ln(III) with L1/L2, $L1_i$ and $L1_{ii}$

4.1a: Ln(III) ions with L1/L2 in aqueous medium (Figure 4.8b and 4.13a)

Species present before addition of L_3 (point O): $Ln^{3+} + 3Cl^-$

$\downarrow L_3$ **(Y^{4-})**

Species present at E.P. (point A_3): $4Na^+ + [Ln–EDTA/DCTA]^- + 3Cl^-$

$\downarrow L_3$ **(Y^{4-})**

Species present after the E.P. (point B_3): $3Cl^- + 4Na^+ + [Ln–EDTA/DCTA]^- + L_3$

Y: Anionic form of ligand*

4.1b: Ln(III) ions with $L1_i$ in aqueous medium (Figure 4.8b) [Y*: Anionic form of ligand*]

Species present before addition of L_2 (point O): $Ln^{3+} + 3Cl^-$

$\downarrow L_2$ **(HY^{3-})**

Species present at E.P. (point A_2): **H^+ (solvated)** + $3Na^+ + [Ln–EDTA] + 3Cl^-$

$\downarrow L_2$ **(HY^{3-})**

Species present after the E.P (point B_2): $3Cl^- + 5Na^+ + [Ln–EDTA] + H_2Y^{2-}$

$\downarrow L_2$**(HY^{3-})**

Species present after the E.P. (point C_2): $3Cl^- + 8Na^+ + [Ln–EDTA] + H_2Y^{2-} + L_2$

4.1c: Ln(III) ions with $L1_{ii}$ in aqueous medium (Figure 4.8b) [Y*: Anionic form of ligand*]

Species present before addition of L_1 (point O): $Ln^{3+} + 3Cl^-$

$\downarrow L_1 (H_2Y^{2-})$

Species present at E.P. (point A_1): **$2H^+$ (solvated)** + $2Na^+ + [Ln–EDTA]^+ + 3Cl^-$

$\downarrow L_1$ **(H_2Y^{2-})**

Species present after the E.P (point B_1): $3Cl^- + 2Na^+ + [Ln–EDTA]^+ + H_4Y$

Further the conductometric titrations of mixtures of two or more lanthanides were carried out using L1 as a ligand. The results obtained for these binary mixtures of Ln(III) ions are given in Table 4.2. Some representative graphs are given in Figure 4.9(a-c). From the figures it can be seen that, the trend of conductivity plots for mixture of two lanthanides remain the same as that for a single lanthanide. The difference in the stability constant values of adjacent lanthanides (log K: Ce(III)–EDTA =15.98 and La(III)–EDTA =15.50, values) is very small and this small difference does not craft a noticeable change in the conductivity value. The equivalence point obtained for these mixtures, however, coincides with the total amount of lanthanide ion present in the system irrespective of the number of lanthanide ions. L1, therefore, gives only the amount of total lanthanides present in system, irrespective of the nature of lanthanide ion. Such specificity could be obtained by:

i. either separating the individual lanthanide ions
ii. or using a chelating agent that form complexes of steadily variable strength across the series
iii. or using another comlexing agent as a masking agent

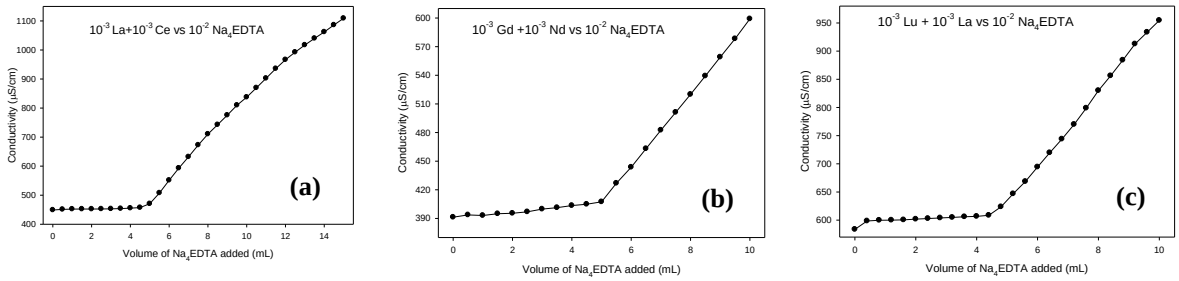


Figure 4.9(a-c): Conductometric titration curves for 25 mL of Ce(III)/ Gd(III)/ Lu(III) (1×10^{-3}M) + 25 mL Ln(III) (1×10^{-3}M) with L1 in absence of HIBA
**Similar results were obtained for other Ln(III)*

Table 4.2: Conductometric titration curves for 25 mL of Ce(III)/ Gd(III)/ Lu(III) (1×10^{-3}M) + 25 mL Ln(III) (1×10^{-3}M) with L1 and L2 in the absence of HIBA

Ln(III)	EDTA*			DCTA*		
	Ce	Gd	Lu	Ce	Gd	Lu
La	5.0	5.0	5.0	5.0	5.0	5.0
Ce	–	5.0	5.0	–	5.0	5.0
Nd	5.0	5.0	5.0	5.0	5.0	5.0
Gd	5.0	–	5.0	5.0	–	5.0
Er	5.0	5.0	5.0	5.0	5.0	5.0
Yb	5.0	5.0	5.0	5.0	5.0	5.0

* Volume of titrant used for equivalence point, mL (Expected E.P. = 5.0 mL)

The separation of neighboring lanthanides is a very difficult and challenging task due to their similar physicochemical properties. To overcome this problem complexing agent α-hydroxyisobutyricacid (HIBA, L_{cl}) was used which acted as a coligand in the system. α-hydroxycarboxylic acids (AHAs) are a class of chemical compounds that consist of a carboxylic acid substituted with hydroxy groups on the adjacent carbon atoms. They have recently been used in analytical separations by ion exchange chromatography or capillary electrophoresis.[29,30] HIBA was first reported as a reagent for the separation of individual lanthanides from there mixture using chromatographic technique in 1956.[31,32] Since then many chelating agents have been tested and used for chromatographic separation of lanthanides but HIBA continues to be the most effective till date. In α-hydroxy carboxylic acids, -OH group has a terminal position, and presence of one carboxylate group promotes the coordination of oxygen atom of the alcoholic -OH group in complexes (Chapter-1,

Figure 1.1). AHAs can form 1:1, 1:2 and 1:3 complexes depending upon concentration availability of AHAs[33,34] and the amount added to titration system was equivalent to the formation of 1:1 complex between Ln(III)–HIBA. During titration, the conductivity decreases because species contributing to conductivity of the solution i.e., released H^+ ions combine with HIBA, as a result of breaking of Ln–HIBA complex and formation of Ln–L1 complex, on addition of L1. The trend in conductometric titration curve for the titration of a mixture of lanthanide ions with EDTA in the presence of HIBA as a coligand is shown in Figures 4.10(a-c) and the results are summarized in Table 4.3. The curves show a decrease in conductivity up to the equivalence point, with a change in slope when the equivalence point of one lanthanide ion is reached and the other lanthanide ion starts to complex with L1, followed by a sudden dip in conductivity near the equivalence point of titration and a subsequent increase in conductivity after the equivalence point has been attained. The decrease in conductivity during the titration is due to uptake of free H^+ ions by HIBA, released from Ln(III)–HIBA complex. Consequently, the titration leads to the formation of new and more stable Ln(III)–EDTA complexes along with the regeneration of HIBA.

Since a change in concentration of free H^+ ions greatly influences the conductivity of any aqueous system, it can be used to follow progress of reactions involving these ions and hence to determine stoichiometry of the Ln(III)–EDTA complexes. HIBA being weaker chelating agent than EDTA is displaced from Ln–HIBA complex (having stability constant values <10) by EDTA to form stronger Ln(III)–EDTA complex (having stability constant values in the range of 15-20). The released deprotonated HIBA takes up the free H^+ ions in the solution resulting in decrease [A to B and B to C in Figure 4.10(a)] in conductivity of solution upto the equivalence point. A further dip observed near the equivalence point region is due to the reaction of L1 with HIBA where HIBA gets deprotonated resulting in the formation of EDTA (H_4Z). The volume of EDTA consumed between points C and D exactly corresponds to the formation of H_4Z. Following this, a sharp and regular increase in conductivity is observed due to the addition of L1 which results in an increase in the number of current carrying species in the system. A schematic representation of various species involved in the titration process is shown in Scheme 4.2.

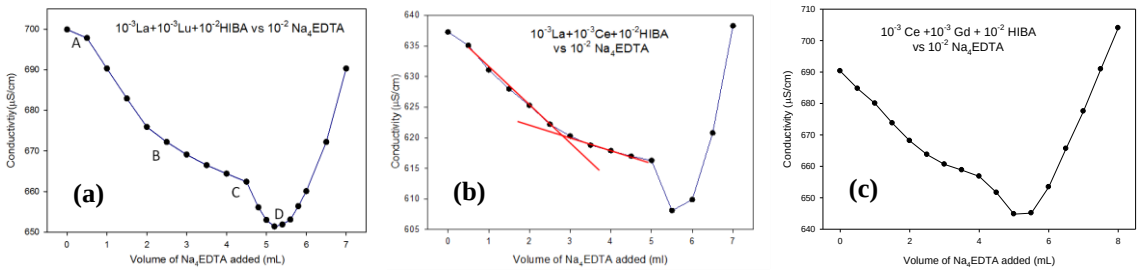


Figure 4.10(a-c): Conductometric titration curves for 25 mL of Ce(III)/ Gd(III)/ Lu(III) (1×10^{-3}M) + 25 mL Ln(III) (1×10^{-3}M) with L1 in presence of HIBA
**Similar results were obtained for other Ln(III)*

Table 4.3: Conductometric titrations for 25 mL of Ce(III)/ Gd(III)/ Lu(III) (1×10^{-3}M) + 25 mL Ln(III) (1×10^{-3}M) with L1and L2 in the presence of HIBA

Ln(III)	EDTA*			DCTA*		
	Ce	Gd	Lu	Ce	Gd	Lu
La	2.5 & 5.0	–	2.5 & 5.0	2.5 & 5.0	–	2.5 & 5.0
Ce	–	2.5 & 5.0	2.5 & 5.0	–	2.5 & 5.0	2.5 & 5.0
Nd	2.5 & 5.0	2.5 & 5.0	2.5 & 5.0	2.5 & 5.0	2.5 & 5.0	2.5 & 5.0
Gd	2.5 & 5.0	–	2.5 & 5.0	2.5 & 5.0	–	2.5 & 5.0
Er	2.5 & 5.0	2.5 & 5.0	2.5 & 5.0	2.5 & 5.0	2.5 & 5.0	2.5 & 5.0
Yb	2.5 & 5.0	2.5 & 5.0	2.5 & 5.0	2.5 & 5.0	2.5 & 5.0	2.5 & 5.0

* Volume of titrant used for equivalence point, mL (Expected E.P. = 2.5 & 5.0 mL)

Scheme 4.2: Various species present in the reaction system at different stages for titration of binary mixture of Ln(III) with L1 in presence of HIBA

Species present before addition of L1 (point A): $Ce^{3+} + La^{3+} + 6Cl^- + HIBA(1\ eq)$

$\downarrow$

$[Ce–HIBA]^+ + [La–HIBA]^+ + \mathbf{2H^+} + 6Cl^-$

$\downarrow L_3$ **(Y^{4-})**

Species present at 1st E.P. (point B): $4Na^+ + [Ce–EDTA]^- + 6Cl^- + [La–HIBA]^+ + \mathbf{H^+}$

$\downarrow L_3$ **(Y^{4-})**

Species present at 2nd E.P. (point C): $6Cl^- + 8Na^+ + [Ce–EDTA]^- + [La–EDTA]^- + L_3 +$ HIBA

Similar conductometric determination procedure was followed for a mixture containing three, four, five as well as six Ln(III) ions. While it was possible to determine up to five

Ln(III) ions present together in the mixture, results for the determination of more than five Ln(III) ions in a mixture were not obtained. Stability constant data dictates that, in a mixture of various lanthanides, the Ln(III) ion having highest stability constant value with the ligand (L1 in this case) should complex first and hence, the first change in slope of the conductometric curve should be due to it, followed by the Ln(III) ion which is immediately next in the order and so on.

4.2.2.1.1 Determination of lanthanides in co-solvent media

Progress in non-aqueous chemistry is restricted by the failure of many tools which are utilized extensively in aqueous solutions. Many fundamental properties of electrolytes have not been investigated in non-aqueous solutions but adequately studied in solvents like water. However, these solvents generally mask many intrinsic solute properties. In this regard, these inert solvents possessing intermediate dielectric constants are particularly useful in studying the natural properties of solutes. The influence of different protic and aprotic solvents on conductometric titrations of Ce(III) with EDTA was studied in mixed solvent systems using 1,4-dioxane (DA), acetonitrile (ACN), Dimethylsulphoxide (DMSO), N,N'-dimethylformamide (DMF), Tetrahydrofuran (THF) and Methanol (MA) as it was expected that their structure, steric bulk, and dielectric constant would affect Ce(III) determination by conductometry.

4.2.2.1.1.1 Optimization of co-solvent concentration: The complexation of ligand (EDTA) with the metal ion [Ln(III)] is significantly influenced by the composition of the solvent system. Thus, for the determination of Ce(III) ions by conductometry, the determination of optimum composition of the co-solvent/solvent system was crucial. To fulfill this purpose six co-solvents at different co-solvent/solvent concentrations were used for determination of Ce(III) ion with EDTA in the presence of α-hydroxy isobutyric acid (HIBA) as a co-ligand, the solvent being double deionized water. The co-solvents included polar solvent: methanol, which is capable of accepting as well as donating electrons through hydrogen bond and other co-solvents which were polar aprotic solvents like ACN, DMSO, THF and DMF and a non-polar aprotic solvent: DA, which are capable of donating electrons through hydrogen bonds. The results obtained for these are shown in Figures 4.11(a-d). The

dielectric constants of all these co-solvents are lower than that of water; therefore, the addition of any one of these to water decreases the dielectric constant of the resultant solution.[35] On increasing the amount of co-solvent (ACN and DA) in the water system, its dielectric constant decreases considerably and ion pair association becomes more favorable.[36,37] This is due to an increase in pK_w of water, as the amount of 1,4-dioxane in the dioxane/water system increases. In co-solvent/ solvent system, the dissociation ability of Ce(III)–HIBA complex (as well as EDTA) decreases as the ratio cosolvent/solvent increases. This behavior is supported by Bjerrum's theory of ion-pair association,[38] according to which the ionization of complex/ligand decreases as the aqueous phase takes on a more organic character. Hence, in consistence with the available literature and the results obtained we can conclude that an increase in co-solvent/solvent concentration in the system leads to a decrease in the dissociation of EDTA as well as Ce(III)–HIBA complex due to which the complete displacement of HIBA by EDTA in Ce(III)–HIBA complex becomes difficult.

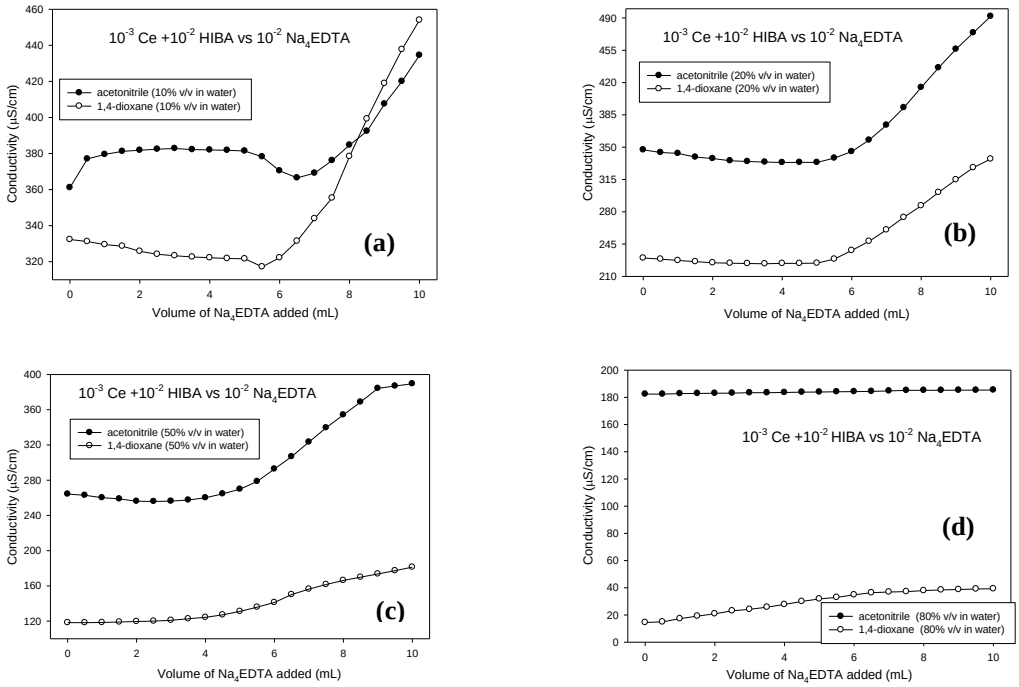


Figure 4.11(a-d): Conductometric titration curves for 1×10^{-3}M Ce(III) *vs* 1×10^{-2}M Na_4EDTA in presence of HIBA in co solvent /water media (co solvents: 1,4-dioxane and acetonitrile) (a)10% v/v (b) 20% v/v (c) 50% v/v (d) 80% v/v

When the concentration of co-solvent becomes >50%, it affects the dielectric constant of the medium to such an extent that it becomes impossible for EDTA to lose its four sodium ions to create sites for complexation with CeIII) ion and also dissociation of Ce(III)–HIBA complex becomes difficult, hence no equivalence point is observed at these co-solvent concentrations. This peculiar behavior is observed due to an increase in tendency of the ionic species to exist as ion pairs. An increase in the amount of DA in DA/water system decreases the dissociation of HIBA (increases the pKa). This is validated by the fact that at different concentrations of DA as 0%, 30% and 50%, the respective values of pKa of HIBA are 3.748±0.004, 4.535±0.008 and 5.21±0.01.[39] This increase in pKa with an increase in concentration of 1,4-dioxane is the net result of increase in solvation and ion-dipole interactions in the medium. Although, well defined equivalence point curvature at 1:1 stoichiometry of Ce(III)–EDTA is observed for co-solvent concentrations below 50% in conductometric plots indicating strong complexation of Ce(III):EDTA. Nevertheless, the conductometric titration curve for co-solvent concentrations above 50% show only small increase in conductivity values, without any indication of change in curvature of slope, at any volume of EDTA added, owing to the incremental addition of EDTA in titration vessel which only slightly increases the number of current carrying species in the titration vessel resulting in an increase in conductivity. From the results summarized in Table 4.4 for the titration of 1×10^{-3}M Ce (III) with 1×10^{-2}M Na_4EDTA in the presence of 1×10^{-2}M HIBA, it was observed that accurate results were obtained for co-solvent compositions from 10-30% for DA and the deviations seen in case of acetonitrile are within tolerance limit. These deviations from equivalence point, however, start increasing as the amount of co-solvent in the system is increased to 40%. At co-solvent concentrations >40%, increase in ion pair association is resumed in the system, which itself is a result of decreasing dielectric constant of the medium, and hence becomes dominant. From the data shown in Table 4.4 it can be concluded that 10%, 20% and 30% co-solvent compositions of the system display maximum accuracy in conductometric determination of cerium. If these co-solvent concentrations are examined closely (Figure 4.11a), a sudden decrease in conductivity can be spotted (dip in the conductometric titration curve) at the equivalence point in case of 10% co-solvent concentration, which is similar to that observed for conductometric titrations of 1×10^{-3}M

Ce(III) + 1×10^{-2}M HIBA *vs.* 1×10^{-2}M Na_4EDTA in pure aqueous media. This 'dip', due to reduction in the number of free H^+ ions in the system, disappears as the concentration of co-solvent is increased to ≥ 20%. Hence, 20-30% of co-solvent composition was found to be optimum for Ce(III) determination by conductometry without any loss of accuracy of equivalence point. Therefore, further study was carried out at 20-30% co-solvent concentration.

Table 4.4: Conductometric titrations of 1×10^{-3}M Ce(III) + 1×10^{-2}M HIBA *vs.* 1×10^{-2} M Na_4EDTA at various co-solvent/solvent compositions

Composition of the analyte and reagent taken for titration	**Concentration of co-solvent (%v/v)**		**Observed Equivalence Point (mL)***	
	Acetonitrile	**1,4-dioxane**	**Acetonitrile**	**1,4-dioxane**
50mL 1×10^{-3}M Ce(III) + 5mL of 1×10^{-2}M HIBA *vs.* 1×10^{-2}M Na_4EDTA	10	10	5.2	5.0
	20	20	5.3	5.0
	30	30	5.3	5.0
	40	40	4.4	5.8
	50	50	4.3	4.0

* Volume of titrant used for equivalence point, mL (Expected E.P. = 5.0 mL)

4.2.2.1.1.2 Nature of co-solvent system: Having established the optimum solvent system composition for Ce(III) determination, studies were conducted in the presence of other lanthanides and interfering ions in different co-solvent media.

Conductometric titrations of Ce(III) ion with EDTA were carried out in the presence of HIBA (as co-ligand) in purely aqueous media at 291.15 K. Figure 4.8(b), demonstrated that the curve obtained was a combination of two linear segments with a well-defined change in curvature at 1:1 Ce(III)–EDTA stoichiometry, which suggests formation of relatively strong complexes. Figure 4.11(b) and 4.12(a-d) show the plots for titration of 1×10^{-3}M Ce(III) *vs.* 1×10^{-2}M Na_4EDTA in the presence of HIBA in different co-solvent/solvent (20% co-solvent) media. Initially, the formation of Ce(III)–HIBA complex releases H^+ ions in solution with sudden increase in initial conductivity of the solution. As the titration against EDTA is started, it is expected that the conductivity of the solution should decrease because of the uptake of free H^+ by the released HIBA, but it is observed that this decrease is much less than that observed in case of pure aqueous media. This behavior can be attributed to the

solvation of these free H^+ ions by the co-solvent (e.g DA, ACN, etc.) molecules, which are polar in nature, resulting in decreased mobility of H^+ ions. This hypothesis also explains why free H^+ ions present in the conductance vessel at the start of titration did not contribute as much to conductivity of the solution in co-solvent/solvent system as they did in purely aqueous media.

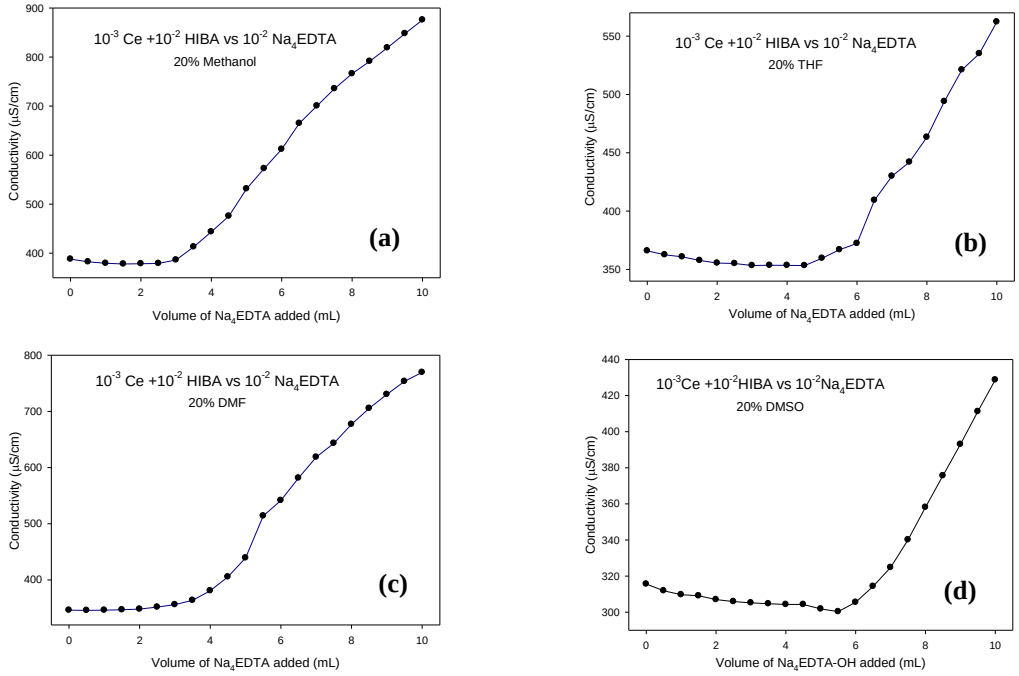


Figure 4.12(a-d): Conductometric titration curves for 1×10^{-3}M Ce(III) *vs*. 1×10^{-2}M Na_4EDTA in presence of HIBA at 20% (co-solvent) concentration (a) MA (b) THF (c) DMF (d) DMSO

Preliminary measurements of molar conductivities of Ce(III)–HIBA solutions in aqueous and co-solvent media suggested that, the conductivity values in co-solvent/solvent media are much lower than those in pure aqueous media indicating that possibly some interaction takes place between Ce(III)–HIBA complex and the co-solvent molecules. For all the solvents in general, conductivity of the initial titration mixture increases as the proton affinity of the co-solvent decreases, (except for DMF, which shows unexpected behavior) proton affinities of DMSO, DMF, ACN, THF, MA and water being 884 µS, 212 µS, 788 µS, 790 µS, 761 µS and 697 µS, respectively, because the H^+ ions released by HIBA are solvated by co-solvent molecules and hence their mobility decreases. Therefore, in the titration vessel, before start of the titration, proton affinity of the co-solvent is dominating factor that determines the

conductivity of solution. As we proceed with the titration, conductivity order is also influenced by factors other than proton affinity of the co-solvent. Factors including the dielectric constant of the medium influence the system. But it is also evident that factors other than dielectric constant of the medium have to be invoked to explain the solution behavior. Nature of the solvent, nature of aquated ion and steric effect of the solvent also play important roles. Interplay of ion association and solvation is seen when we examine the results. According to Burgess the structure around an aqueous metal ion includes several "zones" of hydration or hydration spheres.[40] In the primary hydration sphere, the water molecules are directly bound to the Ce(III)–HIBA complex. Here, ion-dipole interactions dominate and the size of Zone A is determined by the size and charge of the Ce(III)–HIBA complex. In this zone, ion-dipole interactions play basic role in the orientation of water molecules and hydrogen bonding interactions are not important. The second hydration sphere or Zone B consists of water molecules that are ordered due to electrostatic field of the charged Ce(III)–HIBA complex but here the dominating interaction is hydrogen bonding to water molecules of Zone A. Finally, Zone C consists of hydrogen bonded disordered water molecules that have higher entropy than the three dimensional order of the bulk solvent.

When a second solvent i.e., the co-solvent, is added it affects the system in following ways; firstly, by direct interaction i.e., via hydrogen bonding or ion-dipole interactions and secondly, by indirect interaction i.e., by providing a field that impacts ion-ion or ion-dipole interactions. Hence, when co-solvent is added to the pure aqueous system it would disrupt the organization of water molecules around the Ce(III)–HIBA complex. If this co-solvent can participate in hydrogen bonding and is not sterically hindered, it would replace a water molecule in any of the zones of hydration. In contrast, if the second solvent is a larger molecule than water, it would disrupt the water structure around metal ion to a greater extent. If the second solvent is not capable of donating or accepting charge through H-bonding, it would disrupt the whole hydrogen bonding network of the water molecules. Literature suggests that the degree of preferential solvation in the first hydration sphere of solvated lanthanides by various co-solvents in a co-solvent/solvent system is in the order ACN < THF < MA < water < DMF < DMSO.[41] In addition to this, the previous reports have shown that europium is preferentially solvated by water in the first solvation sphere in

mixed DA/water mixtures up to 90%.[42] Further, the complexation of europium and terbium with HIBA in mixed methanol/water media has also been studied[43,44] and it has been established that the trend exhibited by the stability values of Eu(III)–HIBA complexes in mixed methanol/water system is similar to that of 1,4-dioxane/water media. Understanding the behavior of EDTA in a co-solvent/solvent media is needed prior to examining the effect of these water-miscible co-solvents on Ce(III)–EDTA complexation. The donor properties of the solvents are of no importance for the solvation of anions, which are donors themselves due to which the solvation of anions show quite different trends from those observed in case of the cations.[45] As in the interaction of EDTA with co-solvent/solvent, system only electrostatic forces are formed between the EDTA and the dipoles of the solvent molecules surrounding it, apart from the substantially weaker London forces which are a result of solvation.

From the results the following can be concluded about the behavior of complexation of Ce(III) with EDTA by displacing HIBA: DMF and DMSO replace water in the first co ordination sphere around the Ce(III) ions[40] due to which the solvation structure of the Ce(III)–HIBA complex is altered and the ligand has to replace the co-solvent molecules to bind to the Ce(III) ions rather than water molecules. Therefore, in case of DMF and DMSO the observed equivalence points of the system are poorer than other aprotic solvents. Methanol, acetonitrile, THF and 1,4-dioxane do not replace water in the first coordination sphere[41] and hence do not have much effect on the solvation structure of the Ce(III)–HIBA complex and so the conductivity. The magnitudes of conductivity in these cases are lower than those of pure aqueous media due to the reduced dielectric constant of these co-solvents [compare conductivity of titration mixture at zero titrant volume, Figures 4.11(b) and 4.8(b)].

Methanol being protic in nature is an exception to this behavior. It shows highest value of conductivity as compared to other co-solvents/solvent systems except pure aqueous media where the dielectric constant value comes into play. The dielectric constant of methanol (μ= 32.7) is almost half of water due to which the dissociation of ions is low and hence shows lower conductivity values than pure aqueous media. In case of methanol, it was observed

that the value of conductivity and hence, the curvature of conductometric titration curve increases dramatically after 3mL which was due to the free H^+ ions of CH_3OH present in the system. The free H^+ ions in the system affect the conductivity to such a large extent that it suppresses the relatively small change in conductivity at the equivalence point. Tendency to neutralize charge through ion pair formation becomes important when the dielectric constant is lower than 10 and hence, the stabilities of neutral complexes increase dramatically at these values of dielectric constant.[45]

THF and DA have the lowest dielectric constant values (μ = 2.2 and 7.58, respectively) and hence form strong ion pair associations with solvent molecules which is the dominating factor in these co-solvent /water systems. It is expected that during complexation of EDTA with Ce(III) after displacing HIBA from Ce(III)–HIBA complex, the EDTA molecules enter the first solvation sphere by replacing water, whereas 1,4-dioxane is unable to do so and hence, it does not involve in complexation process of EDTA. In case of THF, the conductivity values are not as low as expected from the low dielectric constant valued solvents. The low dielectric constant leads to the formation of ion pairs but due to low value of proton affinity, the free H^+ ions in the system show high mobility and hence, higher conductivity. Table 4.5 and 4.6 summarize the results for the determination of Ce(III) alone and in the presence of Lu(III) in different co-solvent/solvent systems. Since, the results in presence of co-solvents like THF, DMF and MA exhibited large deviation from those expected; they were not used for the determination of cerium in the presence of interfering ions. The results for the determination of cerium in presence of interfering ions in different co-solvent/solvent systems are given in Table 4.7. The reaction composition for the following results was 1×10^{-3}M Ce(III) + 1×10^{-2}M Z + 1×10^{-2}M HIBA *vs*. 1×10^{-2}M Na_4EDTA (where Z = interfering ion). Hydrolysis of Al(III) is a slow process which interferes with the determination of lanthanides in presence of Al(III) in purely aqueous media (Pages 90-92). In 20% DA media the availability of free -OH ions is reduced drastically, as compared to purely aqueous media, due to strong ion pair association and hydrogen bonding between water molecules and 1,4-dioxane molecules. As a result of this hydrolysis of Al(III) is restricted to a certain extent and this effect helps in quantifying both Ce(III) and Al(III) simultaneously in 20% DA media.

From the results in Tables 4.5, 4.6 and 4.7 it can be seen that most accurate results were obtained in case of pure aqueous media. Hence, it can be concluded that pure aqueous media was the best solvent for the determination of cerium by conductometry though 20% 1,4-dioxane media could also be used.

Table 4.5: Determination of Ce(III) in different co-solvent/solvent systems

Co-solvent	**Observed Equivalence point Volume (mL)****		
	1×10^{-3} Ce(III) $+1\times10^{-2}$ HIBA *vs*. 1×10^{-2} Na_4EDTA		
	10% co-solvent	20% co-solvent	30% co-solvent
Water*	5.0	5.0	5.0
1,4-dioxane	5.0	5.3	5.0
Acetonitrile	5.5	5.6	5.5
DMSO	4.0	2.7	4.0
THF	4.0	4.5	3.5
DMF	3.9	3.5	2.6
MA	3.9	3.0	2.5

* Water was taken as solvent
** Volume of titrant used for equivalence point, mL (Expected E.P. = 5.0 mL)

Table 4.6: Determination of Ce(III) in the presence of Lu(III) in different co- solvent/ solvent systems

Composition of analyte and reagent taken for titration	**Co-solvent**	**E.P Observed (mL)****
1×10^{-3}Ce(III) $+1\times10^{-3}$Lu $+1\times10^{-2}$ HIBA *vs*. 1×10^{-2} Na_4EDTA (co-solvent 20%)	Water*	2.5, 5.0
	Acetonitrile	1.7, 5.3
	DMSO	—
	1,4-dioxane	2.2, 5.0
	THF	6.5
	DMF	4.5
	MA	2.3, 4.4

*Water was taken as solvent
**Volume of titrant used for equivalence point, mL (Expected E.P. = 2.5 mL, 5.0 mL)

Table 4.7: Determination of Ce(III) in the presence of interfering ions in different co-solvent/solvent systems (20% co-solvent)

Composition of Titration System							
1×10^{-3}Ce(III) +1×10^{-3}Z + 1×10^{-2} HIBA *vs*. 1×10^{-2} Na_4EDTA* (co-solvent 20%)							
Co-Solvent	**Interfering Ion (Z)**						
	Al(III)	Ca(II)	Co(II)	Cu(II)	Mg(II)	Mn(II)	Pb(II)
Water*	5.5	2.5, 5.0	2.5, 5.7	1.5, 5.5	2.5, 5.0	2.9, 6.0	5.0
AN	4.5	3.1	2.7, 5.5	2.2, 6.0	2.4, 5.5	3.0	2.0, 4.5
DMSO	3.5, 5.0	2.5, 7.0	2.5, 5.0	2.5	X	4.5	5.0
DA	2.9, 5.5	3.0	2.0, 4.5	2.3, 5.5	2.5	2.5, 5.5	2.5, 5.5
MA	7.0	2.5	2.0, 5.0	3.0	X	3.0, 5.0	2.5

*Water was taken as solvent
Volume of titrant used for equivalence point, mL (Expected E.P = 2.5, 5.0 mL)
X*: No equivalence point obtained*

4.2.2.2 Conductometric Titrations Using *Trans*-1,2-Diaminocyclohexane-N,N,N′,N′-tetraacetic Acid (DCTA) As A Complexing Ligand For Lanthanides

A strong metal−ligand interactions in the metal–EDTA and metal–DCTA complexes can be attributed to two sources first being six strong donor atoms in EDTA/DCTA (two nitrogen and four oxygen) that surround the metal ion in the complex in order to achieve the maximal number of possible donor – acceptor interactions and secondly, the anionic character of the ligand that contributes to the stabilization of the complex.[46] Four carboxylate oxygens, each carrying a negative charge, can establish a strong electrostatic attraction with the captured metal ion and, hence, form complexes of different stabilities with different lanthanides.[47] The structural difference between EDTA and DCTA arises from the fact that the ethylene backbone, connecting the two nitrogen atoms, in the former is replaced by cyclohexane ring in the latter (Chapter-1, Figure 1.1). As expected, the replacement of the two bridging methylene groups connecting the two nitrogen donors of EDTA with a cyclohexylene bridge leads to substantial increase in complex stability, as measured by the formation constants, log K**,** of the complexes formed for DCTA (Figure 4.1). This increase in stability can be credited to the rigid cyclohexane ring of *trans*-DCTA that holds its two nitrogens in *trans* arrangement required for coordination to metal ions. In EDTA, by juxtaposition, the low-

energy form of the free ligand is skew, and considerable energy must be expanded in transforming it to the *trans* form required for complex formation. In general, it is expected that DCTA chelates would be more stable due to the increased basicity of the nitrogen atoms and more favorable entropy change upon chelation of the metal ions with DCTA due to the preorientation of the nitrogen atoms.[48-50]

Stability constant values of the lanthanide–L1/L2 complexes (Figure 4.1) largely increase along the lanthanides series. From the stability constant values of Ln(III)–L1/L2 complexes,[51] it can be concluded that DCTA is a stronger complexing agent than EDTA. The log K values increase from 16.26 for the lanthanum complex to 21.51 for the lutetium complex. Consequently, there is no free rotation about the bonds between the nitrogen atoms. A part of the effect of stabilization in cyclohexane ring is related to the presence of charged acetate groups on EDTA, which stabilize the skew relative to the *trans* conformer by electrostatic repulsion.

A quantitative study of interaction of lanthanides with L2 was carried out by performing conductometric titrations of lanthanides using L2 as a ligand. Some typical results are shown in Figures 4.13(a-c) (results continued in Table 4.8) which demonstrated that conductivity changes on complexation with L2 were sufficient for quantitative analysis of individual lanthanide (III) ions. Conductometric titration curves with ligands, L2 exhibited a trend similar to L1, i.e., during complexation, a very small incremental variation in the conductivity of the solution was witnessed until the equivalence point, after which the value of conductivity of the solution increased sharply. The small incremental variation observed up to the equivalence point was a result of formation of $[Ln(III)–L2]^-$ complex and the replacement of highly mobile H^+ ions by less mobile Na^+ ions in the solution. The increase in conductivity after the equivalence point was attained was due to ligand L2 added to the solution which remained unreacted, thereby increasing the number of current carrying species in the solution. Scheme 4.1a gives various species present in the reaction system at different stages of the titration.

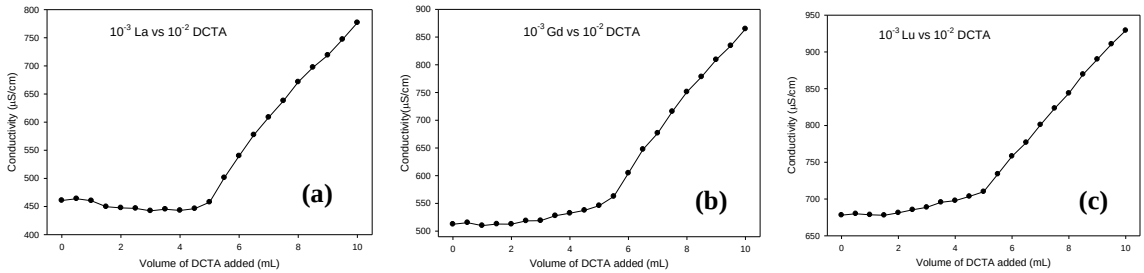


Figure 4.13(a-c): Conductometric titration curves for 50 mL of Ln(III) (1×10^{-3}M) with L2
**Similar results were obtained for other Ln(III)*

Table 4.8: Results for conductometric titration curves for 50 mL of Ln(III) (1×10^{-3}M) with L2, L3 and L4

Ln(III)	DCTA*	EGTA*	EDTA-OH*
La (III)	5.0	4.5	5.5
Ce (III)	5.0	4.5	5.5
Nd (III)	5.0	4.6	5.5
Sm (III)	5.0	3.2	5.5
Eu (III)	5.0	4.5	5.9
Gd (III)	5.0	5.5	6.0
Tb (III)	5.0	4.7	5.4
Dy (III)	5.0	4.7	5.6
Ho (III)	5.0	4.6	6.0
Er (III)	5.0	4.7	5.6
Yb (III)	5.0	4.5	5.6
Lu (III)	5.0	4.0	5.5

*Volume of titrant used for equivalence point, mL (Expected E.P = 5.0 mL)

Further, conductometric titrations of binary mixtures of Ln(III) ions were carried out using L2 as a ligand. The results obtained [Figures 4.14(a-c) and Table 4.2] were analogous to those obtained with L1 i.e., a single equivalence point was obtained, the trend of the curve, too, remained the same.

The equivalence point corresponded to the total Ln(III) ion concentration in binary mixture of different Ln(III) ions. Moving ahead on similar lines as L1, HIBA was used as a co-ligand for the simultaneous determination of Ln(III) ions in their binary mixtures. The results obtained were remarkable [Figure 4.15 (a-c) and Table 4.3]. It was observed that the

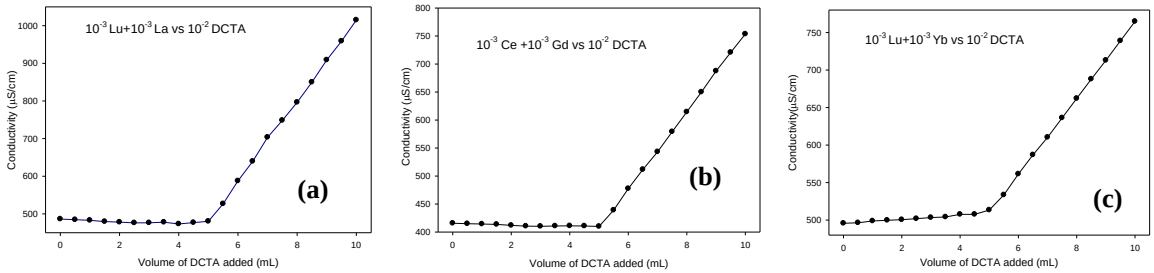


Figure 4.14(a-c): Conductometric titration curves for 25 mL of Ce(III)/ Gd(III)/ Lu(III) (1×10^{-3}M) + 25 mL Ln(III) (1×10^{-3}M) with L2 in the absence of HIBA
**Similar results were obtained for other Ln(III)*

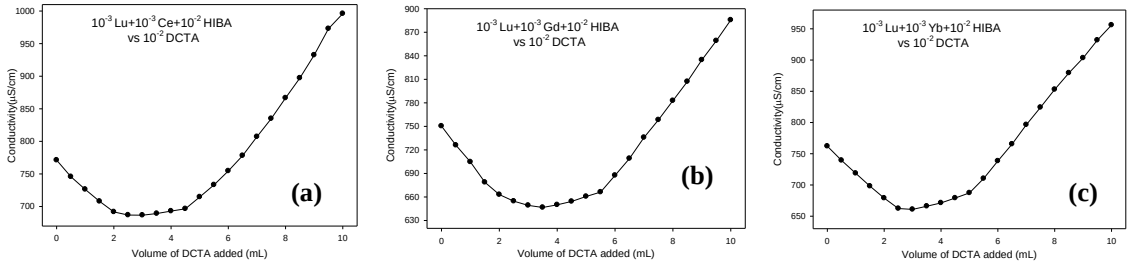


Figure 4.15(a-c): Conductometric titration curves for 25 mL of Ce(III)/ Gd(III)/ Lu(III) (1×10^{-3}M) + 25 mL Ln(III) (1×10^{-3}M) with L2 in the presence of HIBA
**Similar results were obtained for other Ln(III)*

trend of conductometric titration curve for the first equivalence point, corresponding to the formation of a 1:1 Ln(III)–L2 complex followed the same trend as that for the formation of Ln(III)–L1 complex, when L1 was used as a ligand i.e., the conductivity decreased up to the first equivalence point. However, the decrease in case of L2 was more marked as compared to L1. As observed in Figure 4.3a, the large decrease (30 μS) in the case of L2 compared to relatively less decrease (15 μS) for L1 can be explained on the basis of their respective structures. L2 because of *trans*-substituted cyclohexane groups is likely to show more rigidity on complexation than the corresponding change in the case of L1, which is linear in structure and less rigid as compared to L2. This rigidity of the chelate ring is not only due to the presence of cyclohexane bridge but also due to the ability of remaining donor groups of the ligand to get oriented for coordination to metal ions of differing sizes.[52] Schwarzenbach *et al*.,[53] reported, in their studies of the complexing properties of *trans*-DCTA that the effect of the cyclohexylene bridge on stability of *trans*-DCTA relative to EDTA complexes appeared to be dependent on the size of the metal ion.

After the first equivalence point, the slope of the conductometric titration curve illustrated a larger difference for L2 as compared to L1. During this phase of the titration, the second Ln(III) ion present in the system formed Ln(III)–L2 complex. Here it was observed that the conductivity first decreased, stayed almost constant, and then increased until the second equivalence point corresponding to the formation of 1:1 Ln(III)−L2 complex. The results obtained for the determination of binary mixtures of lanthanides were more clearly and distinctly marked for L2 than for L1. The cyclohexane bridge, therefore, proved to be a useful tool in achieving higher selectivity.

4.2.2.3 Conductometric Titrations Using Ethylene glycol-bis(2-aminoethylether)-N,N,N´,N´-tetraacetic Acid (EGTA) as Complexing Ligand for Lanthanides

Another polyaminocarboxylic acid, related to EDTA is EGTA (L3). Due to its favorable geometry of the donor group it forms stable binary complexes with many metal ions and finds enormous applications in medical and biological fields. Having much higher affinity for calcium than for magnesium ions, it is one of the most commonly used chelates in biological research and widely used for making buffer solutions that resemble the environment inside living cells where calcium ions are usually at least a thousand fold less concentrated than magnesium. EGTA has also been used experimentally for the treatment of animals with cerium poisoning and for the separation of thorium from the mineral monazite. These practical applications made EGTA our next choice of PACA ligand for the conductometric determination of lanthanides.

Conductometric titrations of Ln(III) ions with L3 were carried out, the results for which are shown in Figures 4.16(a-c) and Table 4.8. It was spotted that the trend of the titration curves in this case was similar to that of L1 and L2 i.e., there was an incremental increase in conductivity up to the equivalence point followed by which the conductivity of the solution shoots up due to the addition of L3. The incremental increase initially, as explained earlier, was due to complexation of L3 with Ln(III) by displacing the solvent sheath around it resulting in the formation of $[Ln(III)–L3]^-$ complex and the introduction of Na^+ ions to the system in place of initially present H^+. From the start of the titration until the equivalence point was reached the uptake of free Ln (III) ions from, the solution was compensated for by the release of Na^+ ions, resulting in only incremental increase in conductivity. After the

equivalence point had been reached, no further Ln(III) ions were available to complex with L3 and any more addition of L3 only resulted in the increase of $L3^{4-}$ and Na^{+} ions in the solution. Hence, addition of L3, after the attainment of equivalence point only resulted in increase in the number of current carrying species in the mixture resulting in a sharp increase in the conductivity values. This resulted in a sharp change in the slope of the conductometric titration curve after the equivalence point due to which the amount of Ln(III) ion present could be easily determined. It was, however, observed that the equivalence points obtained in case of ligand L3 showed a deviation from the actual equivalence points by a factor of about ±0.5mL i.e. a deviation of 10% in case of all lanthanides.

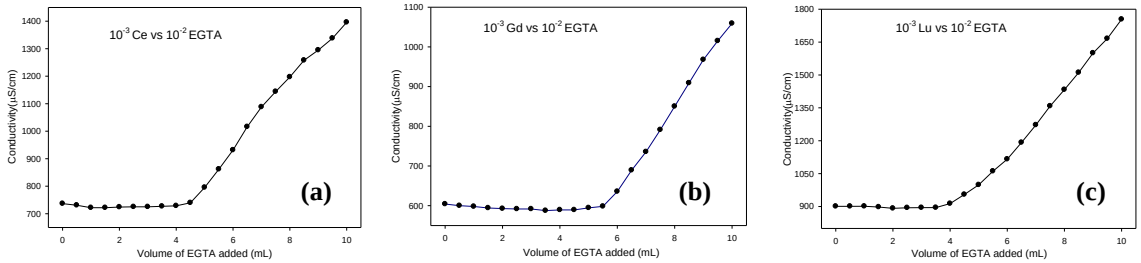


Figure 4.16(a-c): Conductometric titration curves for 50 mL of Ln(III) (1×10^{-3}M) with L3
**Similar results were obtained for other Ln(III)*

The determination of binary mixtures of lanthanides with L3 was carried out, the results for which are shown in Figures 4.17(a-c) and Table 4.9. Similar to L1 and L2, we observed that the nature of the titration curve remained the same as for single lanthanide ion and the equivalence point corresponded to the total concentration of lanthanide ions present in the solution irrespective of the number or nature of lanthanide ions present. Small difference between the stability constants (≈0.1) of different lanthanides made it difficult for the ligand to provide separate equivalence points for different lanthanides present.

Therefore, to increase the specificity, of the ligand the same procedure was followed as for L1 and L2 and carried out the titrations in presence of HIBA, acting as a co-ligand (Figure 4.18 a-c). The curves obtained were V-shaped with a broad tip, although two equivalence points were obtained but the error in determination of each lanthanide ion was not in the permissible limit. Lanthanide cations behave as hard Lewis acids and bind most strongly to

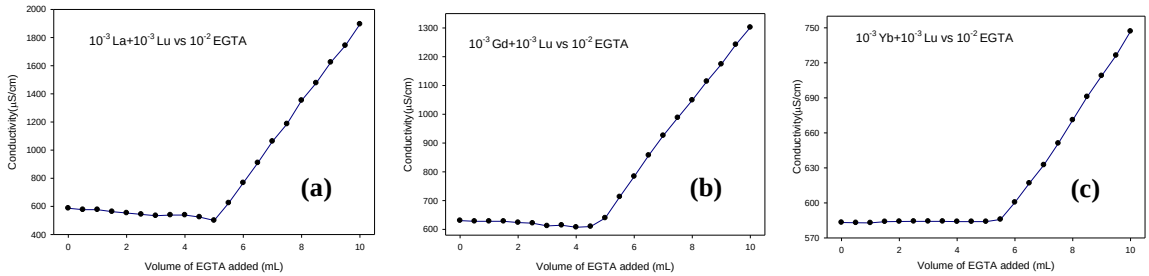


Figure 4.17(a-c): Conductometric titration curves for 25 mL of Ce(III)/ Gd(III)/ Lu(III) (1×10^{-3}M) + 25 mL Ln(III) (1×10^{-3}M) with L3 in the absence of HIBA
**Similar results were obtained for other Ln(III)*

Table 4.9: Conductometric titration curves for 25 mL of Ce(III)/ Gd(III)/ Lu(III) (1×10^{-3}M) + 25 mL Ln(III) (1×10^{-3}M) with L3 and L4 in the absence of HIBA

Ln(III)	EGTA*			EDTA-OH*		
	Ce	Gd	Lu	Ce	Gd	Lu
La	√	–	5.5	√	–	5.5
Ce	–	–	5.5	–	–	5.6
Pr	2.5	2.0	2.0	3.5	3.0	3.0
Nd	5.5	5.5	5.4	6.0	5.0	5.4
Gd	5.5	–	5.4	6.0	–	6.0
Er	5.2	5.5	5.6	6.0	5.5	5.5
Yb	√	5.5	5.6	5.0	4.5	5.0

* Volume of titrant used for equivalence point, mL (Expected E.P. = 5.0 mL)

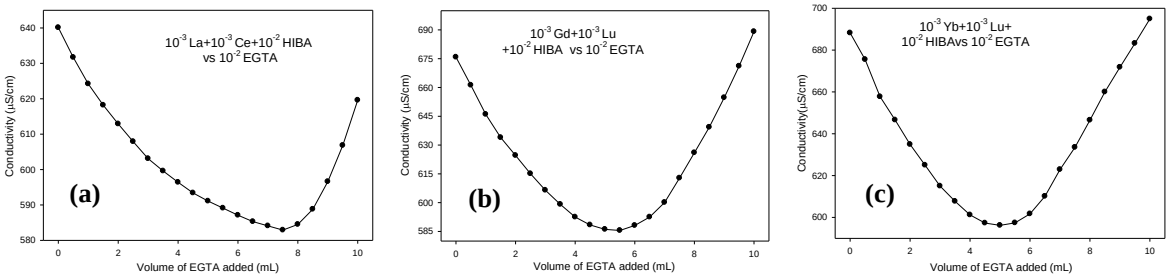


Figure 4.18(a-c): Conductometric titration curves for 25 mL of Ce(III)/ Gd(III)/ Lu(III) (1×10^{-3}M) + 25 mL Ln(III) (1×10^{-3}M) with L3 in presence of HIBA
**Similar results were obtained for other Ln(III)*

hard bases such as oxygen, thus explaining their high affinity for water. Lanthanides typically have 8 to 9 waters of hydration in their inner coordination shell, some of which are displaced upon complexation.[54] Successful complexing agents frequently involve multiple lanthanide-oxygen bonds. Presence of multiple oxygen donor sites in PACA makes them effective ligands for lanthanides binding. Because of their high coordination number even multidentate ligands do not lead to coordinative saturation of lanthanide complexes, therefore, even in their complexed form lanthanides have water molecules in their primary coordination sphere.[55] Literature suggests that lanthanide (III) coordination complexes continuously exchange water molecules with the solution.[56-58] The coordination number of lanthanide (III) ions is known to vary between 8 and 9 in solution.[57-59] Also some members (in the middle of the series) exhibit a coordination equilibrium between the octaaqua and enneaaqua complexes.[57] For higher lanthanides the exchange rate is known to increase toward the middle of the series.[56] The relative stability of 9-coordinate transition state increases as the size of the lanthanide (III) ion increases. This results in higher exchange rates of the octaaqua ions towards the middle of the series in higher lanthanides.[58] When EGTA complexed with Ln(III) ion to form $[Ln(EGTA)(H_2O)_n]^-$, it was expected that the four strongly ligating carboxylate groups pulled the ligand very tightly around the metal center, thus increasing the crowding at water binding site. In addition, the ethyl group bridging the two loosely coordinating glycolic oxygens caused a steric compression resulting in tight pulling of the latter into the first coordination sphere. This further led to high steric constraints on water binding sites[60] in the complex which destabilized the bound water molecule, resulting in an acceleration of the exchange rate. This rapid exchange of water molecules with the system established a dynamic equilibrium between the complex and the solution, due to which a sharp change in conductivity of the solution was not observed at or near the equivalence point and this sharp increase could only be observed after the equivalence point had already been attained and the concentration of L3 was very much in excess and became the dominating factor influencing the graph shape.

Polydentate ligands that present multiple donor atoms for metal binding provide greater complex stability compared with monodentate analogs due to the chelate effect. This effect can be maximized if the number and size of the chelate rings are optimized for the size of

the cation in a way that minimizes steric strain upon metal binding.[61,62] The lower the steric strain in the complex, the more favorable will be the complex formation reaction. This gives rise to the concept of steric efficiency. Since, satisfactory results were not obtained for binary mixtures of lanthanides it was decided not to proceed for the determination of ternary mixtures using this ligand.

4.2.2.4 Conductometric Titrations Using *N*-(2-Hydroxyethyl)ethylenediaminetri acetic Acid (EDTA-OH) as a Complexing Ligand for Lanthanides

N-(2-hydroxyethyl) ethylenediamine-N,N′,N′-triacetic acid (EDTA-OH/ L4) is another ligand that belongs to PACA class of ligands. It has a molecular structure similar to that of ethylenediaminetetraacetic acid (H4edta), except that EDTA-OH has a hydroxymethyl group instead of a carboxyl group i.e., it has three carboxyl groups as against four in case of EDTA. Chelating efficacy of EDTA-OH has successfully been tried in removing several toxic metal ions from biological systems, including manganese,[63] lead,[64] beryllium[65] and aluminum.[66] The complexation of L4 with lanthanides was studied by carrying out the conductometric titrations of lanthanides with L4. L4 forms with rare earth elements complexes in the ratio 1:1 which are generally eight or nine coordinated in which the central lanthanide ion is coordinated to three carboxyl oxygen atoms, a hydroxyl oxygen atom, two nitrogen atoms, and two or three water molecules. In Ln(III)–EDTA-OH complexes the bond length in case of Ln(III)–hydroxyl oxygen bond will be longer than that of Ln(III)–carboxyl oxygen groups, as compared to, same bond lengths in case of Ln(III)–EDTA complex due to four carboxyl groups. This leads to lower symmetry in Ln(III)–EDTA-OH complexes than Ln(III)–EDTA complexes resulting in lower stability constant values for Ln(III)–EDTA-OH complexes. Available reports suggest that in coordination bond of Ln(III) ions with O-donor ligands the major contribution to energy of bond is made by the Coulumbic interactions of O-donor ligands and the stability constants of complexes in solutions are determined most of all by the effective charge on the electron-donor O atom of the ligand.[67]

Figure 4.1 shows the stability constants of various lanthanides with EDTA-OH. The values of stability constants for Ln–EDTA-OH complexes were in the range of 13-16 which are lower than those of L1, L2 and L3. These values dictated that L4 might be less effective in

determination of lanthanides as compared to the three ligands described above; nevertheless, the values were strong enough to effectively show bonding of Ln(III) ions with L4. The trend of conductometric titration curves obtained from these titrations was slightly different from those obtained using L1, L2 and L3 (Figure 4.19 and Table 4.8). Here it was observed, that the value of conductivity went on decreasing till the equivalence point (as opposed to being constant in case of L1, L2 and L3) after which it increased sharply (although the

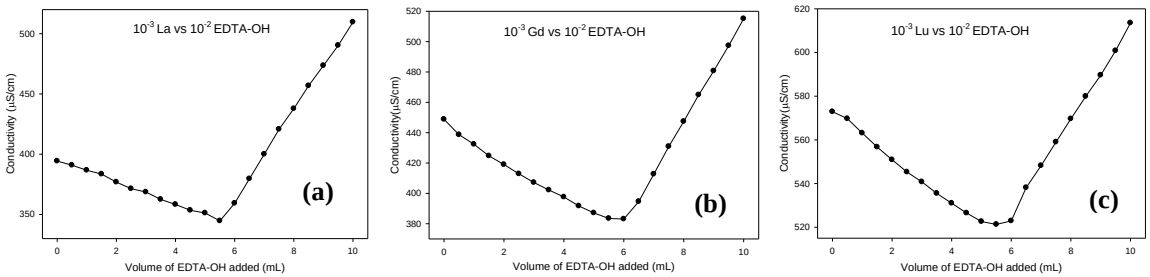


Figure 4.19(a-c): Conductometric titration curves for 50 mL of Ln(III) (1×10^{-3}M) with L4
**Similar results were obtained for other Ln(III)*

increase in this case was not as steep as compared to L1, L2 and L3). It was observed that the equivalence points obtained in case of ligand L4 were shifted from the expected equivalence points. This could be attributed to the fact that low ionic strength of the solution near the equivalence point led to an increase in the tendency of the Ln(III) ions to undergo hydrolyses. It was observed that in the region of equivalence points there was a difference between expected and rear conductivity values, the value of rear conductivity being higher than the expected value of conductivity. This may be due to the H^+ ions released on hydrolyses of EDTA-OH. These released H^+ ions led to an increase in the actual value of conductivity of solution as compared to the expected conductivity value. This was supported by the fact that the stability constant values of lanthanide hydroxo complexes[68-70] were higher than those of Ln(III)–EDTA-OH stability constant values. After all the Ln(III) present in the system had been used up in complexation and theoretical equivalence point had been achieved further addition of L4 led to uptake of free H^+ ions (released by hydrolysis) by Na_3L4 to form H_3L4 resulting in the displacement of highly mobile H^+ ions in solution by Na^+ ions due to which the conductivity kept on decreasing even after the attainment of equivalence point. Hence, the observed equivalence point was higher than the

expected equivalence point A similar trend was observed for titrations of binary mixtures of lanthanides with the ligand in the absence of coligand HIBA (Figure 4.20 and Table 4.9).

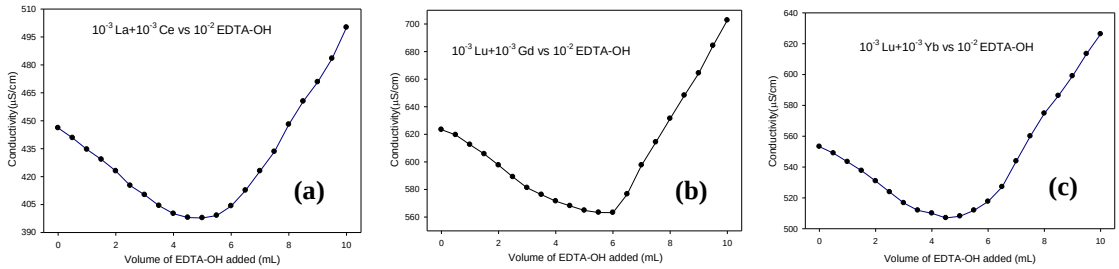


Figure 4.20(a-c): Conductometric titration curves for 25 mL of Ce(III)/ Gd(III)/ Lu(III) (1×10^{-3}M) + 25 mL Ln(III) (1×10^{-3}M) with L4 in the absence of HIBA
**Similar results were obtained for other Ln(III)*

Determination of binary mixtures of lanthanides was carried out in the presence of co-ligand HIBA. It was observed that in this case the difference in the experimental and theoretical equivalence points was even larger than in the absence of coligand (Figure 4.21). Here, the system contained H^+ ions released by the dissociation of HIBA to form Ln(III)–HIBA complex in the initial titration mixture and, as the titration neared the equivalence point, due to hydrolysis of the lanthanide species. This shift in observed equivalence point was accredited to the uptake of H^+ ions by the released $HIBA^{2-}$, to regenerate HIBA, which led to a decrease in the number of H^+ ions in the solution, in addition to the uptake of free H^+ ions by Na_3L4 as explained above. Hence, the decrease in conductivity continued due to the reaction of H^+ with Na_3L4 and $HIBA^{2-}$ to form H_3L4 and HIBA, respectively. After all the available H^+ ions had been used up, an increase in conductivity took place due to the addition of ligand which only increased the number of current carrying species.

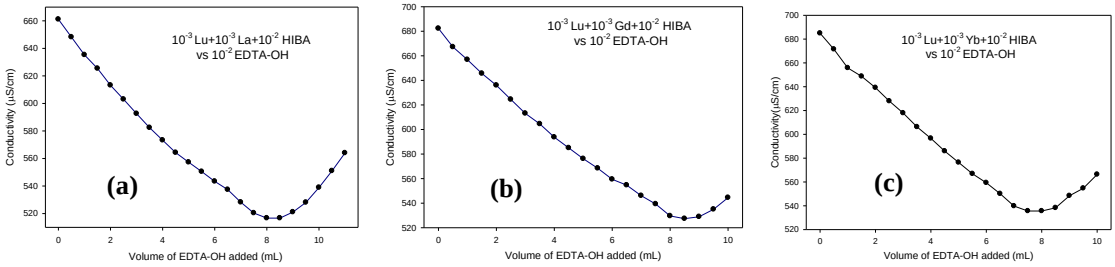


Figure 4.21(a-c): Conductometric titration curves for 25 mL of Ce(III)/ Gd(III)/ Lu(III) (1×10^{-3}M) + 25 mL Ln(III) (1×10^{-3}M) with L4 in the presence of HIBA
**Similar results were obtained for other Ln(III)*

The accuracy of quantitative determination of lanthanides using L4 as a ligand was found to be quite low for single as well as binary mixtures of lanthanides as a result of which it was decided not to proceed to determine ternary mixtures of lanthanides using L4 as a ligand.

4.2.2.5 Conductometric Titrations Using 1,3-Diaminopropane-N,N,N′,N′-tetraacetic acid (TMDTA) as a Complexing Ligand for Lanthanides

TMDTA is a hexadentate ligand with a trimethylene group in place of the ethylene group in EDTA. Ligand TMDTA was used to determine lanthanides by conductometric titration method. From the results shown in Figure 4.22 and 4.23, it is evident that TMDTA does not work well for lanthanide determination in their single ion as well as binary mixtures. This behavior could be attributed to the elongation of central diamine branch by one CH_2 group in going from EDTA to TMDTA. This one CH_2 group forms a part of the metal ion coordination sphere. It does not contain any donor atom in the backbone like EGTA. Literature suggests that TMDTA complexes of lanthanides are weaker as expected from the pKa i.e., the values of log K are about 6 log units lower than expected for the pKa of TMDTA.[71] The stability constant values of EDTA and TMDTA reflect that TMDTA forms weaker, six-membered N-M-N chelate rings compared to the analogous five-membered rings with EDTA. NMR data also indicate weakening of the Ln–N interaction upon expansion of the size of the chelate ring from 5(EDTA) to 6 (TMDTA).[72] This difference in stability of chelate rings of homologous ligands could be explained on the basis of inductive effect and the effect of chelate-ring size. The pentadentate ring formed in case of EDTA complexes of lanthanides changed to hexadentate in case of TMDTA. This longer backbone of TMDTA caused an increase in ring size leading to an increase in lability and hence, a decrease in kinetic inertness of its lanthanide complexes. Also the extra methylene in this hexadentate ring produced an inductive effect that enhanced the donor capability of the nearby N atoms,[73] which led to a decrease in stability of the complex formed. Literature also suggests the values of dissociation constants of Ln(III)–TMDTA complexes to be very high.[74,75] From the literature reports and results obtained it was concluded that the lower value of stability constants of TMDTA, with lanthanides, as compared to other PACA was due to elongation of the diamine branch in the ligand due to which it did not function well as a ligand for conductometric determination of lanthanides. This was also clear from the

results obtained for conductometric determination of binary mixtures of Ln(III) using TMDTA (Figure 4.22 and 4.23). As the results obtained by TMDTA were not satisfactory, therefore, it was not used, further, as a ligand for the determination of lanthanides in the presence of interfering ions.

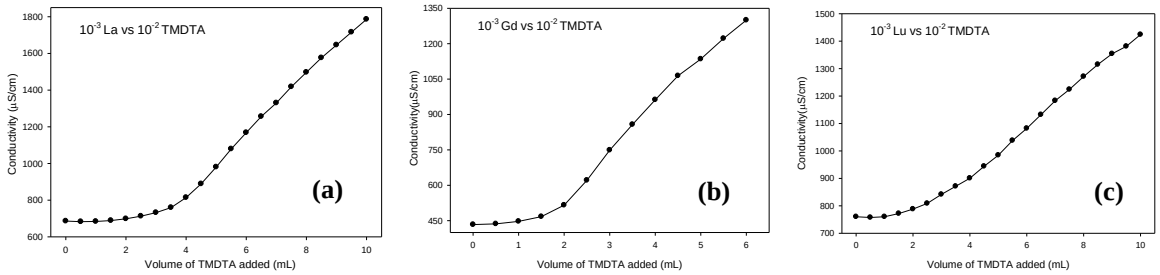


Figure 4.22(a-c): Conductometric titration curves for 50 mL of Ln(III) (1×10^{-3}M) with L5
**Similar results were obtained for other Ln(III)*

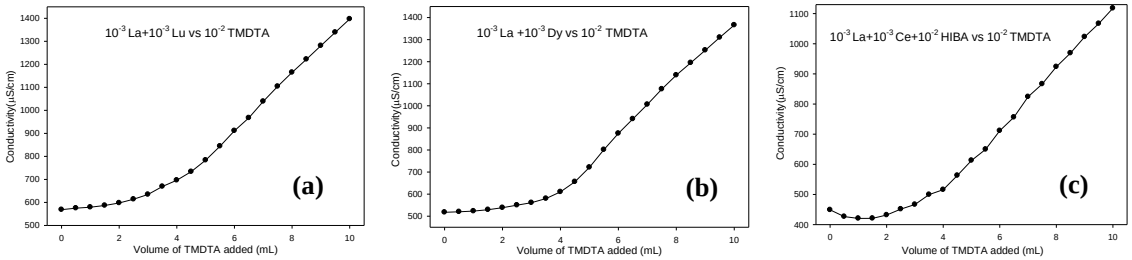


Figure 4.23(a-b): Conductometric titration curves for 25 mL of La(III) (1×10^{-3}M) + 25 mL Ln(III) (1×10^{-3}M) with L5 in the absence of HIBA
4.23(c): Conductometric titration curves for 25 mL of La(III) (1×10^{-3}M) + 25 mL Ce(III) (1×10^{-3}M) with L5 in the presence of HIBA

A comparison of homologous PACA for lanthanide determination by conductometry showed that the structure of the ligand influenced its effectiveness. Effectiveness of EDTA and DCTA could be attributed to the stable chelate rings formed for these two ligands, whereas formation of six-membered N-M-N ring led to lower efficiency in case of TMDTA.

4.2.3 Selectivity of Ligand and Co-Ligand in Conductometric Titration While Determining Lanthanide (III) Ions in Presence of Interfering Ions

Electroanalytical techniques due to their advantages, like inexpensive instrumentation, rapid determination, high reproducibility and accuracy and easy miniaturization for small volume samples, have come to occupy a major standing in present day analytical methods.[75,76] The competence of an analytical method is determined by its ability to furnish results that are

free from any sort of interference and this criterion strongly influences the development of analytical tools and processes. The major goal of analytical processes is to deliver results that are explicitly characteristic of the analyte and are free from influence of any other species present in the system. This ability of an analytical technique to deliver results that are free from interference in known as selectivity.[77] The selectivity of a method measures its ability to distinguish the analyte under study without interference from other components present in a complex mixture. Recent development of highly sensitive and astute methods having the capacity to identify as well as quantify analytes with least interference from other components has led to an evolution of the term selectivity. The choice of analytical method depends on analyte under study, such that the method gives preference to the target analyte with minimum interference from other species present in the system under study. Selectivity of an analytical method expresses the extent to which a particular method can determine analytes in the presence of other components of similar behavior under given conditions. The selectivity of an analytical technique can be enhanced by[78]:

- Avoiding the interferent effect of other components present in the system containing target analyte
- Achieving simultaneous determination of two or more species in the same sample
- Obtaining sequential difference in analytical signals of two or more analytes reacting with the same reagent. This may be a result of difference in the rate constants of reacting species.

Metal complexing agent EDTA has been popular for many purposes since its commercialization in the early 1950s. EDTA is known for its ability to form 1:1 complexes with 62 different metal ions.[79]

Lanthanide metal ions are widely used in a variety of applications like alloys, ceramics, permanent magnets, etc. which are composed of varying amounts of the lanthanide metals in combination with other metals like magnesium,[80] aluminium,[80,81] lead,[82] manganese,[83] cobalt,[83] nickel,[83] copper,[84] etc. Also lanthanides are present together with Th(IV) in spent nuclear fuels. Therefore, a total of 10 interfering ions including alkaline earth metal ions: Mg(II), Ca(II) and Ba(II); Al(III), Pb(II); transition metal ions: Mn(II), Co(II), Ni(II) and

Cu(II) and actinide: Th(IV) were chosen for conducting interference studies in lanthanide determination by proposed technique.

4.2.3.1 Effect of Alkaline Earth Metal Ions

Lanthanides like alkaline earth ions are type A or 'hard' acids i.e they have strong preference for oxygen donor ligands. Their aqueous chemistry largely involves substitution of metal-oxygen bond of solvate water molecules with metal-oxygen bond of ligand although in solid state they might coordinate via nitrogen, sulphur etc. The sizes of hydrated calcium ion and hydrated strontium ion are almost the same whereas, hydrated magnesium ion is the largest hydrated alkaline earth ion. Of the four alkaline earth ions, the metal ion with the largest ionic radius i.e., barium forms the smallest hydrated metal ion. Thus, it can be said that in alkaline earth metal ions a decrease in the ionic radius leads to an increase in number of inner and outer water molecules associated with the metal ion.[85] The bonding of alkaline earth metal ions with EDTA is well known in literature.[85] Literature suggests that the hydrating water molecules are held more loosely by alkaline earth ions and when ligand donor group attacks the hydrated metal ion, it has to displace the water molecules from outer hydration sphere and form ion pair or ion dipole as a result of which metal-water bond present in the hydration co-sphere is broken and the ligand donor atom forms bond there.[85]

Various studies on polyaminocarboxylic acids as calcium binding agents have been carried out in the past. These studies have been related to their practical applications as well as development of classic research models for polydentate chelation.[86] Polyaminocarboxylic acid, EDTA has been commercially used as a sequestrant of Ca(II). The complexation of EDTA and Ca has also been determined from batch extraction experiments where it was seen that a high proportion of K_2H_2EDTA added to the Cal-West soil formed complexes with Ca.[87] Ca–EDTA complex which is hexadentate in nature is expected to have a similar geometry as hexadentate Ln–EDTA complexes with water molecules occupying additional coordination sites.[88] Trivalent lanthanide complexes have higher stability constants with PACA ligands as those of alkaline earth metal ions (Figure 4.1 and Table 4.10).[89]

Table 4.10: Stability constant values of different interfering ions with PACAs[89]

Interfering Ion	Stability Constant Values (log K)			
	EDTA	**DCTA**	**EGTA**	**EDTA-OH**
Mg(II)	8.69	10.32	5.21	7.00
Ca(II)	10.96	12.50	11.00	8.14
Ba(II)	7.76	8.64	8.41	5.54
Al(III)	16.10	18.63	13.90	12.43
Pb(II)	18.04	19.68	14.71	15.50
Mn(II)	13.80	16.78	12.30	10.70
Co(II)	16.31	18.92	12.50	14.40
Ni(II)	18.62	19.40	13.60	17.00
Cu(II)	18.80	21.30	17.80	17.35
Th(IV)	23.20	29.25	20.50	18.50

4.2.3.1.1 Magnesium: Typical results obtained for Ln(III) determination in presence of Mg(II) using various PACA are given in Figures 4.24(a-c), 4.25(a-d) and Table 4.11 − 4.14. Since magnesium has the largest hydrated ion radius in alkaline earth metal ions, when L1/L2 formed a bond with it, it had to displace a large number of water molecules in the solvent sheath whereas in case of calcium and barium due to smaller hydrated ion radius as compared to that of Mg(II), the number of solvent molecules around the metal ion, that needed to be displaced, was less. Therefore, it was concluded that the process of M–L1/L2 bonding for Mg(II) may be a slightly slower than for Ca(II) and Ba(II) due to which to distinct equivalence points were obtained for Ln(III) determination in presence of Ca(II) and Ba(II) whereas these equivalence points were not very well marked for Mg(II) [Figure 4.24(a-b)]. But when the same determination was carried out in the presence of co-ligand HIBA, two distinctly marked equivalence points were obtained (Figure 4.25a and 25b). This observation was similar to that made in case of determination of binary mixtures of Ln(III) using L1 and L2. Using ligand L3, only total concentration of metal ions presents [Ln(III) and Mg(II)] in the system could be determined. For L4 (in absence of HIBA) single equivalence point, corresponding to single metal ions, which was slightly shifted from the expected value, was obtained. This was in accordance with the results obtained for determination of single Ln(III) ions using L4 as ligand. Also, the higher stability constant value of Ce(III)–L4 complex as compared to Mg(II)–L4 complex dictated that Ce(III)–L4

complex should be formed before Mg(II)–L4 complex in a mixture containing Ce(III) and Mg(II). Similar results were obtained for Gd (III) and Lu (III).

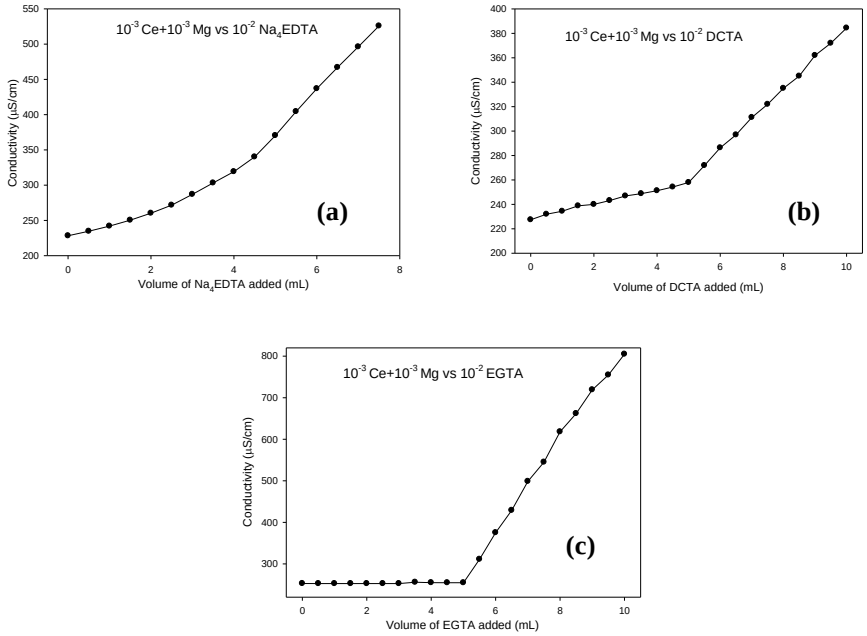


Figure 4.24(a-c): Conductometric titration curves for 25 mL of Ce(III) (1×10^{-3}M) + 25 mL Mg(II) (1×10^{-3}M) with L1, L2, L3 in the absence of HIBA

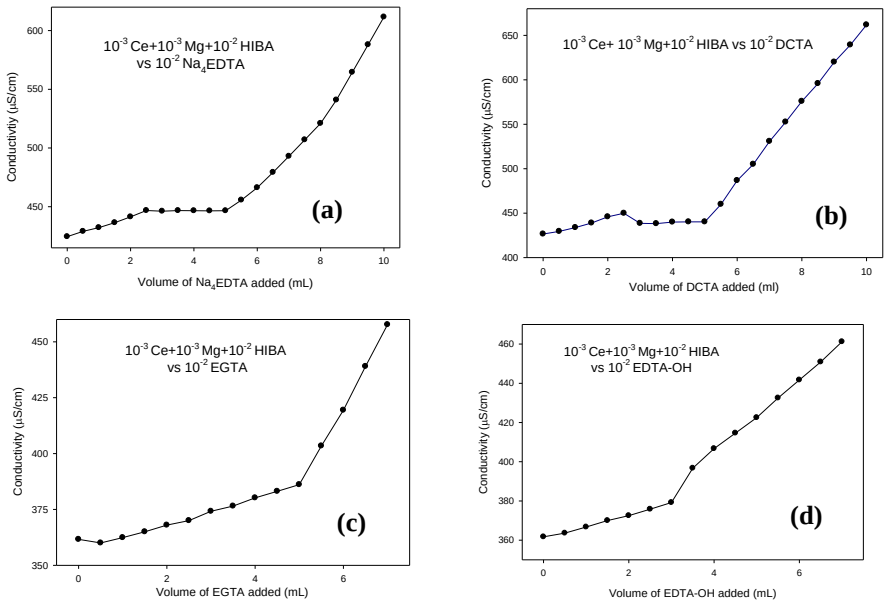


Figure 4.25(a-d): Conductometric titration curves for 25 mL of Ce(III) (1×10^{-3}M) + 25 mL Mg(II) (1×10^{-3}M) with L1, L2, L3 & L4 in presence of HIBA

Table 4.11: Conductometric titrations for 25 mL of Ce(III)/ Gd(III)/ Lu(III) (1×10^{-3}M) + 25 mL Z (1×10^{-3}M) with L1 and L2 in the absence of HIBA

Interfering ion (Z)	EDTA*			DCTA*		
	Ce(III)	Gd(III)	Lu(III)	Ce(III)	Gd(III)	Lu(III)
Mg(II)	T	T	T	T	T	T
Ca(II)	B	B	B	B	B	B
Ba(II)	B	B	B	B	B	B
Al(III)	T	T	T	T	T	T
Pb(II)	T	T	T	T	T	T
Mn(II)	T	T	T	T	T	T
Co(II)	T	T	T	T	T	T
Ni(II)	T	T	T	T	T	T
Cu(II)	T	T	T	T	T	T
Th(IV)	B	B	B	T	T	T

* Volume of titrant used for equivalence point, mL (Expected Equivalence Point, 2.5 & 5.0 mL)
T: total; S: single equivalence point; B: both equivalence points

Table 4.12: Conductometric titrations for 25 mL of Ce(III)/ Gd(III)/ Lu(III) (1×10^{-3}M) + 25 mL Z (1×10^{-3}M) with L3 and L4 in the absence of HIBA

Interfering ion (Z)	EGTA*			EDTA-OH*		
	Ce(III)	Gd(III)	Lu(III)	Ce(III)	Gd(III)	Lu(III)
Mg(II)	T	T	T	T	T	T
Ca(II)	T	T	T	S	S	S
Ba(II)	S	S	S	S	S	S
Al(III)	T**	T**	T**	T**	T**	T**
Pb(II)	T	T	T	T**	T**	T**
Mn(II)	T	T	T	T**	T**	T**
Co(II)	T	T	T	T**	T**	T**
Ni(II)	T	T	T	T**	T**	T**
Cu(II)	T	T	T	T**	T**	T**
Th(IV)	B	B	B	B**	B**	B**

* Volume of titrant used for equivalence point, mL (Expected Equivalence point, 2.5 & 5.0 mL)
** Equivalence points shifted from expected value
T: total; S: single equivalence point; B: both equivalence points

Table 4.13: Conductometric titrations for 25 mL of Ce(III)/ Gd(III)/ Lu(III) (1×10^{-3}M) + 25 mL Z (1×10^{-3}M) with L1 and L2 in the presence of HIBA

Interfering ion (Z)	EDTA*			DCTA*		
	Ce(III)	Gd(III)	Lu(III)	Ce(III)	Gd(III)	Lu(III)
Mg(II)	B	B	B	B	B	B
Al(III)	T**	T**	T**	T**	T**	T**
Pb(II)	B	B	B	B	B	B
Mn(II)	B	B	B	B	B	B
Co(II)	B	B	B	B	B	B
Ni(II)	B	B	B	B	B	B
Cu(II)	B	B	B	B	B	B
Th(IV)	–	–	–	B	B	B

* Volume of titrant used for equivalence point, mL (Expected Equivalence point, 2.5 & 5.0 mL)
** Equivalence point shifted from expected value
T: total; S: single equivalence point; B: both equivalence points

Table 4.14: Conductometric titrations for 25 mL of Ce(III)/ Gd(III)/ Lu(III) (1×10^{-3}M) + 25 mL Z (1×10^{-3}M) with L3 and L4 in the presence of HIBA

Interfering ion (Z)	EGTA*			EDTA-OH*		
	Ce(III)	Gd(III)	Lu(III)	Ce(III)	Gd(III)	Lu(III)
Mg(II)	T	T	T	S	S	S
Ca(II)	S	S	S	–	–	–
Al(III)	B**	B**	B**	B**	B**	B**
Pb(II)	B**	B**	B**	T**	T**	T**
Mn(II)	B	B	B	T**	T**	T**
Co(II)	B	B	B	T**	T**	T**
Ni(II)	B	B	B	T**	T**	T**
Cu(II)	B	B	B	T**	T**	T**

* Volume of titrant used for equivalence point, mL (Expected Equivalence point, 2.5 & 5.0 mL)
** Equivalence point shifted from expected value
T: total; S: single equivalence point; B: both equivalence points

4.2.3.1.2 Calcium: The results obtained for the determination of Ln(III) in presence of interfering ion Ca(II) using various ligands are shown in Figure 4.26(a-d) and Tables 4.11-4.14. From these figures very well marked equivalence points were observed for Ln(III) as well as Ca(II) in case of ligands L1 and L2. Whereas, for L3 these two equivalence points were not as well marked as in case of L1 and L2 and for L4 only a single equivalence point was obtained. Two distinctly visible equivalence points in case of L1 and L2 were due to low value of dissociation constants of Ca–L1/L2 complex, owing to which the complexation reaction of Ca and L1 proceed to completion.[90] In case of L3, the steric compression of the glycolic oxygens might have led to less difference in the stability of Ln(III)–L3 and Ca(II)–L3 complexes due to which the conductometric titration curve did not show very well marked difference in slopes for two metal ions. However, in the presence of HIBA a single equivalence point corresponding to Ln(III) was obtained (Figure 4.26 d). The results obtained for ligand L4 were similar to those obtained for the determination of Ln(III) in presence of Mg(II). Similar results were obtained for Gd(III)& Lu(III).

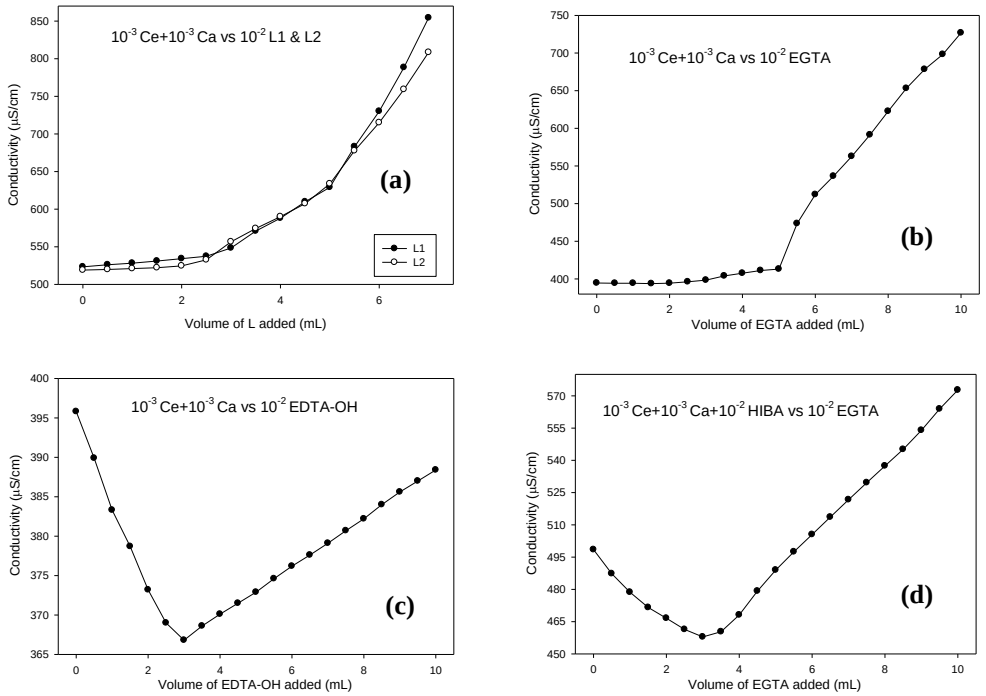


Figure 4.26(a-c): Conductometric titration curves for 25 mL of Ce(III) (1×10^{-3}M) + 25 mL Ca(II) (1×10^{-3}M) with L1, L2, L3 & L4 in the absence of HIBA
4.26(d): Conductometric titration curves for 25 mL of Ce(III) (1×10^{-3}M) + 25 mL Ca(II) (1×10^{-3}M) with L3 in the presence of HIBA

4.2.3.1.3 Barium: Although the stability constant of Ba–L1 is very low still reports found in literature dictate the formation of this complex.[91] The results obtained for L1 and L2 are exactly similar to those obtained for Ln(III) determination in presence of Ca(II) (Figure 4.27a and Table 4.11) i.e both Ln(III) and Ba(II) could be determined simultaneously in mixture. EGTA gave single equivalence point for Ln(III) (Figure 4.27b and Table 4.12), which might be due to low kinetic stability of complex as a result of larger size of EGTA. In case of L4, a single equivalence point for Ln(III) was observed (Figure 4.27c and Table 4.12) due to low stability constant value of Ba–L4 complex. The results are consistent with those obtained for the determination of Ln(III) in presence of Ca(II). Similar results were obtained for Gd (III) and Lu (III).

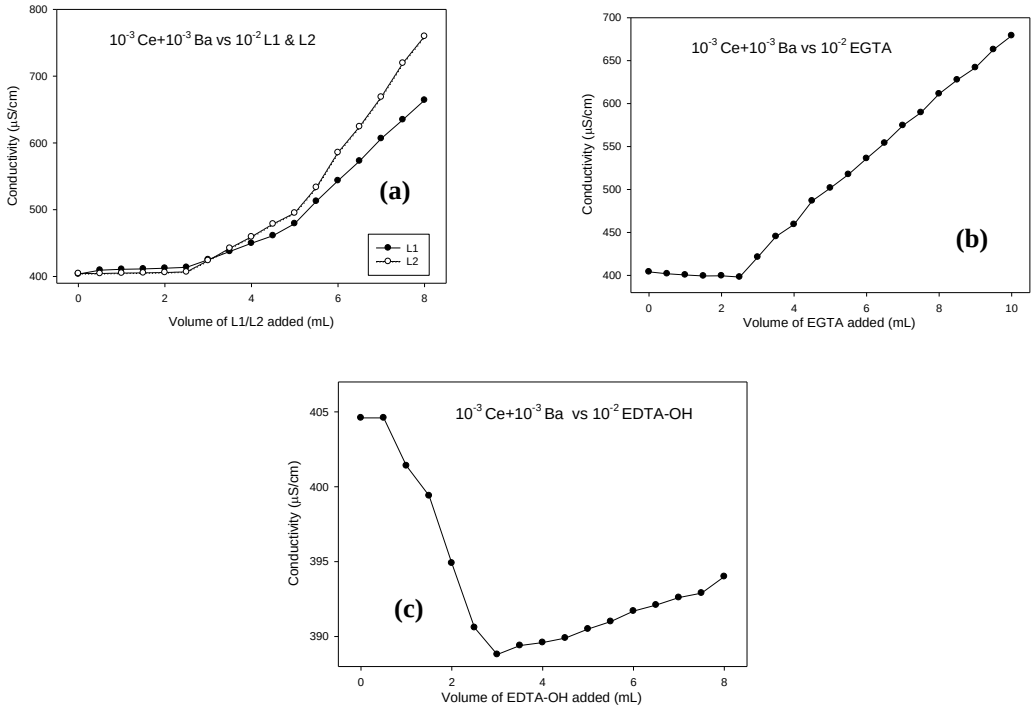


Figure 4.27(a-c): Conductometric titration curves for 25 mL of Ce(III) (1×10^{-3}M) + 25 mL Ba(II) (1×10^{-3}M) with L1, L2, L3 and L4 in absence of HIBA

From the above discussion it can be concluded that both L1 and L2 were best sequestering agents to determine quantitatively lanthanide (III) ions as well as alkaline earth metal ions while L3 was useful to monitor only Ln(III) ions in presence of alkaline earth metal ions.

However, L4 cannot be used due to shifting of equivalence point which is a result of hydrolysis of species.

4.2.3.2 Effect of Aluminium (III) ions

A major source of difficulty encountered with all sequestrating agents was the determination of lanthanides in presence of aluminum(III). This was so because of slow rate of formation of Al(III)–EDTA complex. Therefore, in this thesis the conditions to achieve well marked stoichiometric equivalence points have been carefully optimized for the same, with L1. The determination of Ln(III) in the presence of Al(III) using L1 and L2 gave single equivalence point for total concentration of metal ions present (Figure 4.28a and Table 4.11). For the same titrations carried out in presence of HIBA as a co-ligand, a single equivalence point was obtained which was shifted (towards positive side) from the expected equivalence point (for total amount of metal ions present) (Figure 4.29a and Table 4.13). For L3 and L4 in the absence of HIBA a similar but larger shift was observed (Figure 4.28b-c and Table 4.12). In the presence of HIBA although two equivalence points were observed but the shift from expected value was much greater than with L1 and L2 (Figure 4.29b-c and Table 4.14). A detailed consideration of behavior of Al(III) in aqueous media explains the reason for this shift. Although Al(III) forms complexes with oxygen donor ligands but the interference of metal ion hydrolysis in bond formation is dominant. In neutral solutions the dominant species present is not free aqueous Al(III) and the solubility of $Al(OH)_3$ ions limits the free availability of Al(III) due to which the stability of Al(III) complexes is generally misjudged. Al(III) exists as octahedral hexahydrate $[Al(H_2O)_6]^{3+}$, in solutions having pH<5.[92] Metal ion hydrolysis takes place much sooner than the coordination of Al(III) with uni-dentate ligands.[92] However, Al(III) forms strong complexes with multi-dentate amino- carboxylate ligands such as L1.[93] An important factor, other than stability, that affects metal ion reaction is the rate of ligand exchange in and out of the metal-ion coordination sphere. This factor is particularly important for Al(III) complexation as it is a very slow process.[92] Due to this slow process of hydrolysis, the change in conductivity in the conductometric titration curve was observed much after the actual attainment of equivalence point. Hence, a shift in equivalence point was observed for determination of Ln(III) in presence of Al(III).

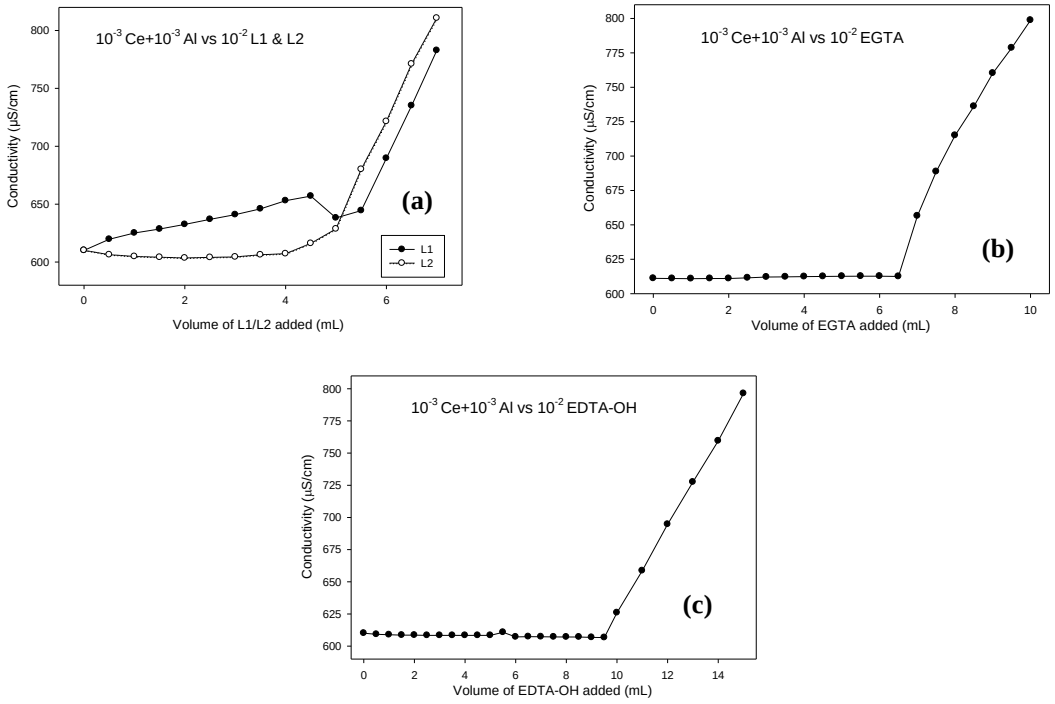


Figure 4.28(a-c): Conductometric titration curves for 25 mL of Ce(III) (1×10^{-3}M) + 25 mL Al(III) (1×10^{-3}M) with L1, L2, L3 and L4 in absence of HIBA

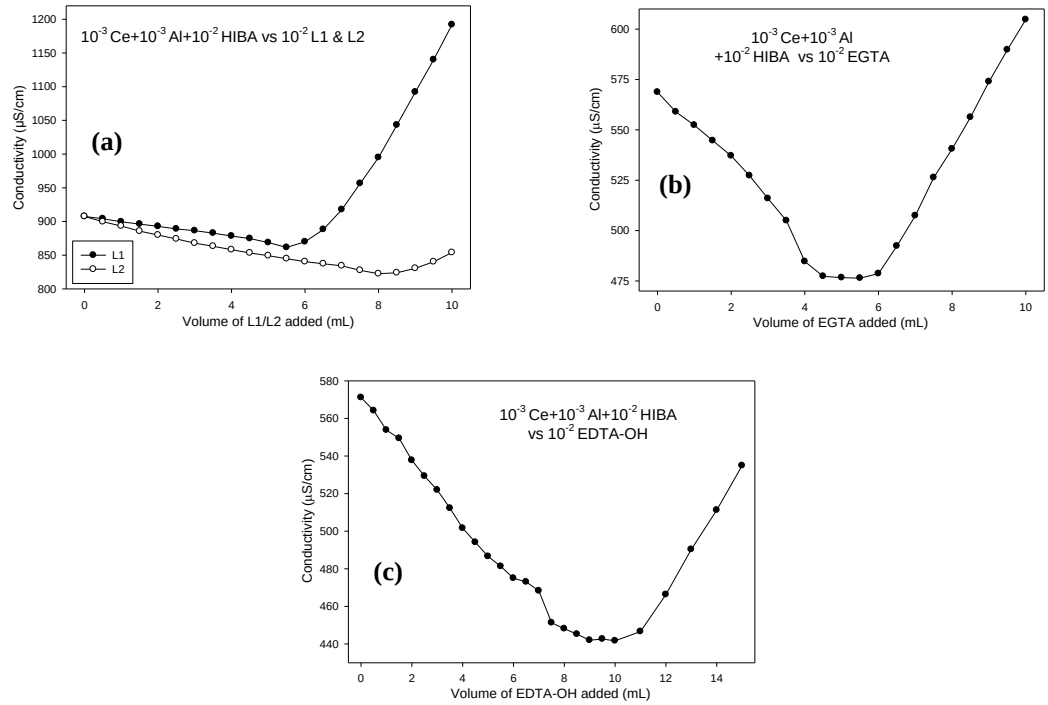


Figure 4.29(a-c): Conductometric titration curves for 25 mL of Ce(III) (1×10^{-3}M) + 25 mL Al(III) (1×10^{-3}M) with L1, L2, L3 and L4 in presence of HIBA

In order to eliminate the interference by Al(III) the same titration was carried out in various co-solvent/solvent media and it was observed that 20% 1,4-dioxane media showed a significant improvement over the previous results (Explained on page 24). The conductometric titration curve in this case [Figure 4.30(a-b)] displayed two distinct equivalence points for Ce(III) and Al(III) using L1 as a ligand. For L2, however, a single equivalence point corresponding to the total amount of metal ions present was obtained.

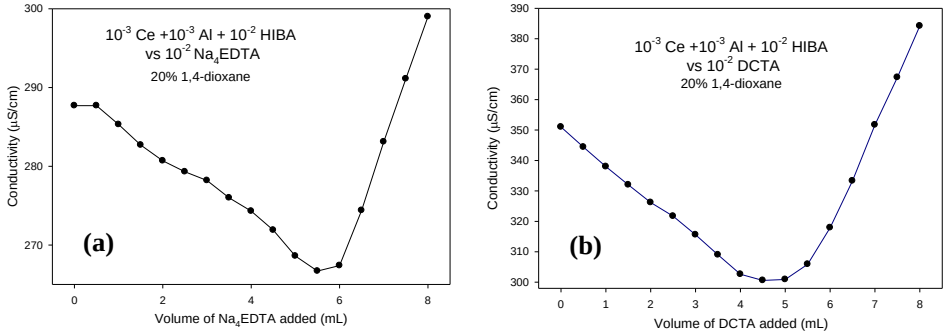


Figure 4.30(a-b): Conductometric titration curves for 25 mL of Ce(III) (1×10^{-3}M) + 25 mL Al(III) (1×10^{-3}M) with L1 and L2 in the presence of HIBA in 20% 1,4-dioxane media

4.2.3.3 Effect of Lead (II) ions

L1 has been extensively used for removal of Pb(II) from contaminated soils.[94,95] Results obtained for the determination of Ln(III) in presence of Pb(II) were similar to those obtained for binary mixtures of Ln(III). In case of L1, L2 and L3 in absence of HIBA a single equivalence point was obtained (Figure 4.31 and Table 4.11-4.12) corresponding to total concentration of metal ions present in the mixture.

This may be due to the fact that the stability constant of Pb(II)–PACA lies in the same range as for Ln(III)–PACA complexes. In the presence of HIBA, however, two equivalence points corresponding to the concentration of Ln(III) and Pb(II) were obtained for L1 and L2 (Figure 4.32 and Table 4.13). Using L3, accurate equivalence point could not be obtained even in presence of HIBA (Figure 4.32c). In case of L4, the equivalence point was shifted from the expected value which shifted on further addition of co-ligand HIBA to the mixture solution (Figure 4.31c-32d and Table 4.12 and 14). This behavior was also similar to that observed for the determination of binary mixtures of Ln(III) in presence of co-ligand HIBA

using L4 which might be due to hydrolysis of species present in the system. Similar results were obtained for Gd(III)& Lu(III).

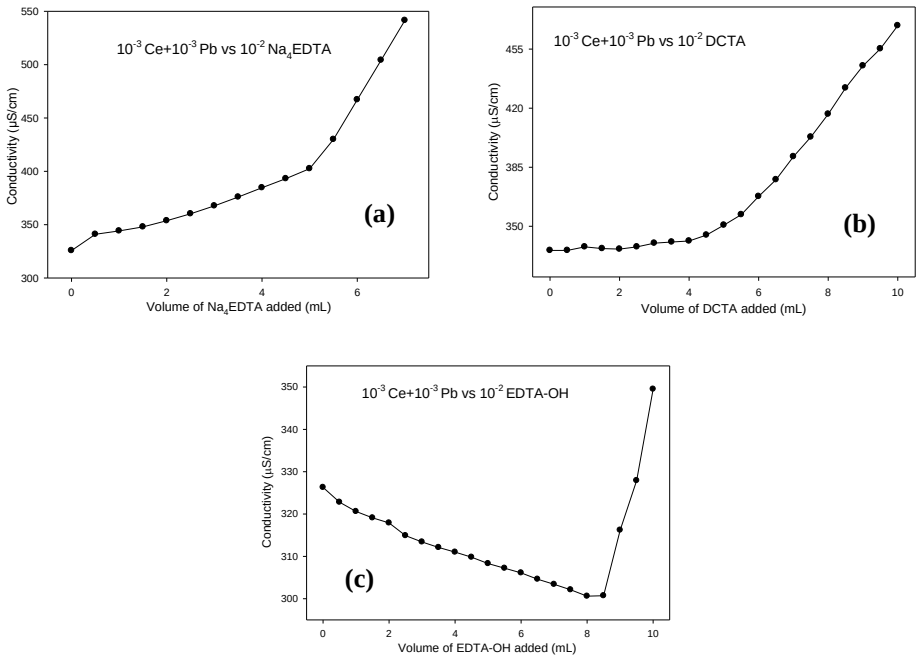


Figure 4.31(a-c): Conductometric titration curves for 25 mL of Ce(III) (1×10^{-3}M) + 25 mL Pb(II) (1×10^{-3}M) with L1, L2 and L4 in absence of HIBA

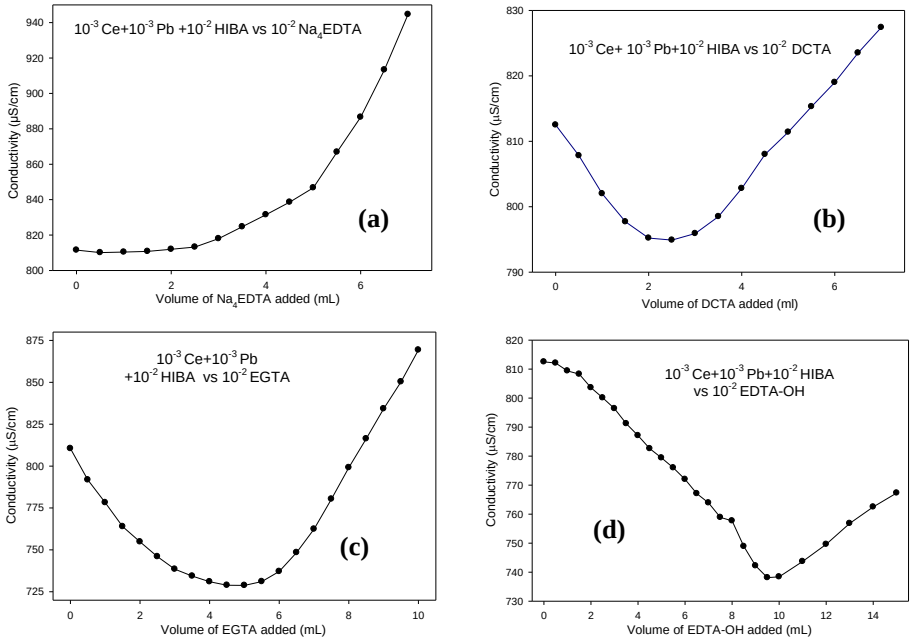
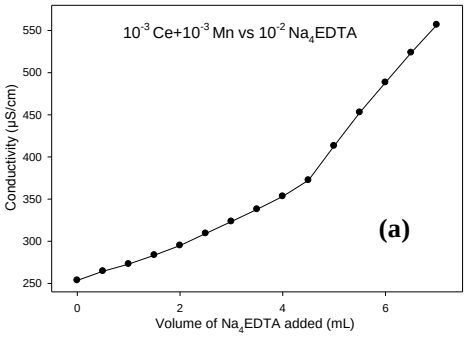
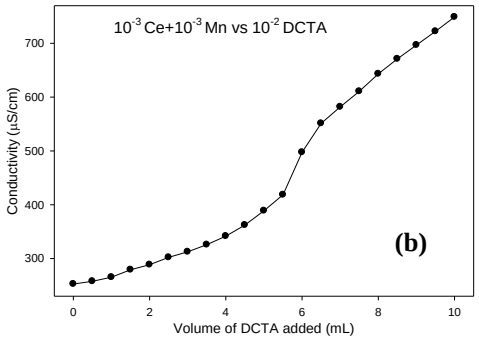


Figure 4.32(a-d): Conductometric titration curves for 25 mL of Ce(III) (1×10^{-3}M) + 25 mL Pb(II) (1×10^{-3}M) with L1, L2, L3 and L4 in presence of HIBA

4.2.3.4 Effect of Transition Metal Ions

The complexation behavior of transition metal ions with PACA has been widely studied and commercially used. Literature suggests the formation of mixed-ligand (L1, water) complexes of nickel at low pH.[96] L1 complex of manganese(II) is reported to have a seven-coordinated structure.[97] L1 aqueous extraction solutions have been used to extract industrial solid wastes containing copper, and manganese.[98] Different PACA have been used for the removal of transition metal ions from contaminated water.[99] Transition metal ions chosen for the study included Mn(II), Co(II), Ni(II) and Cu(II). Transition metal ions have stability constant values similar to Ln(III) ions and the results obtained for all ligands were similar to those obtained for binary mixtures of Ln(III) ions in case of all transition metal ions under study. Typical titration curves obtained with all ligands are shown in Figures 4.33-4.36 and the results are summarized in Tables 4.11-4.14. With L1, L2 as well as L3, single equivalence point corresponding to total concentration of metal ions in a mixture was obtained for conductometric titration of mixture of lanthanide and transition metal ion (Figures 4.33-4.34). Here also co-ligand HIBA was used for determination of Ln(III) ions in a mixture of Ln(III) and transition metal ion. Two equivalence points one each for Ln(III) as well as transition metal ion were obtained on using co-ligand (Figures 4.35-4.36). Thus, for the determination of Ln(III) in the presence of Mn(II), Ni(II), Co(II) and Cu(II) presence of HIBA was required for L1, L2 and L3. In case of ligand EDTA-OH, the results were analogous to those obtained for binary mixtures of Ln(III) with alkaline earth ions i.e, the equivalence point was shifted from the original value which shifted even further on addition of co-ligand HIBA due to hydrolysis of the species as explained earlier for the determination of binary mixtures of lanthanides using EDTA-OH.





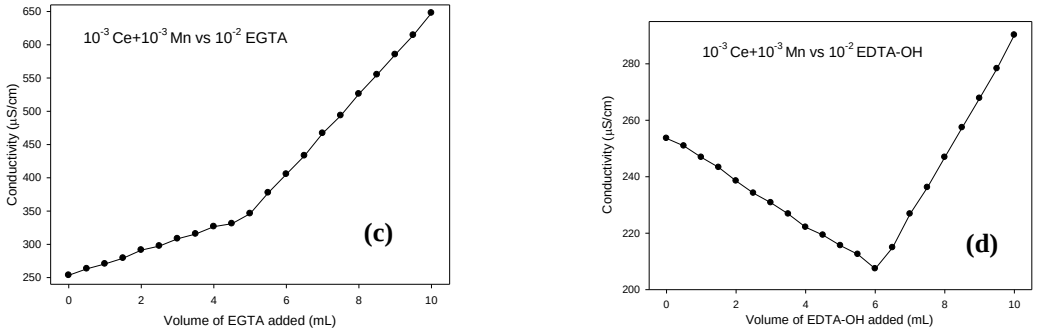


Figure 4.33(a-d): Conductometric titration curves for 25 mL of Ce(III) (1×10^{-3}M) + 25 mL Mn(II) (1×10^{-3}M) with L1, L2, L3 and L4 in the absence of HIBA

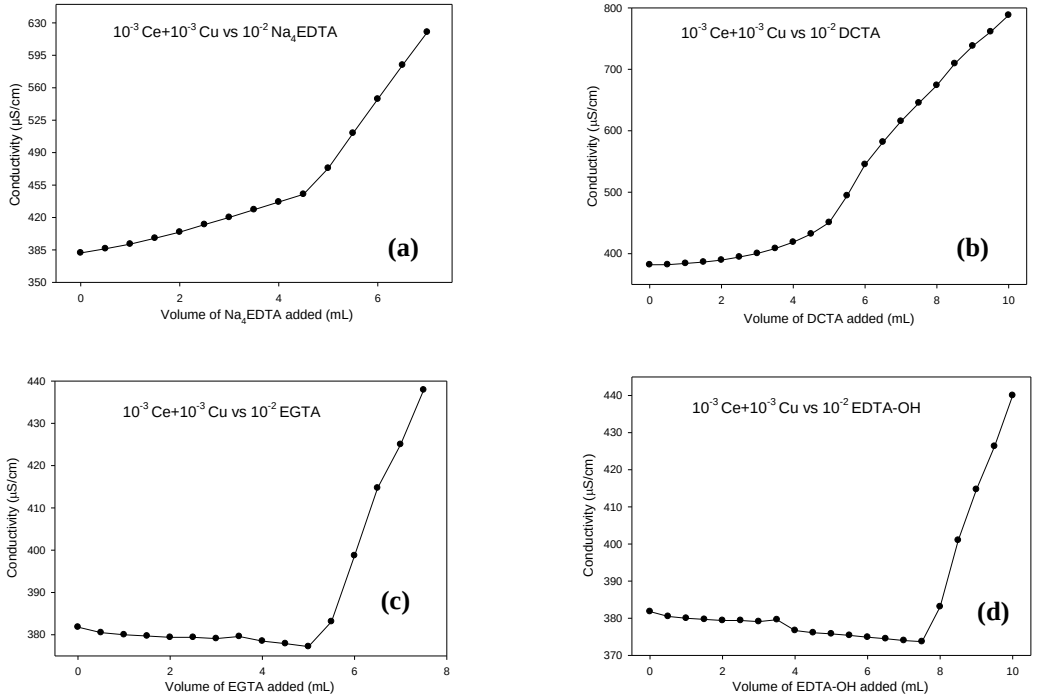
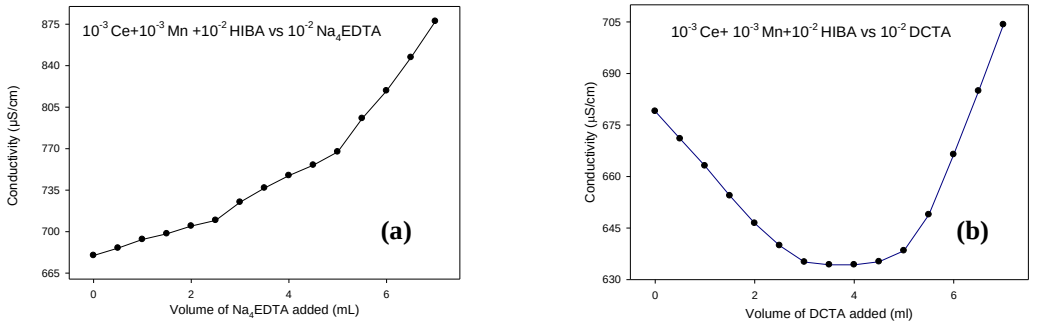


Figure 4.34(a-c): Conductometric titration curves for 25 mL of Ce(III) (1×10^{-3}M) + 25 mL Cu(II) (1×10^{-3}M) with L1, L2, L3 and L4 in absence of HIBA



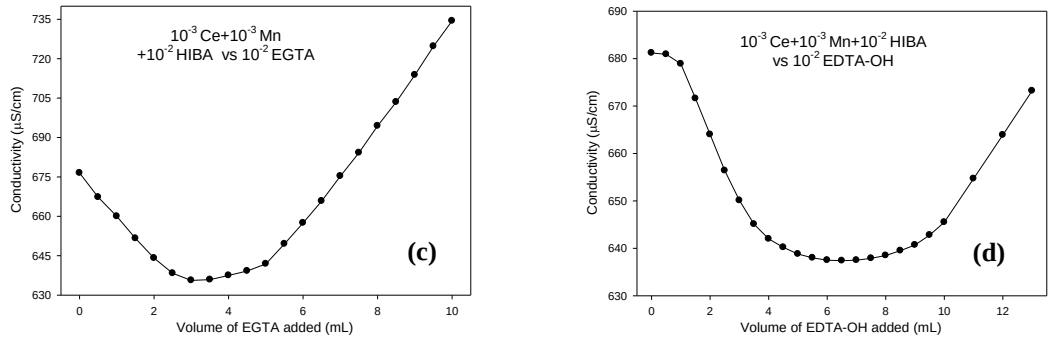


Figure 4.35(a-c): Conductometric titration curves for 25 mL of Ce(III) (1×10^{-3}M) + 25 mL Mn(II) (1×10^{-3}M) with L1, L2, L3 and L4 in presence of HIBA

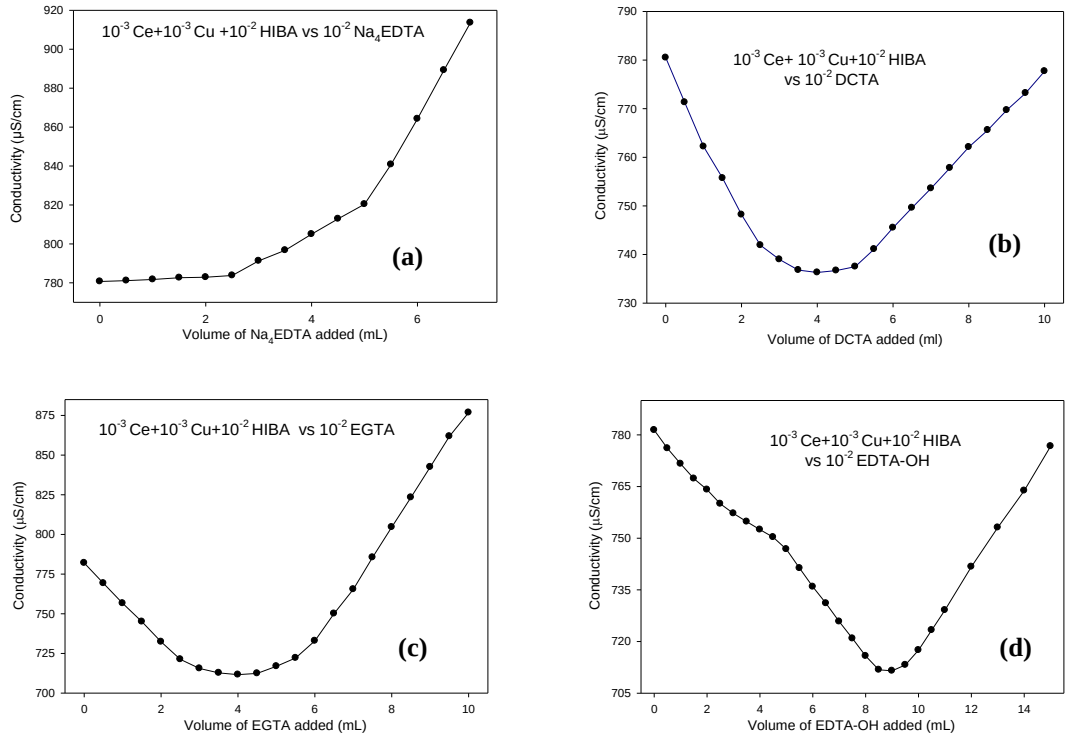


Figure 4.36(a-c): Conductometric titration curves for 25 mL of Ce(III) (1×10^{-3}M) + 25 mL Cu(II) (1×10^{-3}M) with L1, L2, L3 and L4 in presence of HIBA

4.2.3.5 Effect of Thorium (IV) ions

Lanthanide and actinide metals ions demonstrate similar chemical behavior. Lanthanides together with Th(IV) are present in a number of matrices like, monazite sand, spent nuclear fuels, etc. Therefore, the need for their simultaneous determination without preconcentration is vital. The stability constants of Th(IV) with all PACAs under study are much higher than all Ln(III) ions (Figure 4.1 and Table 4.10). Determination of lanthanides Ce(III), Gd(III)

and Lu(III) was carried out in presence of interfering ion Th(IV) using different PACAs under study. It was observed that for Ln(III) determination using L1, two discretely marked equivalence points were obtained for Ln(III) and Th(IV) (Figure 4.37a and Table 4.11) which is a result of large difference in the stability constant values of Th(IV)–L1 and Ln(III)–L1 complexes (Δlog K ≈4-7) Further, we moved to the determination of Ln(III) using L2 where the conductometric titration curve displayed a single equivalence point for the total amount of metal ions present in the system, in the absence of HIBA (Figure 4.37a and Table 4.11). However, two separate equivalence points could be obtained in the presence of HIBA (Figure 4.37d and Table 4.13). Two equivalence points were also obtained using ligands L3 and L4 (Figures 4.37 b and c and Table 4.12). However, a shift in each equivalence point was obtained which is attributed to the hydrolysis of species. Similar results were obtained for Gd(III)& Lu(III).

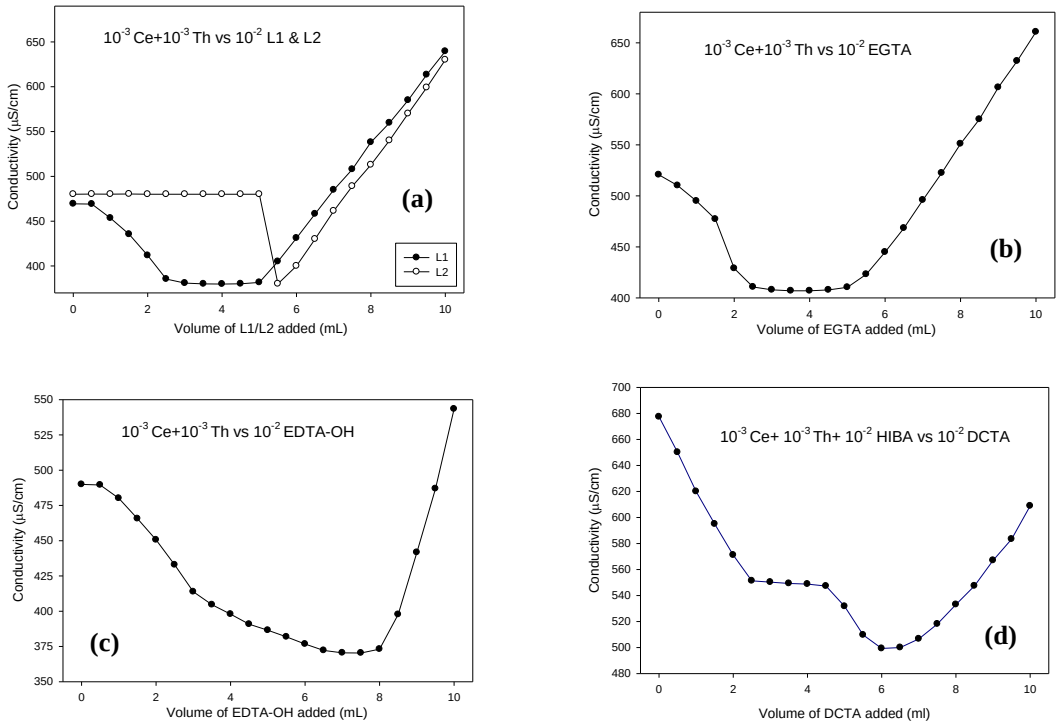


Figure 4.37(a-c): Conductometric titration curves for 25 mL of Ce(III) (1×10^{-3}M) + 25 mL Th(IV) (1×10^{-3}M) with L1, L2, L3 and L4 in absence of HIBA
4.37(d): Conductometric titration curves for 25 mL of Ce(III) (1×10^{-3}M) + 25 mL Th(IV) (1×10^{-3}M) with L2 in presence of HIBA

4.2.4 Determination of Ln(III) Ions In Real Time Samples

The objective of validating an analytical procedure is to demonstrate "suitability for its intended purpose". This can be done by using samples or standards that are similar to unknown samples analyzed routinely. A newly developed method is validated to substantiate that its performance parameters are adequate for use for a particular analytical problem. Therefore, the conductometric titration method established for lanthanide determination was tested on different real time samples for validation. The presence of lanthanides was tested in tap water, river water, clinical waste water and Welsbach gas mantle samples by using spike method. In spike method the sample under study is fortified with known amount of analytes under study. This is done for systems where the expected amount of analyte present in the sample may be too low to be detected clearly. Hence, spiking method helps to increase the signal strength for analyte under study. The presence of lanthanides was also tested in MRI contrast agent.

Tap water and river water samples were spiked with 100 mg L^{-1} of Ln(III) ion mixtures containing La(III) + Ce(III) + Dy(III) + Eu(III) for their simultaneous determination. Ln(III) determination in these spiked samples was carried out using the proposed conductometric titration method, the results for which are summarized in Table 4.15. The results obtained were confirmed with those obtained by spectrophotometry by the use of Arsenazo method. These were found to be in good agreement with those obtained from conductometric titration method. The third sample chosen for real time sample study was clinical waste sample collected from Christian Medical College, Vellore. This sample was tested for Gd(III) and sample was spiked with 100mg L^{-1} of Gd(III). Three replicate measurements were carried out, the average of which indicated Gd(III) = 109 ± 4 mg L^{-1}. Determination of Gd(III) in same samples by the Arsenazo method gave Gd(III) = 107 ± 2 mg L^{-1} which was in satisfactory agreement with the proposed method of conductometry. Forth sample selected for real time study was Welsbach mantle which is used for generating light in gas stoves. The mantle was digested as per the procedure given in Chapter-3 and solution made. This solution was spiked with 100 mg L^{-1} Ce(III) and used for determination. The amount of Ce(III) obtained by conductometric titration method was 110 ± 2 mg L^{-1} and Arsenazo

method gave Ce(III) = 112 ± 3 mg L^{-1}. The results obtained by the two methods were found to be in good agreement.

Table 4.15: Determination of Ln(III) ions in different environment and real time samples using conductometric titration with L1 and spectrophotometric method

S. No.	Sample Environment Used	Ln(III) Present	Amount of Ln(III) Ions Obtained*	
			Conductometric Method	Spectrophotometric Method
1	Tap water	La Ce Dy Eu	98 ± 1 98 ± 2 96 ± 2 95 ± 3	97 ± 2 99 ± 2 94 ± 3 94 ± 2
2	River water	La Ce Dy Eu	102 ± 2 105 ± 4 97 ± 4 98 ± 3	104 ± 3 107 ± 3 95 ± 3 97 ± 4
3	Clinical Waste Sample	Gd	109 ± 4	107 ± 2
4	Welsbach Gas Mantle	Ce	110 ± 2	112 ± 3

* The results obtained were an average of three measurements
** Spiked amount = 100mgL^{-1}

Gadopentetate dimeglumine injection is a sterile solution of N-methylglucamine salt of the gadolinium complex of diethylenetriamine pentaacetic acid (DTPA), and is an injectable contrast medium for magnetic resonance imaging (MRI). Literature states that it is a 0.5mol L^{-1} solution of 1-deoxy-1-(methylamino)-D-glucitol dihydrogen [N,N-bis[2-[bis(carboxy-methyl)amino]ethyl] glycinato (5-)]gadolinate(2-) with a molecular weight of 938 and an empirical formula of $C_{28}H_{54}GdN_5O_{20}$. Figure 4.38 gives its structural formula. Each mL of the injection is reported to contain 469.01 mg gadopentetate dimeglumine.

This was the next sample used for Ln(III) determination using L1. Sample for study was prepared by diluting the contrast. Concentration of the solution obtained by conductometric titration method was found to be 0.49M L^{-1} and was within error limits.

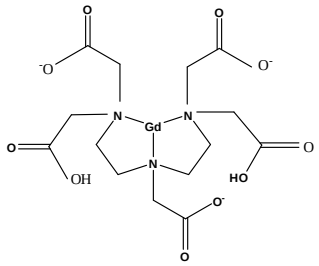


Figure 4.38: Structural formula of Gadopentetate dimeglumine

For all the real time samples under study the results were found to be within the error limit and consistent with results obtained with other methods, hence, proving the validity of the proposed method for Ln(III) determination.

4.3 Conclusions

Simple and rapid conductometric method was established as an analytical method for the quantitative determination of lanthanides with a detection limit of $1x10^{-5}$ M. Use of HIBA as a co-ligand was a necessary condition for determination of lanthanides in their binary mixtures. Changing the number of groups in the ligand backbone, e.g. in going from EDTA to TMDTA, effected the steric requirement of a PACA ligand which appreciably changed the effectiveness of lanthanide ion determination. DCTA as well as EDTA were found to be more effective for determination of single ion as well as binary mixtures of lanthanide as compared to EGTA, EDTA-OH and TMDTA. None of the interfering ions under study was found to interfere with Ln(III) determination except Al(III). The difficulty in determination of Ln(III) in presence of Al(III) observed with both types of electrodes (two-pole, five-ring) was overcome by using a 1,4-dioxane–water (1:4) medium instead of a pure water system.

4.4 References

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Spectrophotometric Determination of Lanthanides (III) Using Arsenazo III as Reagent in Presence of Polyaminocarboxylic Acids

Molecular spectroscopy based on ultraviolet-visible light has been widely used for the identification and determination of many inorganic, organic and biochemical species. Further, it is used for quantitative analysis and is probably more extensively applied in chemical and clinical laboratories throughout the world than any other single method.

Electronic absorption spectra are a result of promotion of valence electrons of the species from their ground states to the excited states due to the impact of electromagnetic radiation. In lanthanides such transitions most commonly involve the excited states which are either components of the ground term or excited states, which may arise from the same $4f^n$ configuration as the ground term. Both of these cases comprise a redistribution of electrons within the 4f orbitals (i.e. f→f transitions). Hence, these transitions like d→d transitions are orbitally forbidden. In case of d→d transitions the selection rule is partially relaxed due to the distortion of symmetry of the metal ion as a result of crystal field effect of the ligand. The same relaxation of selection rule, however, does not apply to lanthanides because the crystal field effects in case of latter are very small. Consequently, the colours of Ln(III) compounds are usually less intense. Another outcome of moderately small effect of crystal field is that the nature of the ligands or thermal vibrations have very low effect on the energies of the electronic states due to which the absorption bands for f→f transitions are very much sharper than those for d→d transitions.[1-2]

Organic reagent named Arsenazo III was synthesized in 1959 by S.B. Savvin and his coworkers at the Vemadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences. It was found to be very promising for analytical chemistry.[3] AsIII {3,6-bis[(2-arsonophenyl)-azo]-4,5-dihydroxy-2,7-naphthalenedisulphonic acid} is a bis-azo derivative of chromotropic acid used extensively for spectrophotometric analysis. Its numerous applications are a result of its high sensitivity, low selectivity and ability to form stable complexes over a wide pH range and in concentrated acid. It forms stable complexes with the lanthanides even in dilute media and gives characteristic electronic spectra which

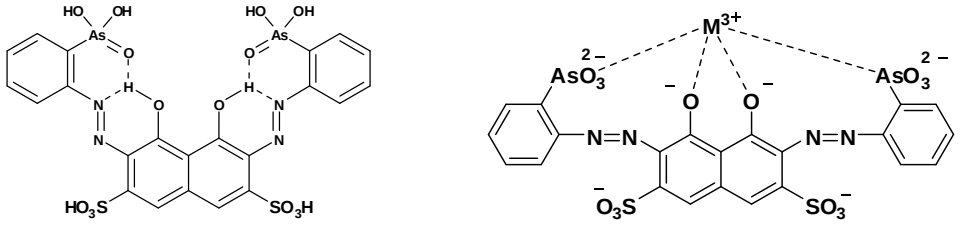
give bathochromic shifts of the bands of complexes of the order of 100-250 nm with respect to the bands of the reagent. Unique analytical properties of Arsenazo III have been studied in detail both in practice and theory. The reagent is widely used in industry and scientific research for the photometric determination of U, Th, Zr, Hf, Pd, Sc, Pa, Np, Pu, Am, Cm, rare earth elements, etc.[4-7] The reagent remains the best for the above elements.[8]

Complexation of lanthanides by arsenazo III and detection of lanthanides have been investigated extensively by spectrophotometry and thermodynamically.[9-13] Literature contains numerous discrepancies regarding the stoichiometry of its lanthanide complexes, these include (Az:Ln): 1:l,[14-17] 2:l,[14,17] 1:2[18] and 2:2.[15,18,19] These discrepancies have been explained to be a result of molecular association at high reagent concentrations.[20] the spectrum of the arsenazo III–lanthanide complex is found to be strongly pH dependent. The chromophore exhibits a high sensitivity to the lanthanides (III) over the range pH 3-4 and is known to give maximum complexation at pH 3.2-3.4. The studies by Rohwer *et al.*[21] indicated that only the 1 : 1 lanthanide–arsenazo III complex is formed at low arsenazo III concentration and in a dilute acidic medium (pH 3.5). Hence, a pH value of 3.5 was chosen for all studies as in this region absorbance is relatively independent of small changes in pH.[21] Also, in the pH range = 3.0 to 3.9 hydrolysis of Nd(III) is avoided which would introduce additional complexity and uncertainty into the analysis of the chemical system.[22] The structure of chromophore Arsenazo III (AsIII) in free as well as complexed form is shown in Figure 5.1(a-b).[23] The activity and stability of Arsenazo III in acidic media prompted interest in studying its behaviour. Due to the low values of formation constants of AsIII–Ln(III) complexes it could be used to study competition with other ligands for the complexation of the same Ln(III) cations. For these studies it was necessary that the competing ligand chosen be more efficient than AsIII but still be capable of bonding with lanthanides, when this ligand competes with AsIII for complexing Ln(III) there would be very little lanthanide left to be complexed by AsIII. Hence, the effect of PACA on AsIII–Ln(III) complexes can be studied.

5.1 Reagents and Experimental set up

The detailed discussion regarding reagents and experimental set up is given in Chapter-3,

Materials and Methods.



(a) **(b)**

Figure 5.1: Structure of Arsenazo III in (a) uncomplexed and (b) complexed forms

5.2 Results and Discussion

5.2.1 Spectrophotmetric behaviour of AsIII in the presence and absence of Na_4EDTA

UV spectra of AsIII molecule exhibited λ_{max} at 538 nm Figure 5.2. From the absorbance values at λ_{max}, $5x10^{-5}$M was taken as the optimum concentration for further studies as lower concentration of solution gave very low absorption, whereas absorbance for 10^{-4}M solution was high and may not have followed the Beer Lambert law. Absorbance spectra of AsIII, in the presence of Na_4EDTA were taken by adding Na_4EDTA (1 mL) to a solution of AsIII ($5x 10^{-5}$M, 1 mL) and buffer of pH =3.5 (1 mL) and the results are given in Figure 5.3. The spectrum of AsIII was affected by the phenomenon of hypochromic effect in the presence of Na_4EDTA. This could be due to substantial overcrowding of Na_4EDTA molecule on active functional groups of arseanzo III.

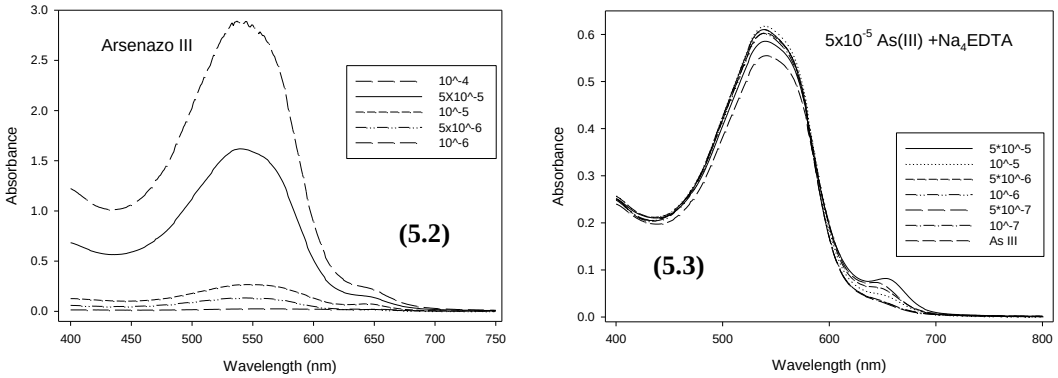


Figure 5.2: Absorbance *vs*. wavelength plots of AsIII at its different concentrations**;**
Figure 5.3: Absorbance *vs*. wavelength plots of AsIII (1 mL of $5x10^{-5}$M) in the presence of different concentrations of Na_4EDTA (6 mL)

5.2.2 Spectrophotmetric behaviour AsIII–Ln(III) complex

UV-Visible spectra of solutions containing fixed concentrations of AsIII (1mL of $5x10^{-5}$M) and variable concentrations of La(III) (10^{-9} M – 10^{-4} M) (in presence of buffer pH=3.5, 1 mL) were carried out for which concentration *vs.* absorbance curves were plotted to establish the detection limit. The results obtained are given in Figures 5.4a and 5.4a′. The notable trend is the decrease in intensity at 610 and 654 nm bands of La(III)–AsIII complex with decrease in concentration of La (III) solution.

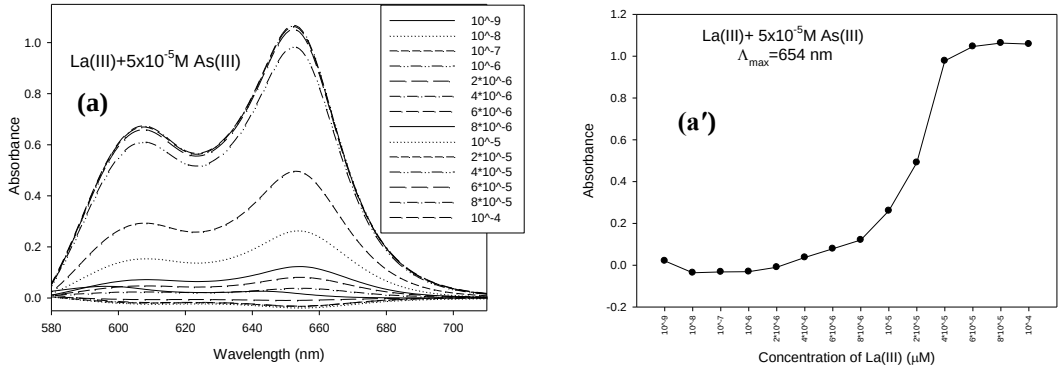


Figure 5.4 (a-a′): (a) Absorbance *vs*. wavelength plots of AsIII–La(III) complex
(a′) Absorbance *vs*. concentration plots of AsIII–La(III) complex

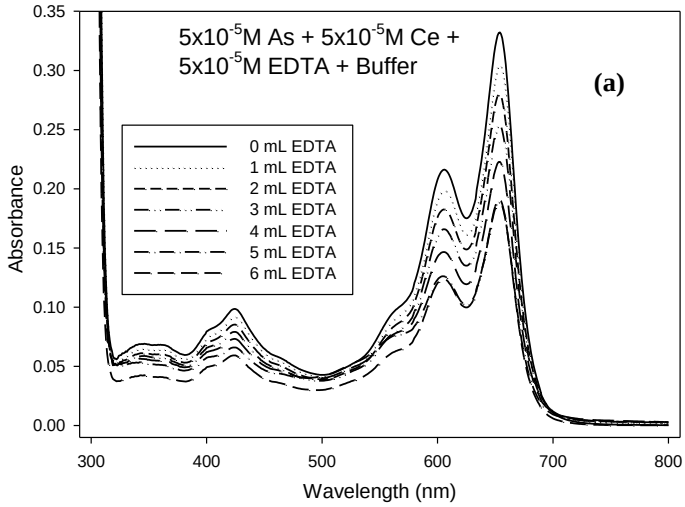
From absorbance *vs*. concentration plots as shown in Figure 5.4(b), $6x10^{-5}$M – $8x10^{-6}$M can be taken as the detection range. It is assumed that any part of the titration curve might be considered to represent adequately the whole system. The absorption band in the curve at 538 nm due to free AsIII disappears on addition of La(III) solution and two sharp bands at 610 nm and 654 nm appear, which are characteristic of AsIII–Ln(III) complex.[11] Free Arsenazo III molecule (Figure 5.1a), is symmetrical and both the the chromophore systems are identical resulting in only one absorption band due to coincident absorption spectra. The appearance of two absorption bands in the complex of Arsenazo III with elements is indicative of a symmetry breakdown in the complex molecule (Figure 5.1b). The spectrum shows that absorbance reaches its maximum at 2 mL of La(III) added which corresponds to 1:1:: AsIII:La(III) stoichiometry. The fact that these two peaks correspond to two electronic transitions in the same molecule is indicated by their simultaneous decrease upon successive additions of any Ln in the solution.

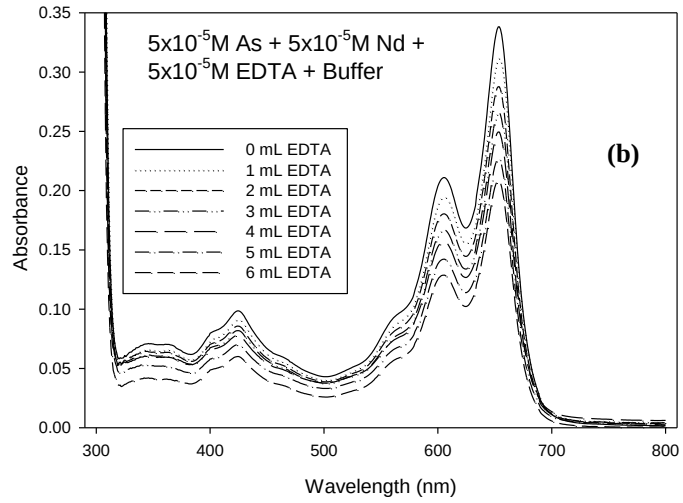
5.2.3 Spectrophotmetric behaviour arsnazoIII–Ln(III) complex in presence of PACA

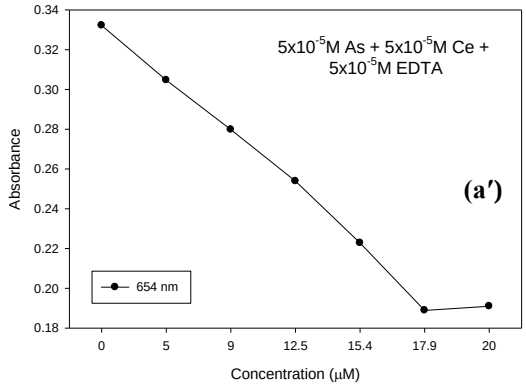
To study the effect of PACA on Ln(III)–AsIII complexes five lanthanides representing the lighter and heavier lanthanides in series, namely: Ce(III), Nd(III), Dy(III), Tm(III)and Lu(III), were chosen.

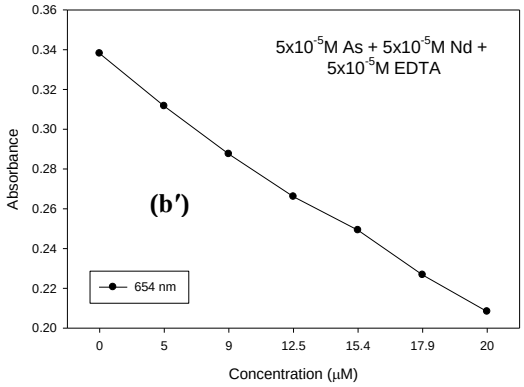
5.2.3.1 Spectrophotometric titrations of Ln(III)–AsIII complexes with EDTA

As seen from Figures 5.5a and 5.5b the broad band at 538 nm due to AsIII group disappeared on addition of lanthanide solution of equimolar concentration. The new peaks that appeared at 610 nm and 654 nm in place of a broad band at 538 nm were probably due to phenolate and azide groups of AsIII complexed with Ln(III) ions. The possibility of singlet to triplet transitions between the highest occupied and lowest unoccupied energy levels of the complex and the reagent might be a cause of the main-band (538 nm) splitting.[8] The absorption peak at 610 nm was due to ionization of phenolic groups of AsIII in an extended form and bore resemblance to the peak formed at high pH in the absence of bivalent cations. When AsIII molecule wraped around a large metal ion, the conformational changes in the molecule led to a change in orientation of the diazo bonds which gave a peak at 654 nm.[24] On further addition of EDTA (5×10^{-5}M) to the solution containing AsIII (1 mL, 5×10^{-5}M) and Ln(III) (6 mL, 5×10^{-5}M) ions the following changes were observed: If the solution contained lanthanides Ce(III) and Nd(III), the absorbance of 610 nm and 654 nm peaks decreased continuously with each addition of EDTA made [Figure 5.5a′ and 5.5b′] whereas if the solution contained lanthanides Dy(III), Tm(III) and Lu(III) further, addition of EDTA resulted in disappearance of peak at 610 nm while peak at 654 nm survived [Figure 5.5c – 5.5e and 5.5c′ – 5.5e′]. A new band at 538 nm appeared which was due to free AsIII in the solution, released by the displacement of AsIII from AsIII–Ln(III) complex. It was interesting to note that the absorbance at 538 nm did not increase in intensity on increasing the concentration of EDTA in the mixture solution and the absorbance at 654 nm disappeared on further addition of EDTA. This was due to the reason that after the formation of 1:1 complex between EDTA and Ln(III) species no further change in the intensities were expected due to absence of interaction between AsIII and EDTA.


5x10-5M As + 5x10-5M Ce +
5x10-5M EDTA + Buffer
(a)
0 mL EDTA
1 mL EDTA
2 mL EDTA
3 mL EDTA
4 mL EDTA
5 mL EDTA
6 mL EDTA
Absorbance
Wavelength (nm)


5x10-5M As + 5x10-5M Nd +
5x10-5M EDTA + Buffer
(b)
0 mL EDTA
1 mL EDTA
2 mL EDTA
3 mL EDTA
4 mL EDTA
5 mL EDTA
6 mL EDTA
Absorbance
Wavelength (nm)


5x10-5M As + 5x10-5M Ce +
5x10-5M EDTA
(a′)
654 nm
Absorbance
Concentration (μM)


5x10-5M As + 5x10-5M Nd +
5x10-5M EDTA
(b′)
654 nm
Absorbance
Concentration (μM)

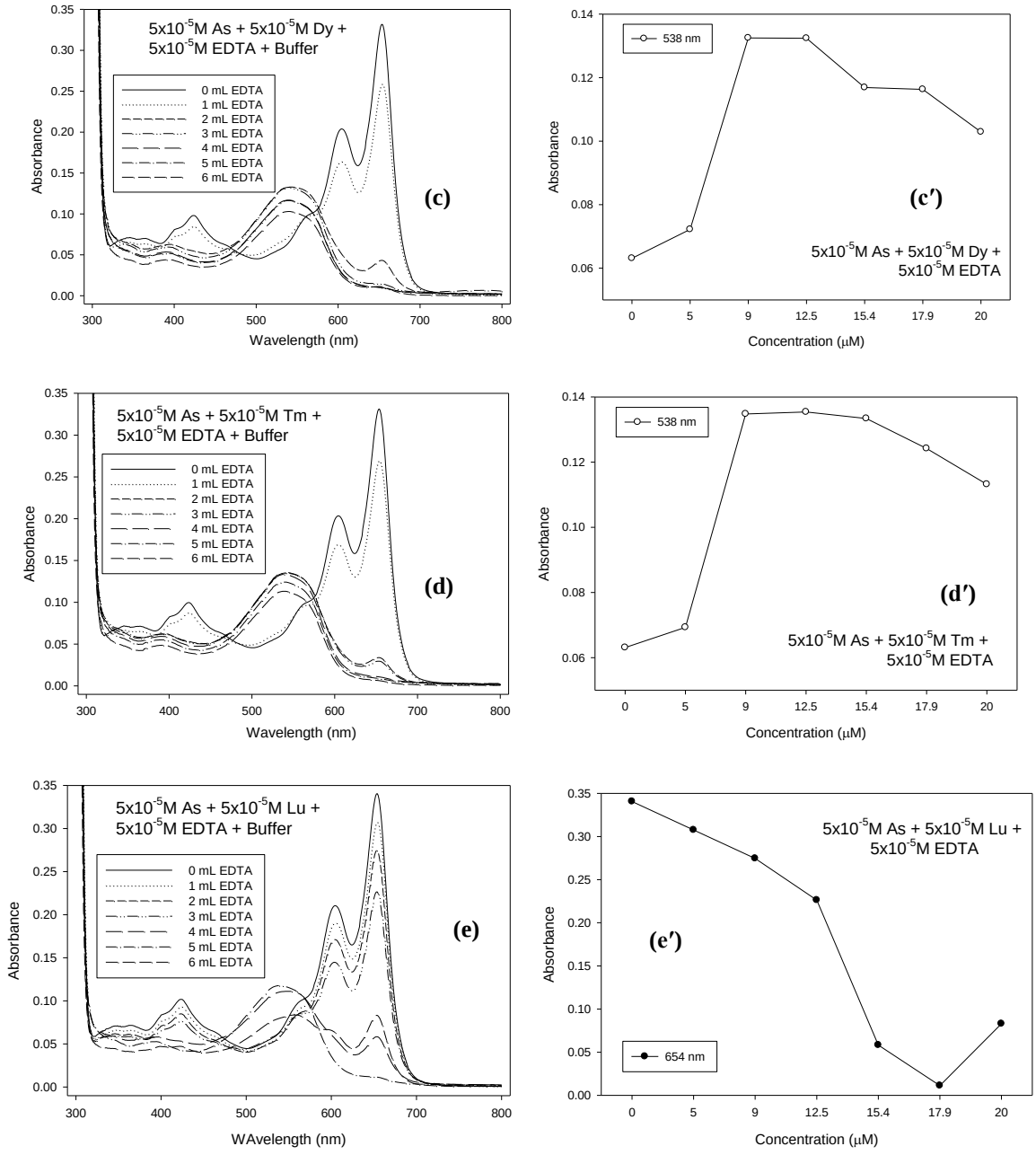


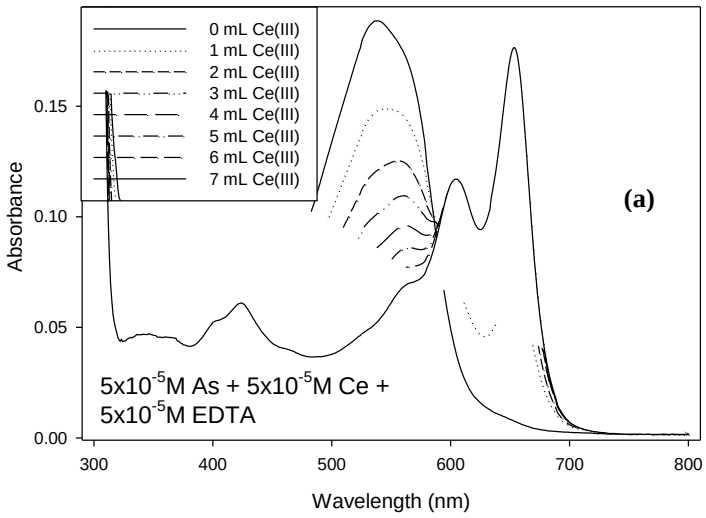
Figure 5.5(a-e): Absorbance *vs*. wavelength plots for AsIII–Ln(III) complex in the presence of different concentrations of EDTA

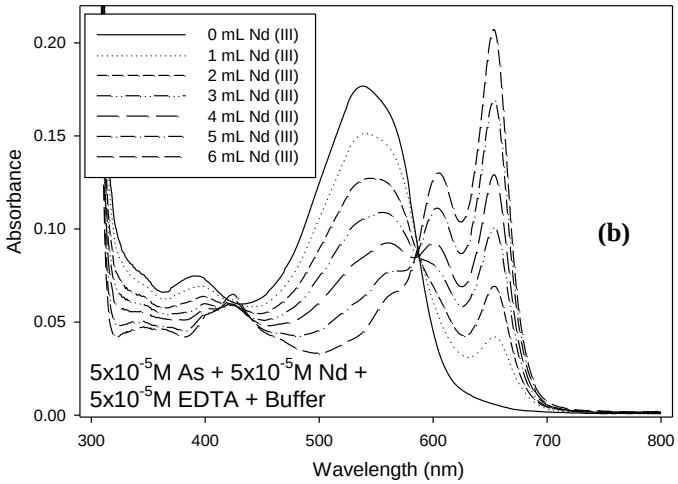
5.5 (a′-e′): Absorbance *vs*. concentration plots for AsIII–Ln(III) complex in the presence of different concentrations of EDTA

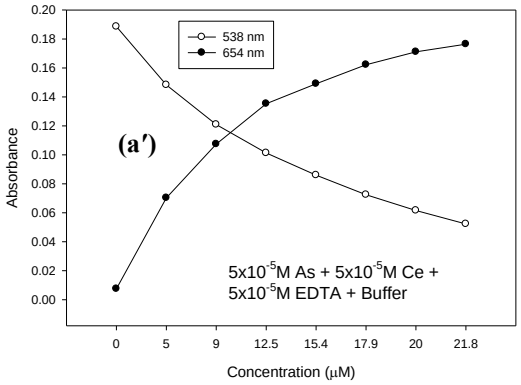
5.2.3.2 Spectrophotometric titrations of mixture of AsIII and EDTA with Ln(III)

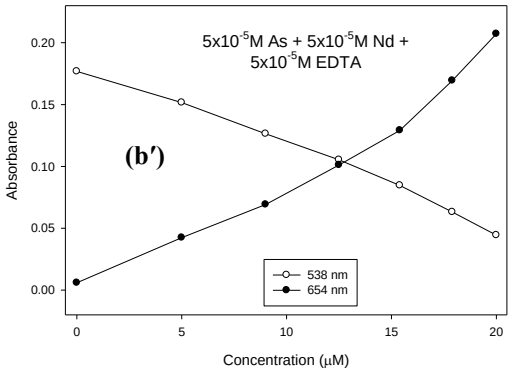
On titrating a solution containing AsIII (1 mL, 5×10^{-5}M) and EDTA (6 mL, 5×10^{-5}M) with Ln(III) (5×10^{-5}M) the absorbance due to AsIII (538 nm) underwent a change in position to 610 nm (sh) and 654 nm (sh) on addition of lanthanides (Figures 5.6a and 5.6b) similar to that observed previously in Figure 5.4. In case of Ce(III) and Nd(III), the addition of 1mL of equimolar lanthanide solution showed low intensity peaks at 654 nm due to the formation of 1:1 complex. This observation was further strengthened with increase in intensity of peaks on addition of Ln(III) [Figure 5.6a′ and 5.6b′]. On addition of lanthanides to a solution containing AsIII and EDTA, it was observed that the peak at 538 nm gradually disappeared i.e., diminished in intensity after each addition upto 3mL, due to decrease in the availability of free AsIII present in the solution, and then finally disappeared at 4mL giving rise to a new peak at 610 nm which is due to the formation of Ce(III)/Nd(IIII)–AsIII complex. The increase in peak intensity 610nm and 654 nm with each addition of lanthanide solution might be due to the fact that EDTA and AsIII were competing with each other for complexing with Ln(III) and for each milliequivalents of Ln(III) added some amount complexed with AsIII and the rest with EDTA leaving some free AsIII in the system to complex with EDTA on further Ln(III) addition, hence, resulting in an increase in the amount of Ce(III)/Nd(III)–AsIII complex on each addition.

In case of heavier lanthanides like Dy(III), Tm(III) and Lu(III) (Figure 5.6c - 5.6e and 5.6c′ - 5.6e′) a decrease in peak intensity at 538 nm was observed, on each subsequent addition of Ln(III) to AsIII–EDTA solution which was attributed to the decrease in concentration of AsIII in solution after each addition. The absence of peaks at 610 and 654 nm indicated that the formation of weak Ln(III)–AsIII complex might be suppressed by Ln(III)–EDTA complex. Moreover, the added Ln(III) solution formed complexed with the EDTA available in solution this is because the difference between stability constant value of Ln(III)–EDTA complexes and Ln(III)–AsIII complexes are much higher for heavier lanthanides [log K Dy(III)–AsIII and Dy(III)–EDTA, being 7.63 and 18.30, respectively].


0 mL Ce(III)
1 mL Ce(III)
2 mL Ce(III)
3 mL Ce(III)
4 mL Ce(III)
5 mL Ce(III)
6 mL Ce(III)
7 mL Ce(III)
(a)
5x10-5M As + 5x10-5M Ce +
5x10-5M EDTA
Absorbance
Wavelength (nm)


0 mL Nd (III)
1 mL Nd (III)
2 mL Nd (III)
3 mL Nd (III)
4 mL Nd (III)
5 mL Nd (III)
6 mL Nd (III)
(b)
5x10-5M As + 5x10-5M Nd +
5x10-5M EDTA + Buffer
Absorbance
Wavelength (nm)


538 nm
654 nm
(a′)
5x10-5M As + 5x10-5M Ce +
5x10-5M EDTA + Buffer
Absorbance
Concentration (μM)


5x10-5M As + 5x10-5M Nd +
5x10-5M EDTA
(b′)
538 nm
654 nm
Absorbance
Concentration (μM)

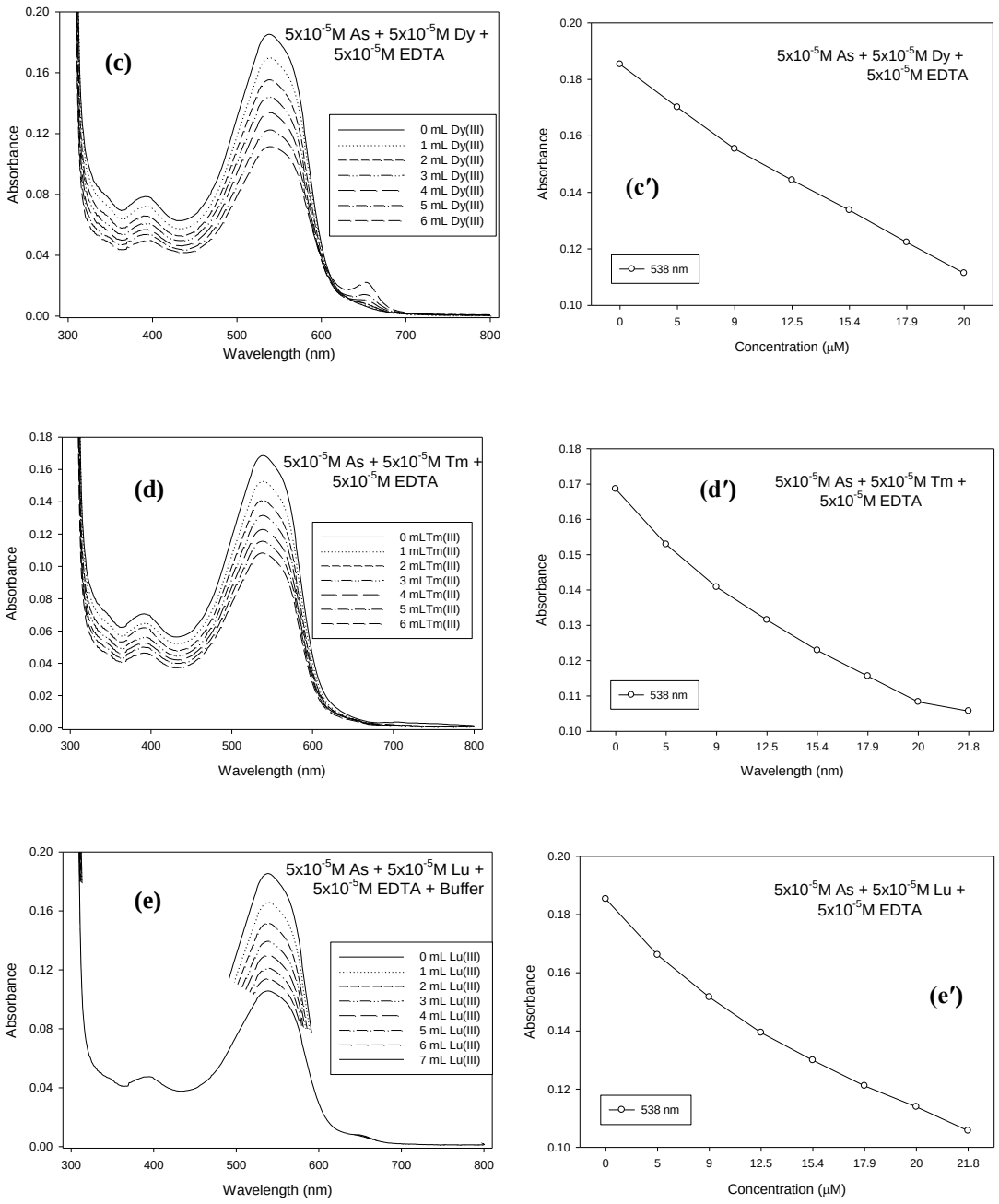
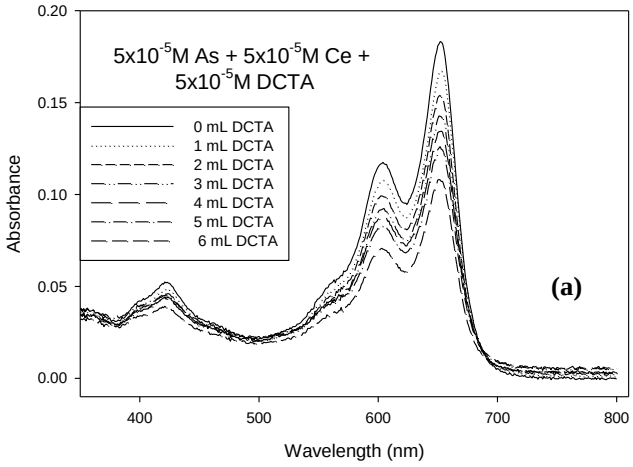


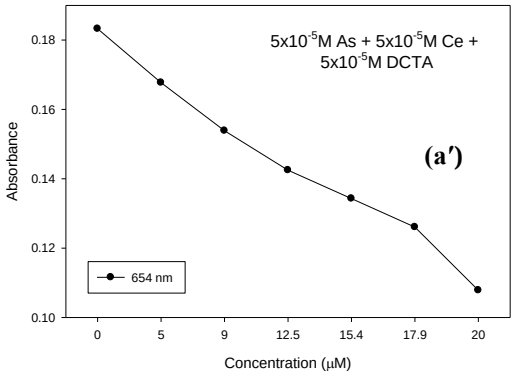
Figure 5.6 (a-e): Absorbance *vs*. wavelength plots for titration of mixture of AsIII and EDTA with Ln(III)

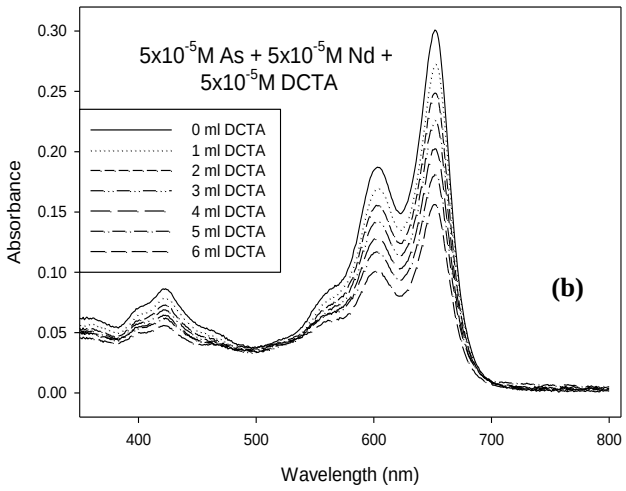
5.6 (a′-e′): Absorbance *vs*. concentration plots for titration of mixture of AsIII and EDTA with Ln(III)

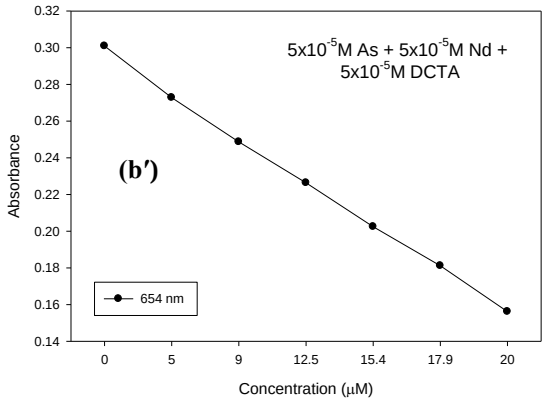
5.2.3.3 Spectrophotometric titrations Ln(III)–AsIII complexes with DCTA

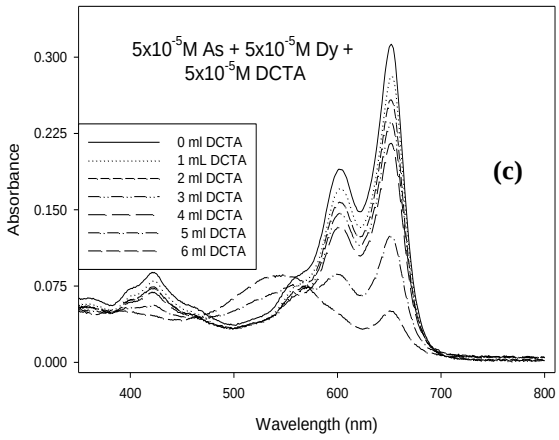
On adding DCTA (5×10^{-5}M) to a solution containing AsIII(1 mL, 5×10^{-5}M) and Ln(III) (6 mL, 5×10^{-5}M), the changes observed in the absorption spectra, in case of all five Ln(III) ions, were similar to those observed in the case of EDTA (Figures 5.7a- 5.7e and 5.7a′-5.7e′). For solutions containing lighter lanthanides like Ce(III) and Nd(III), the intensity of peaks at 610 nm and 654 nm decreased continuously with each addition of DCTA whereas, for the solutions containing heavier lanthanides like Dy(III), Tm(III) and Lu(III) addition of DCTA led to a decrease and subsequent disappearance of peak at 610 nm and 654 nm giving way to a new band at 538 nm which was attributed to the uncomplexed AsIII dye molecule. Further addition of DCTA did not result in any major change in the intensity of peak at 538 nm which might be due to the reason that all the AsIII present in the system as AsIII–Ln(III) complex was displaced by DCTA added to the system.

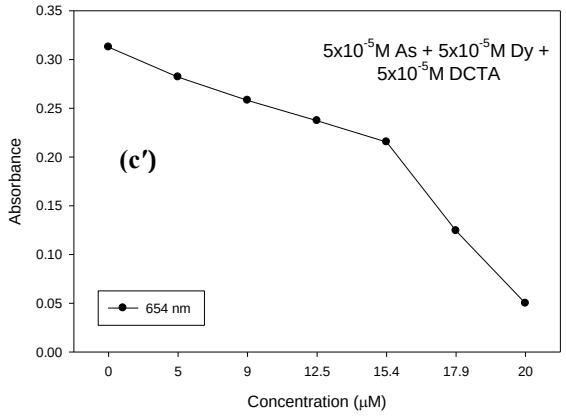





5x10-5M As + 5x10-5M Nd +
5x10-5M DCTA
0 ml DCTA
1 ml DCTA
2 ml DCTA
3 ml DCTA
4 ml DCTA
5 ml DCTA
6 ml DCTA
(b)
Absorbance
Wavelength (nm)


5x10-5M As + 5x10-5M Nd +
5x10-5M DCTA
(b′)
654 nm
Absorbance
Concentration (μM)


5x10-5M As + 5x10-5M Dy +
5x10-5M DCTA
0 ml DCTA
1 mL DCTA
2 ml DCTA
3 ml DCTA
4 ml DCTA
5 ml DCTA
6 ml DCTA
(c)
Absorbance
Wavelength (nm)


5x10-5M As + 5x10-5M Dy +
5x10-5M DCTA
(c′)
654 nm
Absorbance
Concentration (μM)

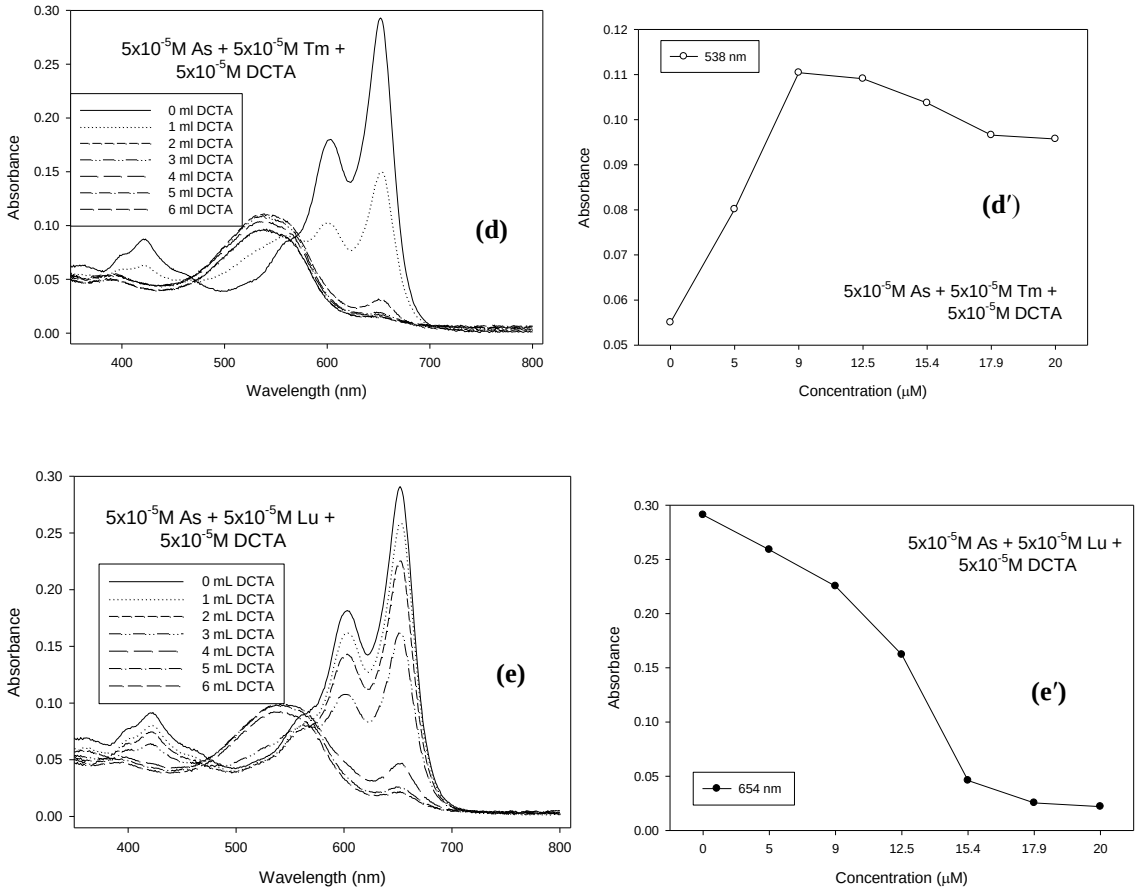


Figure 5.7 (a-e): Absorbance *vs*. wavelength for AsIII–Ln(III) complex in the presence of different concentrations of DCTA

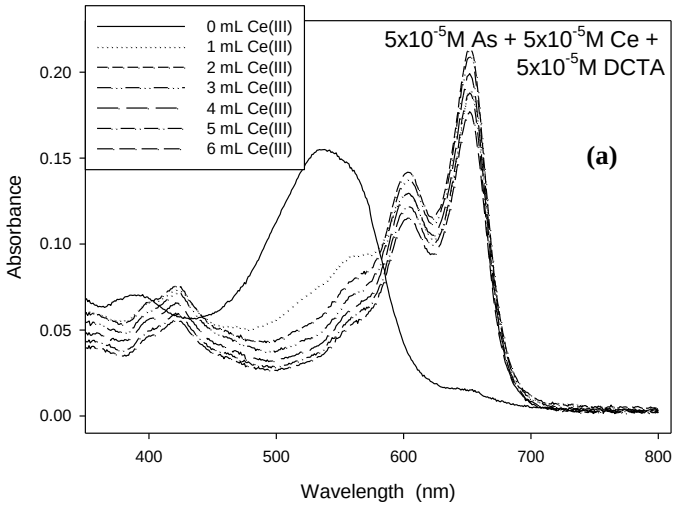
5.7 (a′-e′): Absorbance *vs*. concentration for AsIII–Ln(III) complex in the presence of different concentrations of DCTA

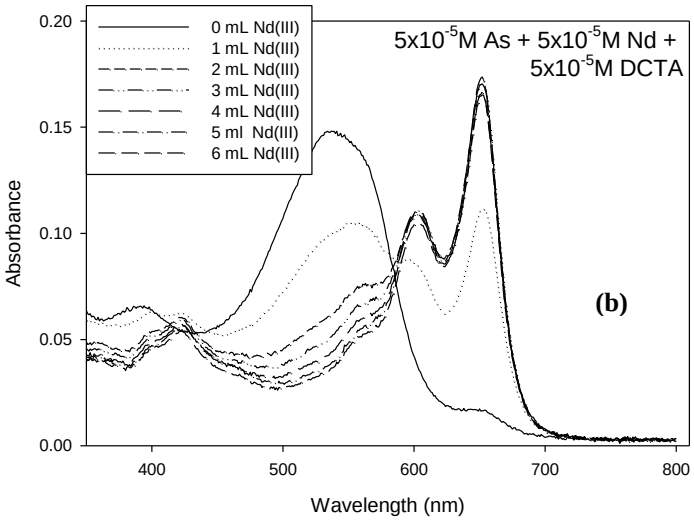
5.2.3.4 Spectrophotometric titrations of mixture of DCTA and AsIII with Ln(III)

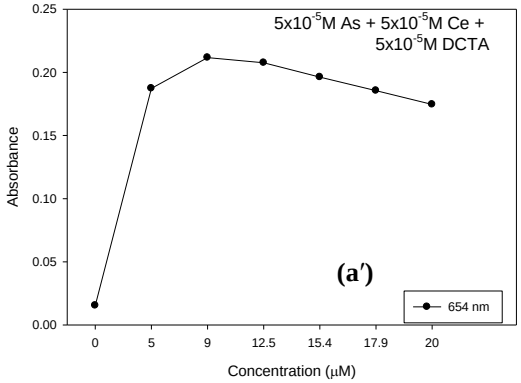
Spectrophotmetric titrations of solution containing AsIII (1 mL, 5×10^{-5}M) and DCTA (6 mL, 5×10^{-5}M) with Ln(III) (5×10^{-5}M) followed trends similar to those obtained for EDTA. The peak at 538 nm due to free AsIII disappeared on addition of 1mL of equimolar Ln(III), in case of lighter lanthanides [Ce(III) and Nd(III)], and two new peaks at 610 nm and 654 nm appeared, which were characteristic of AsIII–Ln(III) complex formation. In case of Ce(III) it was observed that further addition of Ce(III) did not have much effect on the intensity of the peaks showing that all the AsIII present in the system had complexed with Ce(III) added during the first addition (Figures 5.8a and 5.8a′). However, in case of Nd(III), the behaviour observed was similar to that observed with EDTA i.e. the peak at 538 nm

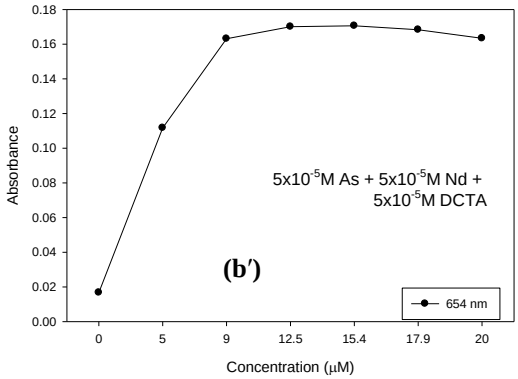
disappeared gradually giving rise to peaks at 610 and 654 nm till 2 mL addition of Nd(III), after which the intensity of peaks remained almost constant (Figures 5.8b and 5.8b′). This might be due to the reason that on going from Ce(III) to Nd(III) in the lanthanide series the stability constant values of Ln(III)–DCTA complexes increase by approximately 1 unit due to which DCTA starts competing with AsIII for bonding with Nd(III) and on first addition of Nd(III) some amount of Nd(III) complexes with AsIII and the rest with DCTA (similar to the EDTA), second addition of Nd(III) results in formation of more AsIII–Nd(III) complex using up all the free AsIII present in the system due to which no increase in peak intensity was observed on further addition of DCTA.

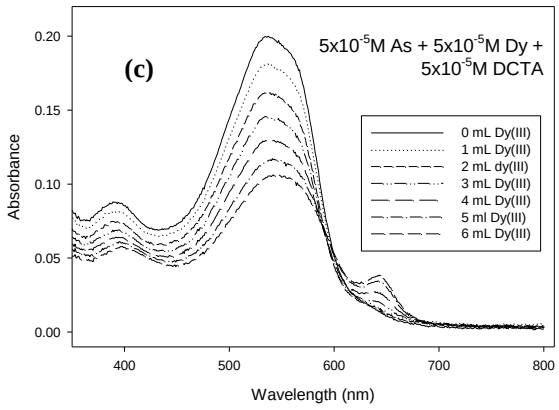
In case of heavier lanthanides i.e., Dy(III), Tm(III) and Lu(III) (Figures 5.8c - 5.8e and 5.8c′- 5.8e′) a decrease in peak intensity at 538 nm was observed after each subsequent addition of Ln(III) to AsIII–DCTA solution which might be due to a decrease in concentration of AsIII in solution. The peaks at 610 nm and 654 nm did not appear, in case of heavier lanthanides, showing once again that the formation of Ln(III)–AsIII complex did not take place and Ln(III) solution added only complexed with DCTA present due to large difference in the stability constant values of Ln(III)–DCTA complexes as compared to Ln(III)–AsIII complexes.

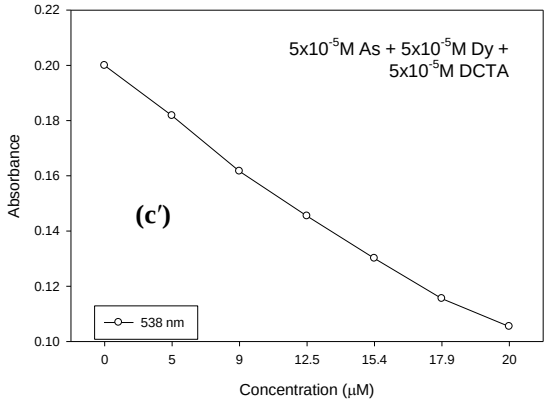



0 mL Nd(III)
1 mL Nd(III)
2 mL Nd(III)
3 mL Nd(III)
4 mL Nd(III)
5 ml Nd(III)
6 mL Nd(III)
5x10-5M As + 5x10-5M Nd +
5x10-5M DCTA
(b)
Absorbance
Wavelength (nm)


5x10-5M As + 5x10-5M Ce +
5x10-5M DCTA
(a′)
654 nm
Absorbance
Concentration (μM)


5x10-5M As + 5x10-5M Nd +
5x10-5M DCTA
(b′)
654 nm
Absorbance
Concentration (μM)


(c)
5x10-5M As + 5x10-5M Dy +
5x10-5M DCTA
0 mL Dy(III)
1 mL Dy(III)
2 mL dy(III)
3 mL Dy(III)
4 mL Dy(III)
5 ml Dy(III)
6 mL Dy(III)
Absorbance
Wavelength (nm)


5x10-5M As + 5x10-5M Dy +
5x10-5M DCTA
(c′)
538 nm
Absorbance
Concentration (μM)

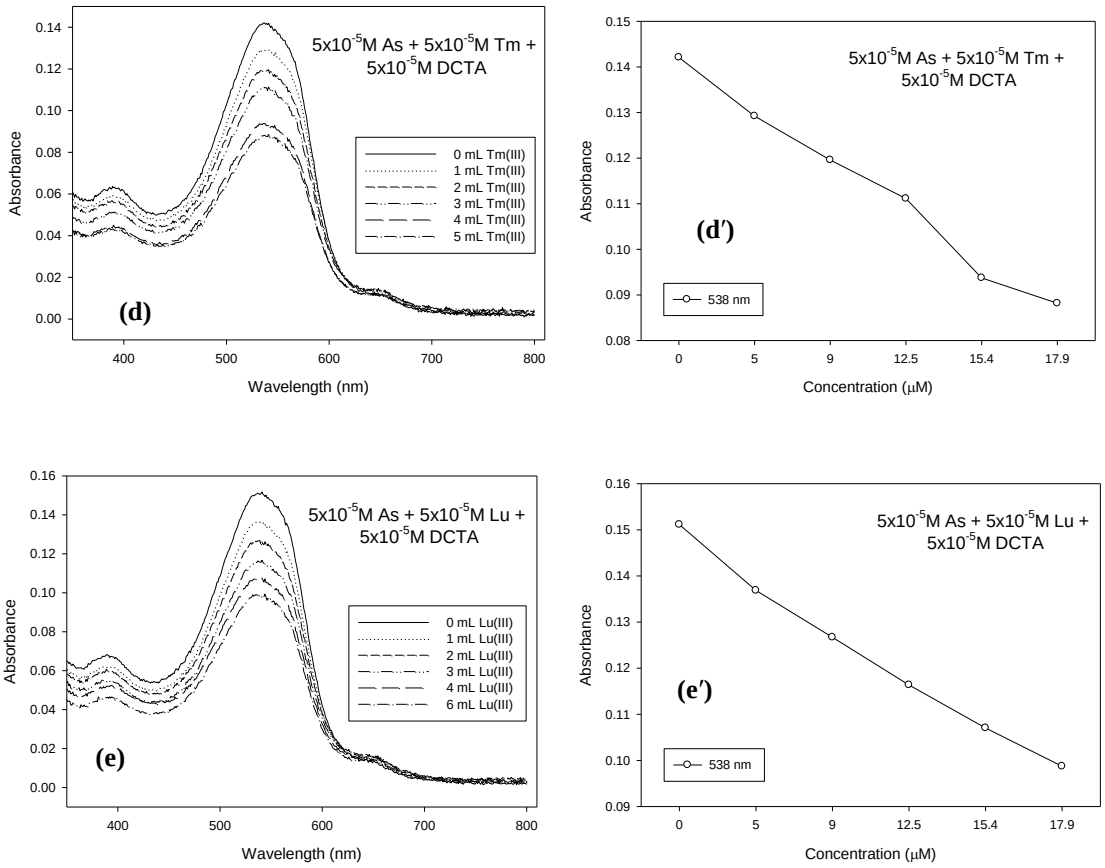


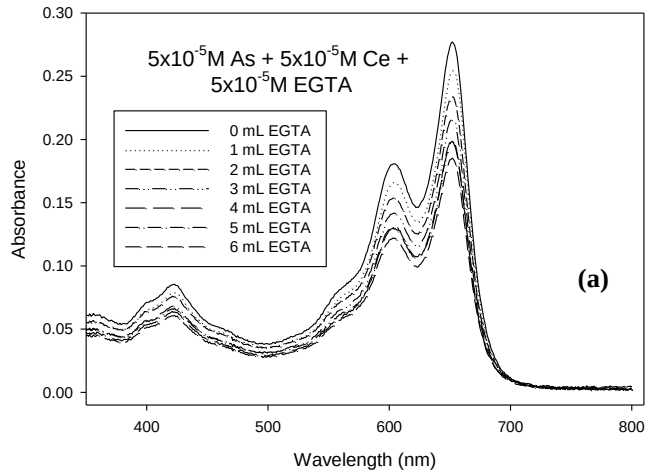
Figure 5.8(a-e): Absorbance *vs*. wavelength plots for titration of mixture of AsIII and DCTA with Ln(III)

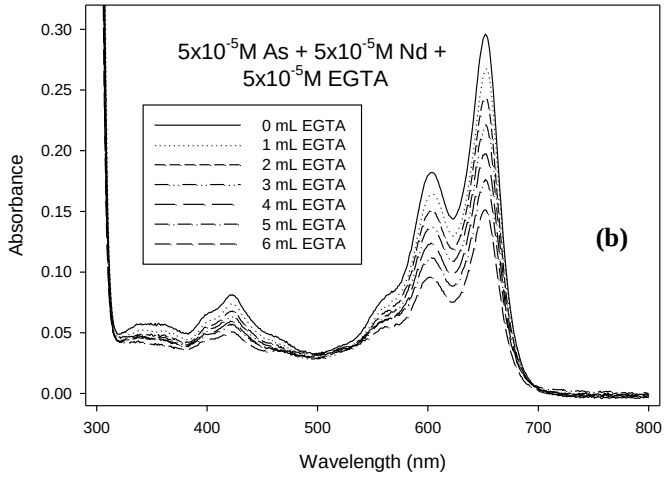
5.8 (a′-e′): Absorbance *vs*. concentration plots for titration of mixture of AsIII and DCTA with Ln(III)

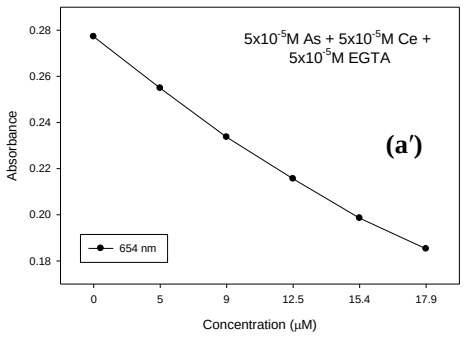
5.2.3.5 Spectrophotometric titrations Ln(III)–AsIII complexes with EGTA

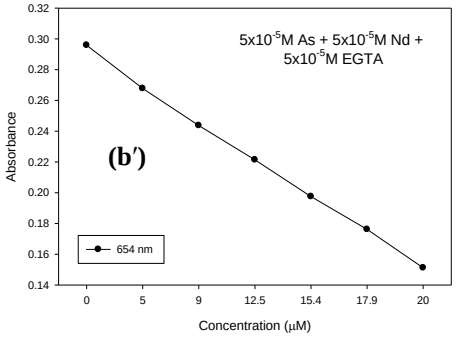
The results obtained for titrations of AsIII–Ln(III) complexes with EGTA (5×10^{-5}M) are given in Figures 5.9a - 5.9e and 5.9a′ - 5.9e′. The results were similar to those obtained for EDTA and DCTA in case of lighter lanthanide; however, they did not coincide for heavier lanthanides. In case of EGTA all five lanthanides [Ce(III), Nd(III), Dy(III), Tm(III) and Lu(III)] under study gave similar results. On each successive addition of EGTA to AsIII–Ln(III) solution a decrease in absorbance at 610 and 654 nm was observed. Here, the disappearance of peaks at 610 nm and 654 nm and subsequent appearance of 538 nm peak for free AsIII was not observed for heavier lanthanides unlike EDTA and DCTA. This was indicative of the fact that EGTA was unable to displace AsIII from AsIII–Ln(III) complex

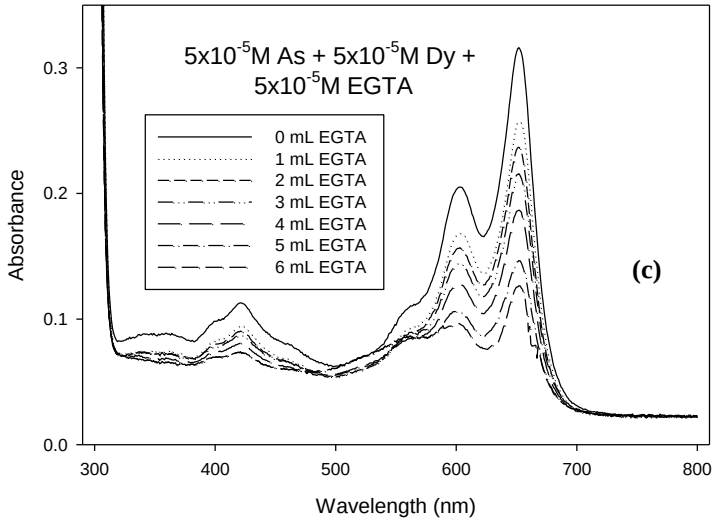
even in case of heavier lanthanides. This might be due to high steric constraints on water binding sites in the complex which destabilized the bound water molecule and hence, decreased stability of Ln(III)–EGTA complex (already explained in the previous chapter, Chapter-4, page 76).

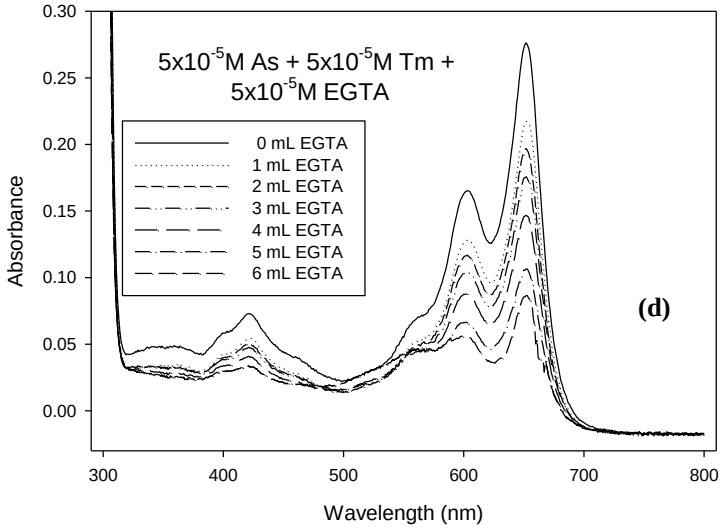


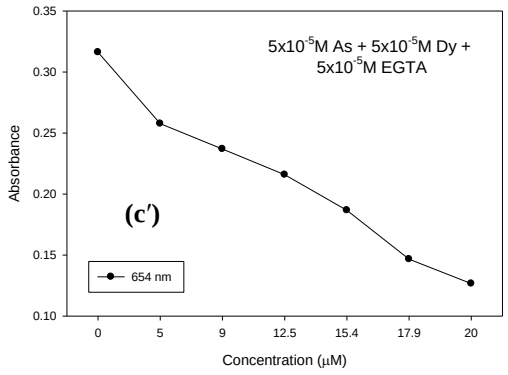


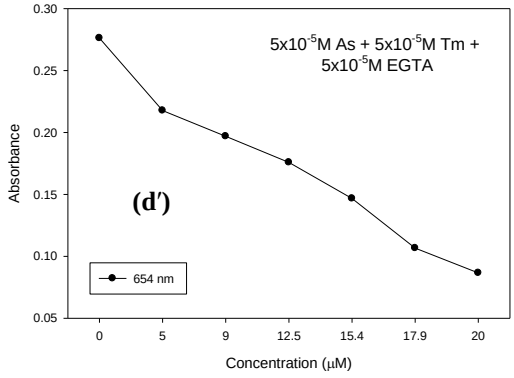





5x10-5M As + 5x10-5M Dy +
5x10-5M EGTA
0 mL EGTA
1 mL EGTA
2 mL EGTA
3 mL EGTA
4 mL EGTA
5 mL EGTA
6 mL EGTA
(c)
Absorbance
Wavelength (nm)


5x10-5M As + 5x10-5M Tm +
5x10-5M EGTA
0 mL EGTA
1 mL EGTA
2 mL EGTA
3 mL EGTA
4 mL EGTA
5 mL EGTA
6 mL EGTA
(d)
Absorbance
Wavelength (nm)


5x10-5M As + 5x10-5M Dy +
5x10-5M EGTA
(c′)
654 nm
Absorbance
Concentration (μM)


5x10-5M As + 5x10-5M Tm +
5x10-5M EGTA
(d′)
654 nm
Absorbance
Concentration (μM)

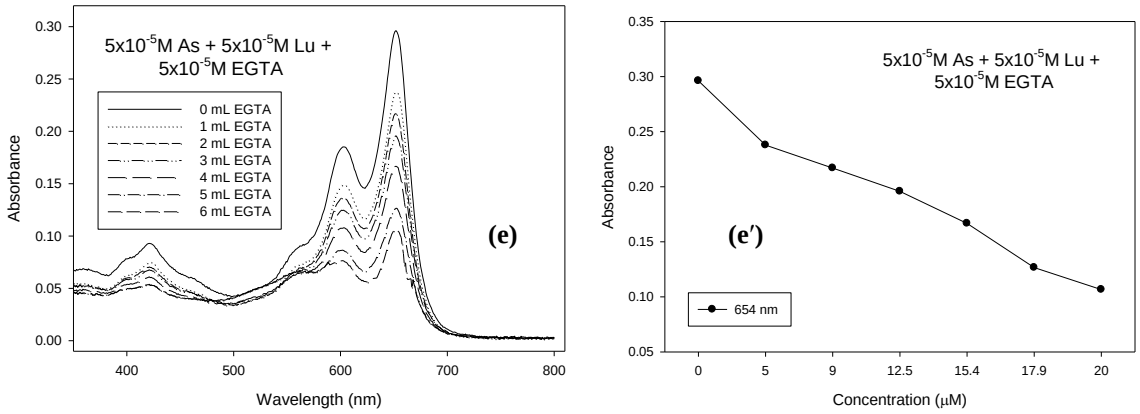
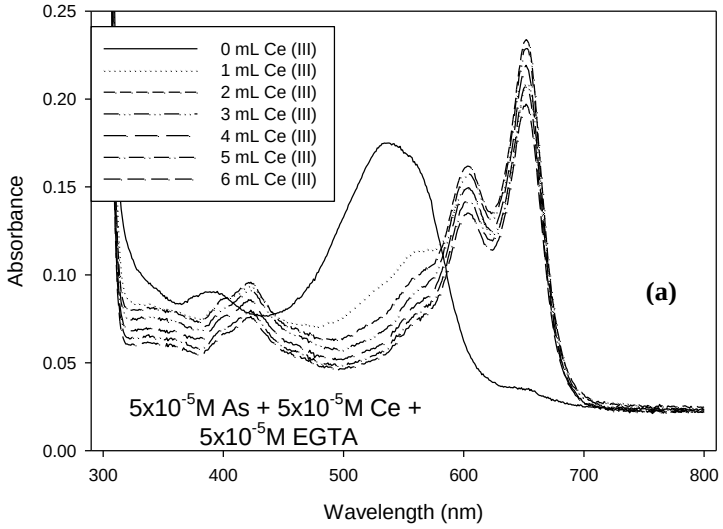


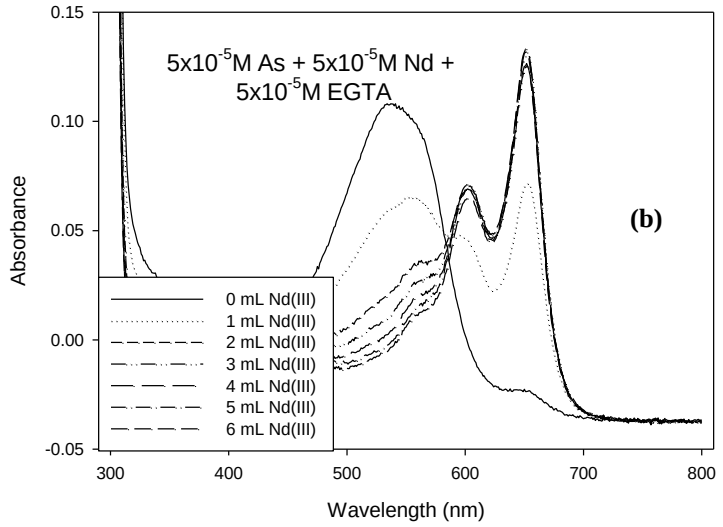
Figure 5.9 (a-e): Absorbance *vs*. wavelength plots for AsIII–Ln(III) complex in the presence of different concentrations of EGTA

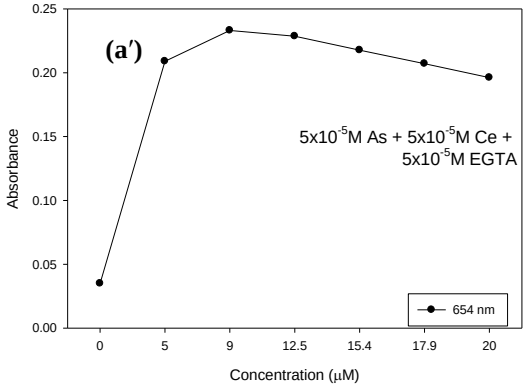
5.9 (a′-e′): Absorbance *vs*. concentration plots for AsIII–Ln(III) complex in the presence of different concentrations of EGTA

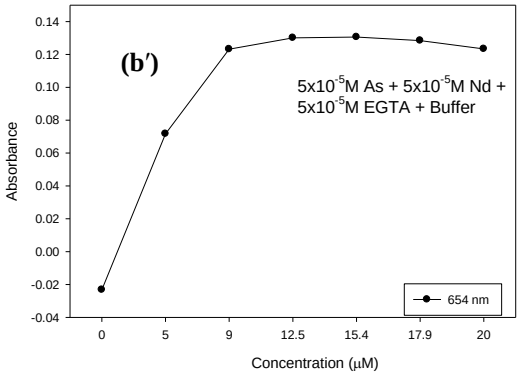
5.2.3.6 Spectrophotometric titrations of mixture of EGTA and AsIII with Ln(III)

For the titration of solution of AsIII (1 mL, 5×10^{-5}M) and EGTA (6 mL, 5×10^{-5}M) with equimolar Ln(III), the results obtained were analogous to those obtained for EDTA and DCTA. Addition of 1 equimolar Ce(III)/ Nd(III) to a mixture of AsIII and EGTA led to the disappearance of 538 nm peak and appearance of two sharp peaks at 610 and 654 nm which showed that the free AsIII initially present in the mixture had complexed with Ln(III) to form Ce(III)/Nd(III)–AsIII complex. Further addition of Ce(III)/Nd(III) did not result in any noticeable change in the absorption at λ_{max} shown figure 5.10a, 5.10b, 5.10a′ and 5.10b′. In case of Dy(III), Tm(III) and Lu(III), the addition of Ln(III) solution only led to a decrease in the peak intensity at 538 nm showing that the Ln(III) added preferably complexed with EGTA leaving free AsIII in the solution shown figure 5.10c - 5.10e and 5.10c′ - e′.


0 mL Ce (III)
1 mL Ce (III)
2 mL Ce (III)
3 mL Ce (III)
4 mL Ce (III)
5 mL Ce (III)
6 mL Ce (III)
5x10-5M As + 5x10-5M Ce +
5x10-5M EGTA
(a)
Absorbance
Wavelength (nm)


5x10-5M As + 5x10-5M Nd +
5x10-5M EGTA
(b)
0 mL Nd(III)
1 mL Nd(III)
2 mL Nd(III)
3 mL Nd(III)
4 mL Nd(III)
5 mL Nd(III)
6 mL Nd(III)
Absorbance
Wavelength (nm)


(a′)
5x10-5M As + 5x10-5M Ce +
5x10-5M EGTA
654 nm
Absorbance
Concentration (μM)


(b′)
5x10-5M As + 5x10-5M Nd +
5x10-5M EGTA + Buffer
654 nm
Absorbance
Concentration (μM)

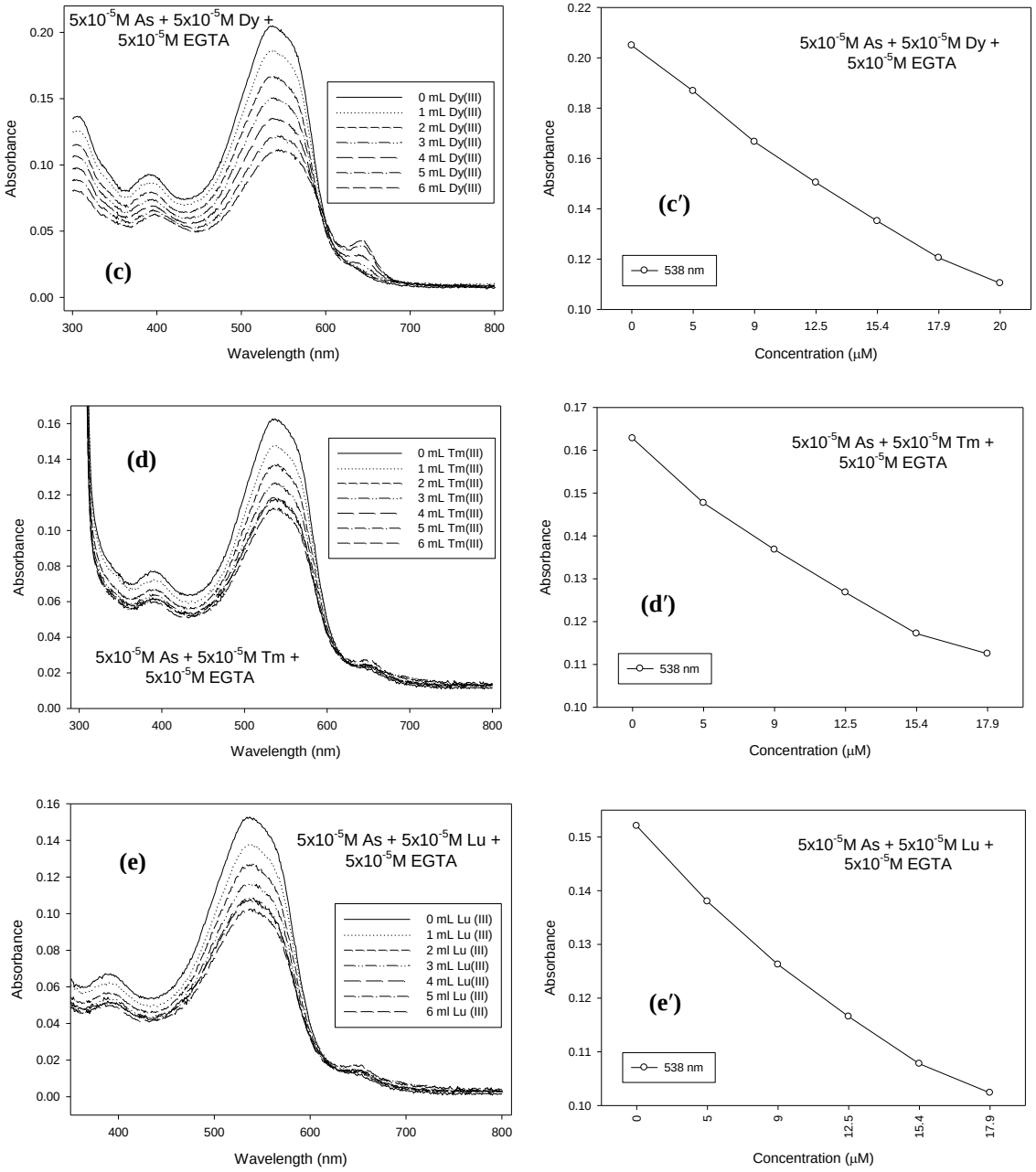
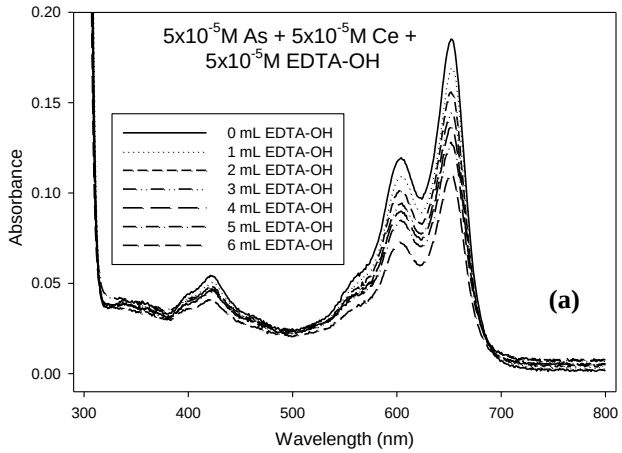


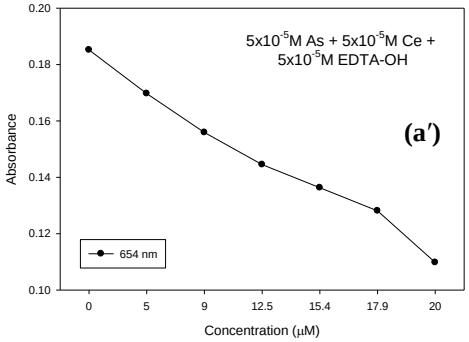
Figure 5.10 (a-e): Absorbance *vs*. wavelength plots for titration of mixture of AsIII and EGTA with Ln(III)

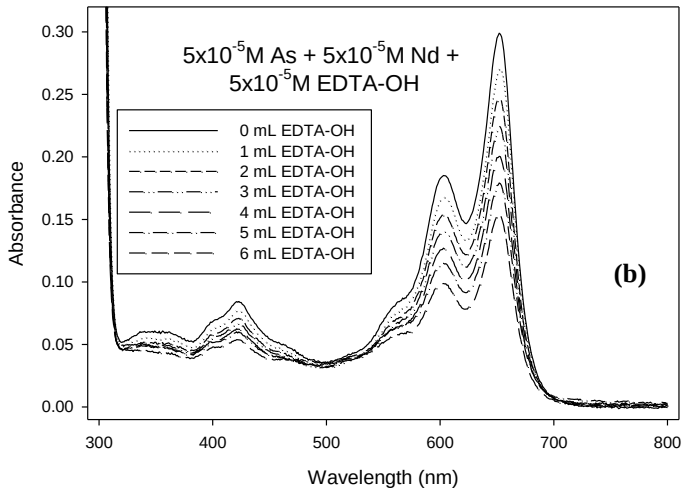
5.10 (a′-e′): Absorbance *vs*. concentration plots for titration of mixture of AsIII and EGTA with Ln(III)

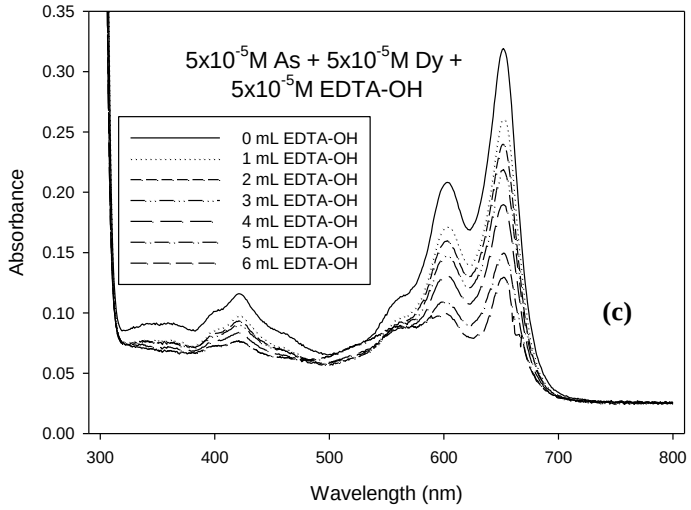
5.2.3.7 Spectrophotometric titrations Ln(III)–AsIII complexes with EDTA-OH

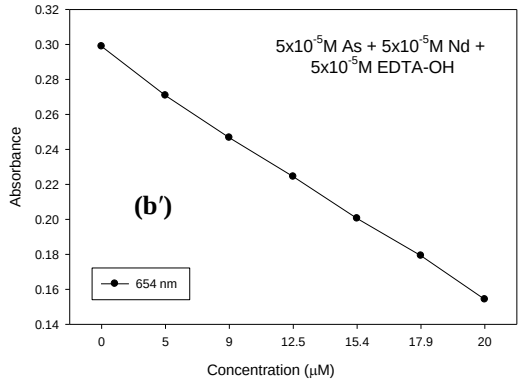
Titrations of AsIII–Ln(III) complexes were carried out with EDTA-OH (5×10^{-5}M) and the results were found to be exactly similar to those obtained for titrations of AsIII–Ln(III) complexes with EGTA as shown Figures 5.11a - 5.11e and 5.11a′ - 5.11e′ i.e., all lanthanides, lighter and heavier behaved in a similar fashion. The absorbance peaks at 610 nm and 654 nm, due to AsIII–Ln(III) complex, decreased with each addition of EDTA-OH. Unlike EDTA and DCTA the appearance of 538 nm, peak due to free AsIII, was not observed for heavier lanthanides indicating that EDTA-OH, like EGTA, was unable to displace AsIII from AsIII–Ln(III) complex. This may be due to lower stability constant values of Ln(III)–EDTA-OH complexes as compared to Ln(III)–EDTA/DCTA complexes and also due to hydrolysis of species which functions as a competing reaction (explained in chapter-4, page 78). The hydrolysis of species was also the main reason for inefficiency of EDTA-OH as a ligand in lanthanide determination by conductometry (Already explained at page 78, Chapter-4).

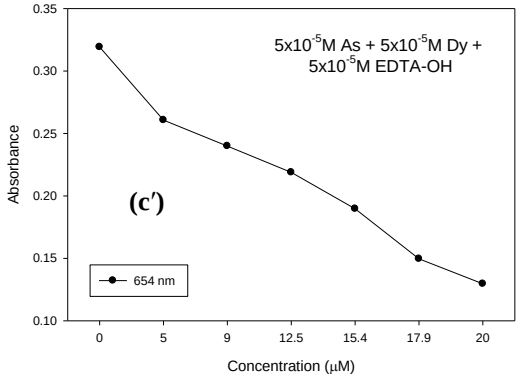





5x10-5M As + 5x10-5M Nd +
5x10-5M EDTA-OH
0 mL EDTA-OH
1 mL EDTA-OH
2 mL EDTA-OH
3 mL EDTA-OH
4 mL EDTA-OH
5 mL EDTA-OH
6 mL EDTA-OH
(b)
Absorbance
Wavelength (nm)


5x10-5M As + 5x10-5M Dy +
5x10-5M EDTA-OH
0 mL EDTA-OH
1 mL EDTA-OH
2 mL EDTA-OH
3 mL EDTA-OH
4 mL EDTA-OH
5 mL EDTA-OH
6 mL EDTA-OH
(c)
Absorbance
Wavelength (nm)


5x10-5M As + 5x10-5M Nd +
5x10-5M EDTA-OH
(b′)
654 nm
Absorbance
Concentration (μM)


5x10-5M As + 5x10-5M Dy +
5x10-5M EDTA-OH
(c′)
654 nm
Absorbance
Concentration (μM)

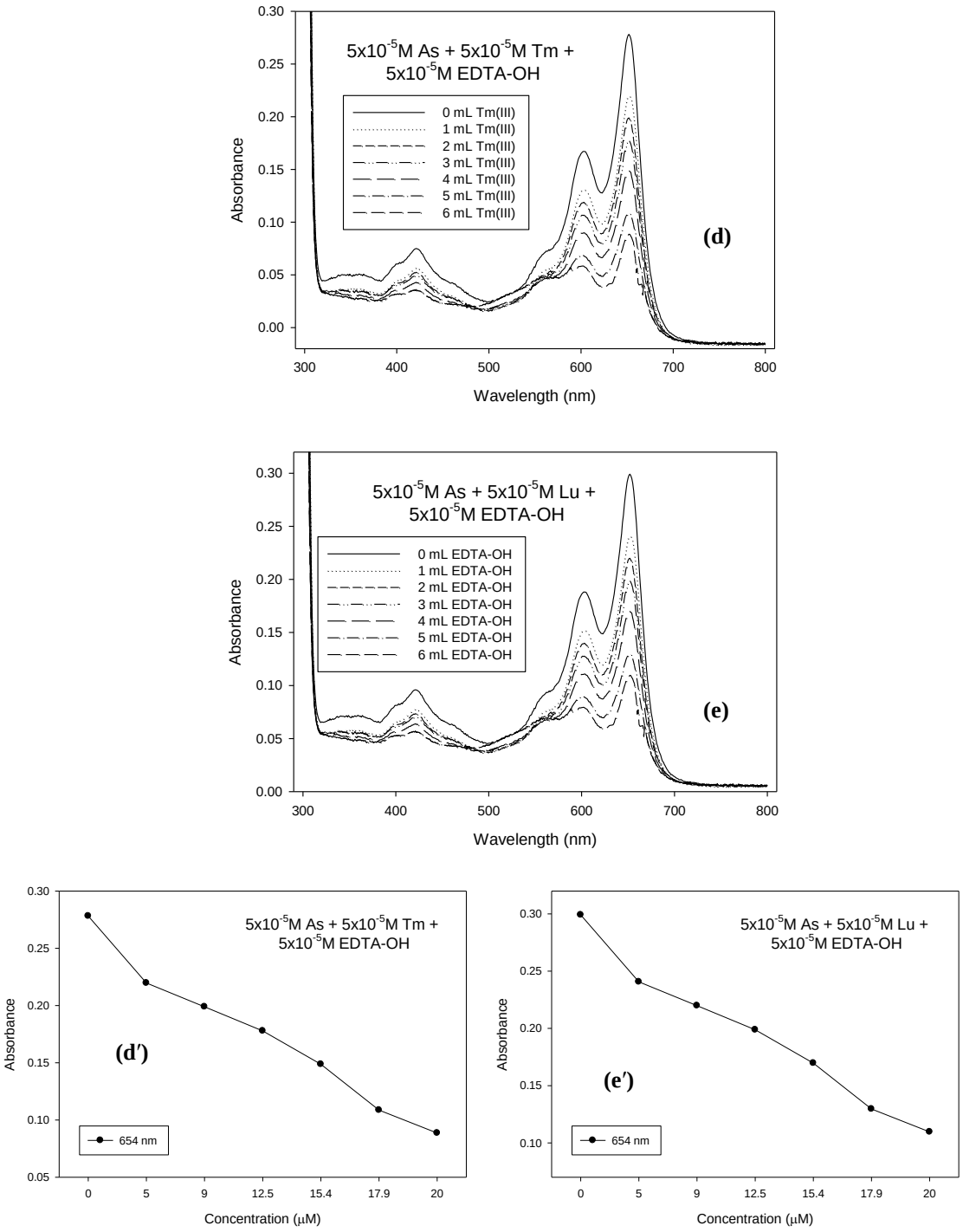
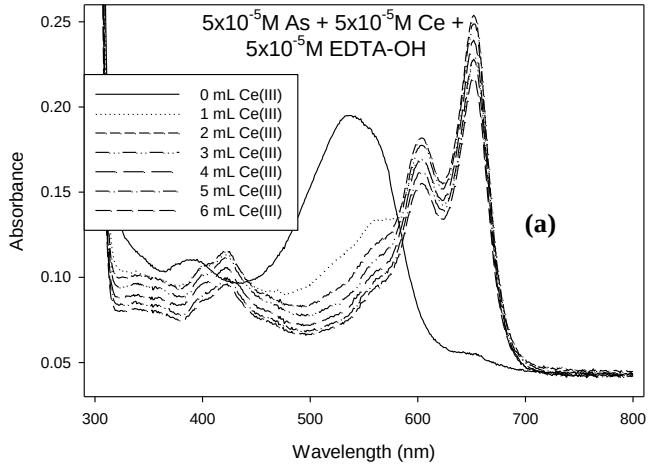


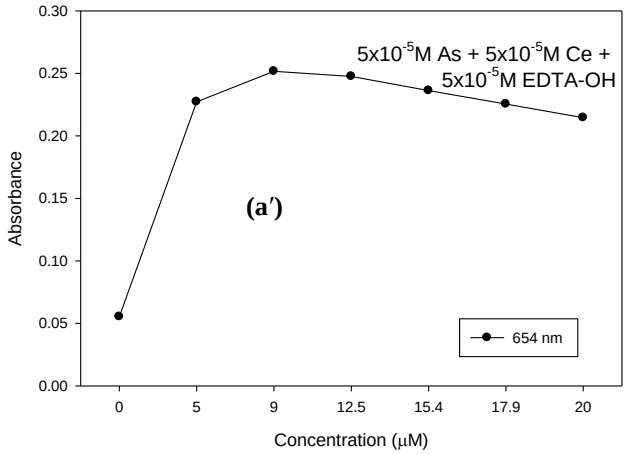
Figure 5.11 (a-e): Absorbance *vs*. wavelength plots for AsIII–Ln(III) complex in the presence of different concentrations of EDTA-OH

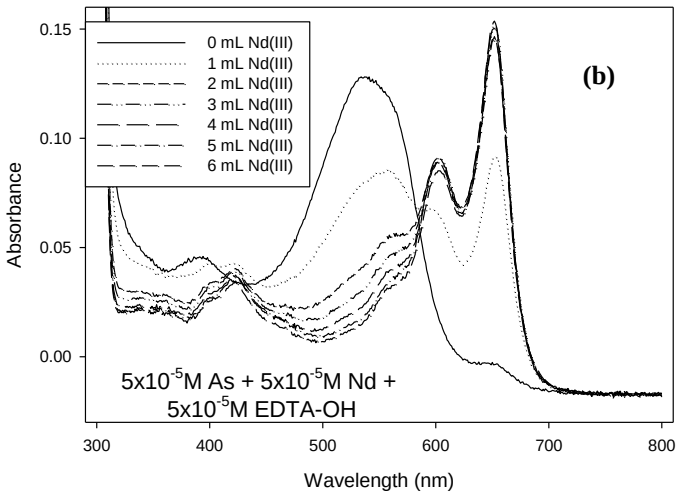
5.11 (a′-e′): Absorbance *vs*. concentration plots for AsIII–Ln(III) complex in the presence of different concentrations of EDTA-OH

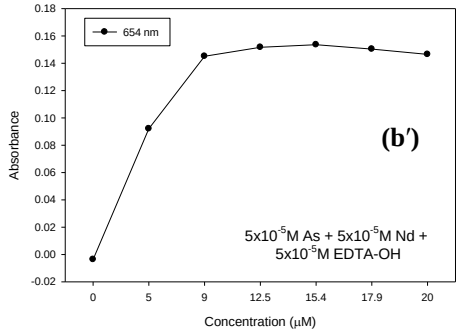
5.2.3.8 Spectrophotometric titrations of mixture of EDTA-OH and AsIII with Ln(III)

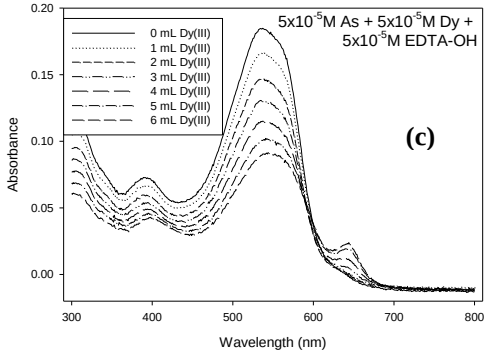
In this case also, the results obtained were similar to those observed in case of EGTA (Figures 5.12a – 5.12e and 5.12a′ – 5.12e′) i.e., disappearance of 538 nm peak was observed on the addition of 1 equimolar Ce(III)/ Nd(III) to a mixture of AsIII (1 mL, 5×10^{-5}M) and EDTA-OH (6 mL, 5×10^{-5}M) solution and two sharp peaks at 610 and 654 nm appeared showing the formation of Ce(III)/ Nd(III)–AsIII complex. Any further addition of Ce(III)/ Nd(III) did not result in any noticeable change in the intensity of peaks. For heavier lanthanides, a decrease in peak intensity of 538 nm was observed with each successive addition of Ln(III) solution showing that the Ln(III) added preferably complexed with EDTA-OH leaving free AsIII in the solution.

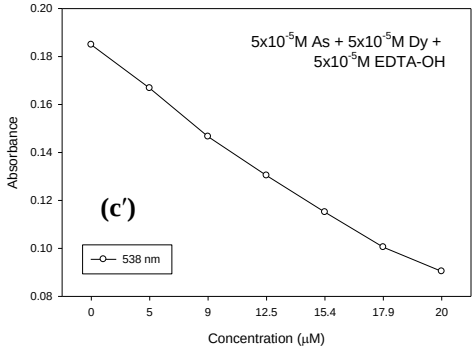


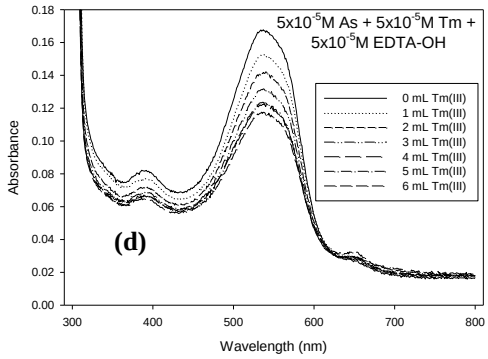


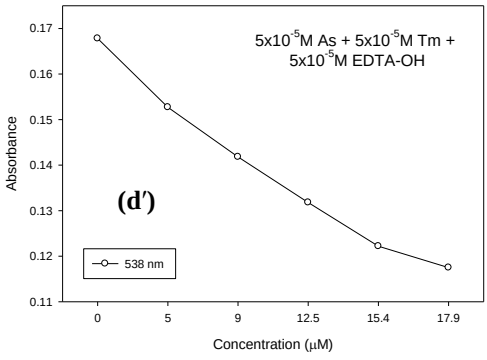

0 mL Nd(III)
1 mL Nd(III)
2 mL Nd(III)
3 mL Nd(III)
4 mL Nd(III)
5 mL Nd(III)
6 mL Nd(III)
(b)
5x10-5M As + 5x10-5M Nd +
5x10-5M EDTA-OH
Absorbance
Wavelength (nm)


654 nm
(b′)
5x10-5M As + 5x10-5M Nd +
5x10-5M EDTA-OH
Absorbance
Concentration (μM)


0 mL Dy(III)
1 mL Dy(III)
2 mL Dy(III)
3 mL Dy(III)
4 mL Dy(III)
5 mL Dy(III)
6 mL Dy(III)
5x10-5M As + 5x10-5M Dy +
5x10-5M EDTA-OH
(c)
Absorbance
Wavelength (nm)


5x10-5M As + 5x10-5M Dy +
5x10-5M EDTA-OH
(c′)
538 nm
Absorbance
Concentration (μM)


5x10-5M As + 5x10-5M Tm +
5x10-5M EDTA-OH
0 mL Tm(III)
1 mL Tm(III)
2 mL Tm(III)
3 mL Tm(III)
4 mL Tm(III)
5 mL Tm(III)
6 mL Tm(III)
(d)
Absorbance
Wavelength (nm)


5x10-5M As + 5x10-5M Tm +
5x10-5M EDTA-OH
(d′)
538 nm
Absorbance
Concentration (μM)

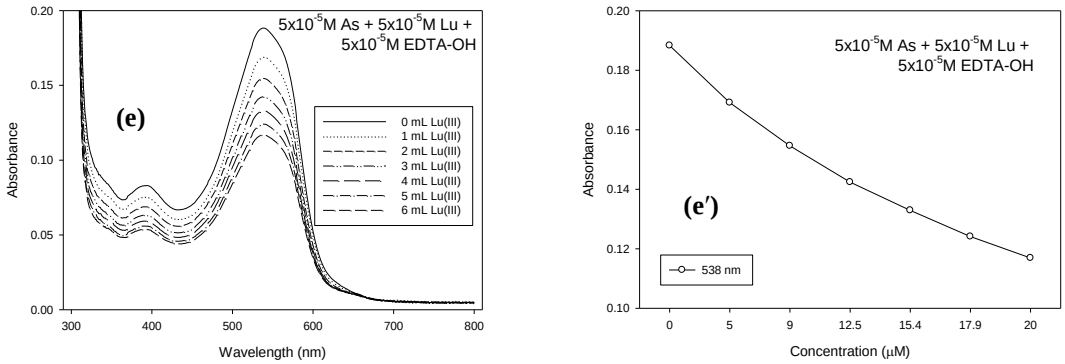


Figure 5.12 (a-e): Absorbance *vs*. wavelength plots for titration of mixture of AsIII and EDTA-OH with Ln(III)
5.12 (a′-e′): Absorbance *vs*. concentration plots for titration of mixture of AsIII and EDTA-OH with Ln(III)

The overall results obtained for studying the effect of EDTA-OH on AsIII – Ln(III) bonding were analogous to those obtained with EGTA which proved that AsIII and EDTA-OH present in the solution compete for bonding with Ln(III). While, Ln(III) would preferably bond with EDTA-OH in a solution containing free AsIII and EDTA-OH but EDTA-OH cannot displace AsIII from AsIII–Ln(III) complexes.

5.3 Conclusions

Characteristics wave length maximum absorption peaks of AsIII–Ln(III) complex in presence and absence of PACA given below:

I. Three absorption bands at 538, 610 and 654 nm were observed during spectrophotometric titration of mixture of EDTA and AsIII with Ce(III)/Nd(III). At 538 nm absorbance decreased while at 610 nm and 654 absorbance increased on successive additions of Ce(III). λ_{max} at 654 nm was selected for the calibration curve.

II. Spectrophotometric titration of mixture of DCTA/EGTA/HEDTA and AsIII with Ce(III)/Nd(III) produced 3 peaks: 538, 610 and 654 nm. At 538 nm absorbance decreased with the removal of AsIII as Ln(III)–AsIII complex. Simultaneously, intensity of absorbance bands at 610 nm and 654 increased upto 3 equivalents. On further addition of Ln(III), no change in intensity was observed.

III. Spectrophotometric titration of mixture of EDTA/DCTA/EGTA/HEDTA and AsIII with Dy(III)/Tm(III)/Lu(III) produced only one band at 538 nm. The absorbance band intensity decreased with further addition of Ln(III).

IV. Ln(III) preferably bonds with EDTA-OH/EGTA in a mixture of free AsIII and EDTA-OH/EGTA but EDTA-OH/EGTA does not displace AsIII from AsIII–Ln(III) complexes.

5.4 References

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Conclusions and Futuristic Aspects

Generally, conductometric method is used for quantitative determination of acids/bases. It is accepted as a simple, inexpensive and easy to operate technique. This thesis work attempts to establish conductometry as an analytical technique for lanthanide determination. The technique does not require pre-requisites like preconcentration, separation, etc. and provides reasonable selectivity and detection limits.

8.1 Conclusions from the present studies

A new conductometric method for accurate determination of individual lanthanides up to concentration level (1×10^{-5} M) has been developed. HIBA has been used as a co-ligand during complexometric titrations of binary mixtures of lanthanides with EDTA for achieving separate equivalence points for lanthanides. These measurements of individual lanthanides were achievable only with polyaminocarboxylic acids (PACA) as complexing agents. Hence, the presence of co-ligand was found to be a necessary condition for determining lanthanides in their mixtures. The method was tested for selective determination of individual lanthanides in the presence of interfering ions like selected alkali, alkaline earth, and transition metal ions. It did not suffer interference from any of these species. The method established was tested on different real time samples for validation and the results were found to be matching to those obtained by arsenazo method (spectrophotometry).

Performance of two pole conductivity cell and five-ring conductivity cell was inspected using complexing reagents EDTA and DCTA. The five-ring conductivity cell was ascertained to be a better electrode for determination of binary, ternary and quaternary mixtures of lanthanides. Using a two pole cell as conductivity tool it was not possible to obtain separate equivalence points for each lanthanide in binary mixtures.

Usefulness of ligands EDTA, DCTA, EGTA, EDTA-OH and TMDTA was studied for lanthanide determination by conductometry. These ligands were used for titrating solutions of individual lanthanides, their binary mixtures and lanthanides in presence of other metal ions as interfering ions.

Order of effectiveness of ligands for single Ln(III) determination was found to be:

EDTA ≈ DCTA > EGTA > HEDTA > TMDTA

Order of effectiveness of ligands for determination of binary mixtures of lanthanides was found to be:

DCTA > EDTA > EGTA > HEDTA > TMDTA

Order of effectiveness of ligands for lanthanide in presence of interfering ions:

EDTA ≈ DCTA > EGTA > HEDTA

The apparent increase in log K value is larger in going from EDTA to *trans*-DCTA than in going from EDTA to EGTA. This makes DCTA a better ligand than EGTA, as the thermodynamic stability of the metal chelate is the primary consideration in the selection of a chelating agent for many chelometric methods. On moving along the lanthanide series from LaY^- to LuY^- a release of strain is expected as a result of decrease in the ionic radius (lanthanide contraction) which contributes to a large increase in stability of the order of about 5 units. This makes DCTA a better ligand for determination of lanthanides in their binary mixtures, as compared to EDTA, giving very distinctly marked and precise equivalence points.

Low dielectric constant solvent like 1,4-dioxane did not solvate Ce(III) ions to the extent of primary solvation sphere in mixed solvent system but due to lower conductivity range, the endpoints became sharper in binary titrations. Order of increasing influence of co-solvents on conductometric titrations of Ce(III) against ligand EDTA can be given as:

DA < ACN < MA < DMSO < THF < DMF

The difficulty in determination of lanthanides in presence of aluminum was observed with both types of electrodes (two-pole, five-ring) and was overcome by using a 1,4-dioxane – water (1:4) medium instead of a pure water system.

Effect of PACA on AsIII–Ln(III) complexes was studied by spectrophotometric titrations. The work was divided into two cases, with respect to each ligand, to see the performance of PACA as a substituting ligand with respect to AsIII for complexing with Ln(III). The results obtained by spectrophotometry were in agreement with those obtained by conductometry.

EDTA and DCTA performed good as substituting ligands i.e. they complexed not only with Ln(III) in the presence of As III but also displace AsIII from its complex with the former to form Ln(III)–EDTA/DCTA complexes confirming the high stability of these complexes and, hence, commending the proficiency of these ligands for conductometric determination of lanthanides.

Ligands like EGTA and EDTA-OH, on the other hand, complexed with lanthanides in the presence of As III, showing that their complexation was favorable, but were unable to displace the arsenazo from its complex with Ln(III). The results for EGTA and EDTA-OH, in case of heavier lanthanides, displayed peaks for both free As III and AsIII–Ln(III) complex demonstrating the formation of latter as well as Ln(III)–EGTA/EDTA-OH complex. The inability of ligands EGTA and EDTA-OH to displace As III from its complexes with lanthanides ratifies the low efficiency of these ligands in conductometric determination of lanthanides due to steric constraints and competing hydrolysis reactions, hence, demonstrate the low stability of these complexes.

Thus, the observations made by conductometry regarding the complexation behavior of different PACA with Ln(III) were confirmed due to examination of similar behavior in spectrophotometry.

8.2 Future recommendations

Determination of major actinides like Th(IV), U(IV) and Pu(IV) in various matrices has become increasingly significant and several techniques have also been used. Moreover quantification of different oxidation states of plutonium species is an extremely challenging task. In view of the observations of getting separate equivalence points from the mixture of Ln(III) and Th(IV), it is anticipated that the analytical method for lanthanides shall be workable for actinides, as well.

PUBLICATIONS

Publications in International Journals

1. Komal Matharu, Susheel K Mittal, Ashok Kumar, S.K., A novel method for the determination of individual lanthanides using an inexpensive conductometric technique. **Analytical Methods** 2011, 3, 1290 (RSC; IF: 1.547)

2. Komal Matharu, Susheel K Mittal, Ashok Kumar S.K. Conductometric Performance of 2-pole and 5-ring conductivity cell probes for lanthanide determination using EDTA and DCTA as potential sequestering agent. **Industrial and Engineering Chemistry Research** 2012, 51, 11328−11334 (ACS; IF: 2.237)

3. Komal Matharu, Ashok Kumar, S.K., Susheel K Mittal. Improvised response in 1,4 Dioxane as co-solvent during selective determination of lanthanides in binary mixtures by conductometry. **Current Analytical Chemistry** (Bentham Science Publisheres; IF: 1.000) [Manuscript Accepted for Publication. doi:10.2174/15734110113099990013]

4. Komal Matharu, Ashok Kumar SK and Susheel K Mittal. Effect of EDTA on ArsenazoIII-Lanthanide (III) complexation. [**Manuscript under preparation**]

5. Komal Matharu, Susheel K Mittal and Ashok Kumar SK. Selectivity of ligand and co-ligand in conductometric titration while determining lanthanide (III) ions in presence of interfering ions. **[Manuscript under preparation]**

6. Komal Matharu, Ashok Kumar SK and Susheel K Mittal. A comparison efficiency of various polyaminocarboxylic acids used for lanthanide determination by conductometry. [**Manuscript under preparation**]

7. Komal Matharu, Ashok Kumar SK and Susheel K Mittal. Conductometry as an analytical technique: A review. [**Manuscript under preparation**]

Publications in Conference Proceedings

1. Komal Matharu and Ashok Kumar S.K. In Search of New Selective Determinations of Lanthanides Using Some Sequestering Agents. 12th CRSI National Symposium in Chemistry and 4th CRSI-RSC Symposium in Chemistry from 4-7 February 2010 at IICT, Hyderabad.

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