NEW REAGENTS IN LIQUID-LIQUID EXTRACTION STUDIES OF RARE EARTHS

THESIS SUBMITTED TO THE UNIVERSITY OF KER
IN PARTIAL FULFILMENT OF THE REQUIREMEN
FOR THE DEGREE OF
Doctor of Philosophy
IN CHEMISTRY

BY

S. SREELATHA

REGIONAL RESEARCH LABORATORY (CSIR)
THIRUVANANTHAPURAM-695 019
INDIA

FEBRUARY, 1993

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वैज्ञानिक एवं औद्योगिक अनुसंधान परिषद्
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INDIA

CERTIFICATE

This is to certify that the thesis bound herewith is an authentic record of the research work carried out by **Sreelatha S., M.Sc.** under our supervision in partial fulfilment of the requirements for the **Degree of Doctor of Philosophy in Chemistry** of the University of Kerala and further that no part thereof has been presented before for any other Degree.

C.S. Narayanan
(Supervising Teacher)

T. Prasada Rao
(Supervising Teacher)

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DECLARATION

I hereby delcare that this thesis is a bonafide record of the research work done by me and no part of the thesis has been presented earlier for any degree, diploma or similar title of any other University.

S. Sreelatha

SREELATHA S.

February 1993

Thiruvananthapuram

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S. Sreelatha

Sreelatha S.

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CHAPTER I

INTRODUCTION

INTRODUCTION

Rare earths exhibit close similarity in their chemical properties due to identical outer electronic configuration of their atoms. The separation of these sixteen elements from one another is regarded as one of the most difficult problems in inorganic chemistry. The increasing use of rare earth elements in the preparation of lasers, magnets and superconducting materials necessitated in obtaining individual rare earths at high purities. This has resulted in search of various techniques[1,2] for the separation of rare earth elements both at trace and macro levels. This in turn led to the growth of a voluminous literature on the separation of rare earths.

1.1 DISCOVERY, OCCURRENCE AND USES

1.1.1 Discovery

Arrhenius[3] in 1787 discovered a dark coloured mineral in the ytterby feldspar quarry near Stockholm, Sweden. In 1794 Gadolin[4] isolated yttria from gadolinite, a mineral now known to contain yttrium, middle and heavy rare earths. In 1803 Klaproth[5] discovered another substance that was similar to yttria in some respects and different in some other respects and it was named ceria. In 1804 Berzelin and Hisinger[6] analysed these substances and found neither yttria nor ceria was a pure substance. Mosander[7] in 1839 pyrolysed ceria into dissimilar oxides, one being readily soluble in dilute nitric acid and the other very resistant to the acid. He named the readily soluble oxide as lanthanum oxide and the other oxide as cerium oxide. Another new element, didymium was isolated two years later (1842) from lanthana itself by Mosander[8]. In 1843 he[9] again succeeded in obtaining three rare earths; yttria, erbia and terbia by the fractional precipitation of Gadolin's yttria with ammonia. Nearly forty years later, in 1878, Marignac[10,11] isolated ytterbia from Mosander's erbium nitrate and gadolinia from Samararskite. Boisbaudran[12,13] in 1879 isolated samarium from didymium. Fredrik[14] isolated scandia from euxenite and Cleve[15] resolved erbia into holmia, erbia and thulia in 1879. In 1885 Welsbach[16] resolved didymium into neodymium and praseodymium by fractional crystallisation of the double ammonium nitrates. Boisbaudran[17] separated holmia into dysprosia and holmia. Europium was isolated from samarium fractions by Demarcay[18] in 1901. Urbain[19,20] and Von Welsbach in 1907 independently obtained lutetia from ytterbia. Moseley's[21] determination of atomic numbers and Bohr's theory of atomic structure provided a clear idea of the number of elements in the rare earth series and their arrangement in the periodic table. An element with atomic number 61 was not isolated in any of the above separation studies. Later in 1945 Marinsky and Glendenin[22] isolated promethium (atomic number 61) from fission products. Considerable delay in the discovery of this element was due to its radioactive nature. So it was concluded that rare earths consist of sixteen elements viz. yttrium (atomic number 57 to 71). Of these elements promethium (61) does not occur in nature.

1.1.2 Occurrence[3]

The rare earths as a group constitute 8 x 10^{-3} % by weight of the earth's crust. They occur in a variety of minerals chiefly in pegmatites. The commercial sources of rare earth minerals are monazite, xenotime, bastnaesite and gadolinite. Usually thorium occurs along with the rare earths. Uranium, zirconium, hafnium, titanium, tantalum and niobium are also found in lesser extents. The ores are usually phosphate, silicate, carbonate and fluoride.

1.1.3 Uses[3]

Rare earths are used industrially as the naturally occurring mixture derived from monazite. Rare earths find an increasing demand in the electronic material industry. The rare earths are of interest in atomic energy development as control and shut down materials and in the manufacture of ceramic capacitors. Yttrium iron garnets are used as magnetic components for microwave circuits. Cerium is used in photosensitive glass, optical coatings and as catalysts. Neodymium and praseodymium are used for colouring glass and enamels. Rare earth fluorides and oxides are used as core materials in carbon electrodes for arc lumination due to high light intensity. High purity lanthanum is used for the manufacture of glass for instrument and camera lenses. A mixture of rare earth chlorides are used for the manufacture of misch metal which is used in lighter flints. Addition of rare earths to alloys has high temperature properties. The mechanical properties can be enhanced by the addition of rare earths to stainless steel[23] and aluminium metal[24]. Recently the use of Nd-Fe-B permanent magnets with superior magnetic properties are based on the compound $Nd_2Fe_{14}B$. High strength high temperature ceramics are used for cutting tools and turbine blades in the exhaust gas streams and major engine parts. Recently RE oxides have come to use in the manufacture of variety of superconducting materials[25]. Sm-Co alloy have been employed in lasers particularly solid-state lasers. These lasers provide high intensity coherence and directionality.

1.2 SEPARATION TECHNIQUES[26]

Various separation techniques have been adopted for separating the rare earth elements. Precipitation method depending on charge change had been perfected for isolating cerium and europium. Amalgam extraction methods[27,28] have also been developed for the isolation of samarium, europium and ytterbium. The only way of obtaining the remaining rare earths in a pure state relied entirely on fractional crystallisation processes. Although these methods provided a means of separating light rare earths, they were much less effective in the isolation of the heavy rare earths. This situation was completely changed by the application of two modern techniques namely ion-exchange chromatography[1] and liquid-liquid[2] or solvent extraction.

Ion exchange chromatography is one of the efficient means of separating the rare earth elements in a pure state. But inspite of this, this technique is tedious and time consuming. Another limitation imposed by this technique is that it is feasible only for small scale operations and in large scale there are many disadvantages. Solvent extraction is the most exhaustively employed technique due to its simplicity, versatility and ready adaptability to scaling up of the process for various hydrometallurgical processes.

1.3 SOLVENT EXTRACTION THEORY[3]

Berthelot and Jungfleisch[29] first enunciated a law governing the distribution of a metal species between two immiscible phases. The theory of extraction of metal chelates has been developed by Kolthoff and Sandell[30] , Irving and Williams[31] and more recently by Rydberg[32] who has shown the inter-relationships of the formation constants of the chelate, distribution coefficient of the chelate, pH and ionisation constant of the reagent in determining the distribution. The distribution equilibria between two phases are governed by the Gibbs phase rule. Nernst[32] derived the distribution law governing the distribution of metal between the aqueous and organic phases which is stated as

$$D = C_1/C_2$$

where D is the distribution coefficient, C_1 and C_2 are the concentration of the metal in the organic to that in the aqueous phases. D depends on the activity coefficients of the solute in the two phases. However, at low solute concentration, the activity coefficients approach unity, so that D remains constant. The distribution coefficient and percentage extraction E are related by the following equation

$$\% E = \frac{100 D}{D + \frac{V_{aq}}{V_{org}}}$$

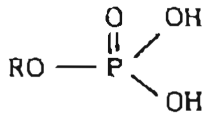
where V_{aq} and V_{org} are the volumes of the aqueous phase and organic phase respectively. Separation factor β gives the extent of separation of two metals, is given by

$$\beta = D_1/D_2$$

where D_1 and D_2 are the distribution coefficients for metal(1) and metal(2) respectively.

1. Acidic extractants[3] which involve compound formation. There are two main types of extractant in this category. (a) acidic organophosphorus extractants: This type of extractants include extractants with structures of the type

1.



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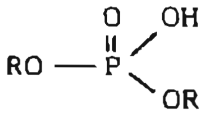

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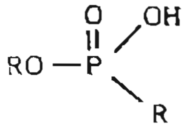

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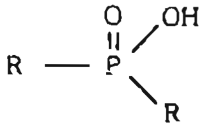
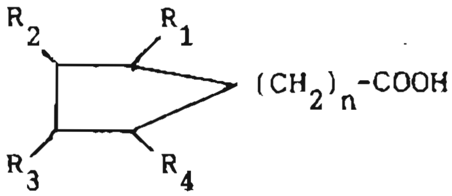


where R can be alkyl or aryl substituents. In this type of extractants the most important and commercially used ones are di(2-ethylhexyl) phosphoric acid (DEHPA) and 2-ethylhexyl-mono-2-ethylhexyl ester of phosphonic acid (EHEHPA).

b. Carboxylic acids: These extractants can be mainly divided into two types: extractants having the following two structures

1.



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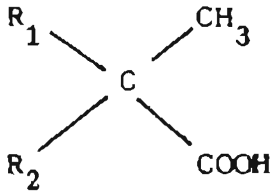
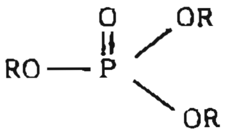


Among these type of extractants the commercially used ones are naphthenic acid and versatic acid.

2. Neutral extractants: These include organophosphorus esters and ketones. The mostly commonly used extractant in this class are tri-n-butyl phosphate (TBP)

1.



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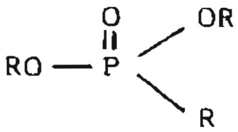

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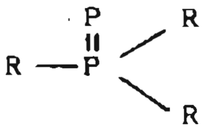


Tri-n-octyl phosphine oxide (henceforth TOPO).

3. Basic extractants are usually (a) primary amines, (b) secondary amine, (c) tertiary amine, and (d) quaternary amines having the following structures:

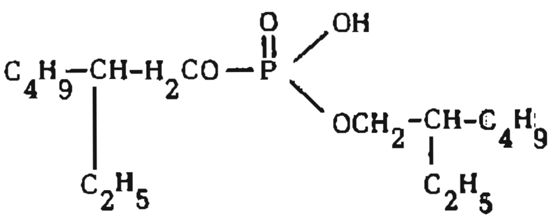
a. $R\text{-}NH_2$ b. R_2NH c. R_3N d. $R_4N^+Cl^-$

Quaternary ammonium salt like tricapryl methyl ammonium chloride (Aliquat 336) is used for commercial purposes.

1.3.1 Acidic extractants

Acidic organophosphorus extractants:

The various acidic organophosphorus extractants used for the extraction of rare earths are phosphoric, phosphonic and phosphinic acids. The phosphoric acids used mainly are mono(2-ethylhexyl) phosphoric acid (MEHPA)[33] and DEHPA (I)[34-39].



(I)

Peppard and coworkers[40] were the first to report the use of DEHPA as an extractant for the separation of rare earths. DEHPA is dimerised in aromatic diluents which are inert[41]. The mechanism of extraction of rare earth elements by DEHPA in aromatic diluents has been reported as follows:

$$Ln^{3+} + (\overline{HX})_2 \rightleftharpoons \overline{Ln(HX_2)_3} + 3\,H^+$$

where Ln stands for rare earth element and $(\overline{HX})_2$ refers to the dimeric form of the extractant. These extractants act as cation exchangers.

Several investigators (Peppard et al[42], Harada and Smutz[43], Michelson and Smutz[44], Thomas and Burkhart[45] and Reddy et al[46]) have reported studies with DEHPA. The extraction of rare earths using DEHPA increases with increase in atomic number i.e. from lanthanum to lutetium. The extractability of DEHPA was restricted by the formation of a gelatinous third phase when the metal concentration of the solvent phase becomes high. Pierce and Peck[47] have found an average separation factor of 2.4 ± 0.87 between the adjacent rare earth elements using DEHPA as the extractant. Reports showed that the extraction behaviour of yttrium with respect to DEHPA lies between holmium and erbium. In the rare earth separation by DEHPA, it has been found that chloride medium is preferable compared to nitrate or sulphate systems. One of the most successful applications of DEHPA for the large scale separation of rare earths was demonstrated in the year 1965 by the Molybdenum Corporation of America[48]. The enrichment of europium from didymium carbonate containing 50% La_2O_3, 7% Pr_6O_{11}, 35% Nd_2O_3, 6% Sm_2O_3 and other rare earths including yttrium 2% derived from Indian monazite sand containing only about 0.03% Eu_2O_3 was reported by Venkateswarlu et al[49] in 1971. Their liquid-liquid extraction process with 1M DEHPA in kerosene as extractant involved three stages of extraction followed by scrubbing and stripping, resulting in 20 fold enrichment of europium.

A 14-stage countercurrent extraction process for the preparation of 99.8% La_2O_3 was developed by Nair and Smutz[50]. A didymium chloride feed containing 45% La_2O_3, 35% Nd_2O_3, 10% Pr_6O_{11} and 5% of Sm_2O_3 using 1M DEHPA in AMSCO as an extractant was used for the recovery of La_2O_3. Minagawa et al[51] developed a novel process for the separation of yttrium from heavy rare earths. The process involves contacting 1M DEHPA in aliphatic or aromatic diluent with an aqueous solution containing diethylene triaminepentaacetic acid (DTPA) and yttrium ions along with one or more of the heavy rare earths viz. Gd to Lu (atomic number 64 to 71). The ratio of DEHPA employed is usually more than one equivalent or preferably 1.5 to 3 equivalent to the total of Y ions and other rare earth ions. A pH $>$ 1.5 was maintained for the aqueous phase, preferably about 6.0 to 9.0 from the industrial point of view. The concentration of DTPA was more than one equivalent to the heavy rare earth ions.

A liquid-liquid extraction process for the production of pure Sm_2O_3 and Gd_2O_3 using DEHPA/Shellsol A system was successfully developed to pilot plant scale by Brown[52].

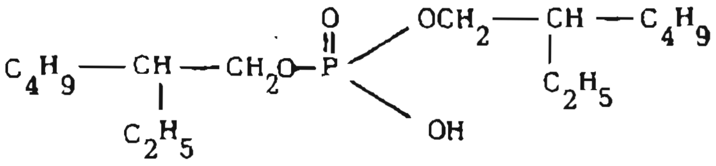
Alstad and Farbu[53] have developed a liquid-liquid process for the extraction and separation of element in the lanthanide series. The extraction of the rare earths was carried out from sulphate medium. The loaded organic phase containing the rare earths was subjected to stripping with sulphuric acid. The contact time between the aqueous and organic phase in the stripping stage was controlled so that the desired rare earth elements are back extracted into the aqueous phase. The contact time was regulated and was less than the total extraction equilibrium time between the phases. This process has made possible the separation of erbium, terbium and yttrium.

A process for upgradation of yttrium oxide using solvent extraction was reported by Mishra et al[54]. The enrichment of yttrium oxide from 60% to 92% yttrium oxide using DEHPA as extractant involves 8 stages of countercurrent extraction with a feed solution having an acidity of 1.5 M hydrochloric acid followed by 10 stage scrubbing with 4.5 M hydrochloric acid. The loaded organic phase was then back extracted with oxalic acid to precipitate the yttrium along with heavy rare earths.

The resulting oxalates were converted into oxides. Reddy et al[46] have also described a countercurrent extraction process for the separation of some rare earths from yttrium concentrate (Y_2O_3 55%, Dy_2O_3 25%, Tb_4O_7 6.2%, Ho_2O_3 3.6%, Gd_2O_3 9% and Er_2O_3 1%) from chloride solution using 1 M DEHPA in kerosene as extractant.

DEHPA is potentially the most useful and powerful reagent for the commercial separation of the whole range of rare earths. However one of the major draw backs in the use of DEHPA as an extractant for the rare earths is the gelation or the formation of insoluble polymers at approximately around 50% saturation. In non-polar solvents such as xylene or kerosene DEHPA exists as dimer, probably as a result of hydrogen bonding. In the case of rare earths this dimeric structure appears to favour the formation of complexes by substitution of hydrogen ions by rare earth cations. In the presence of excess rare earths, it is possible to displace both hydrogens in each dimeric unit. This results in the three dimensional cross linkages set up between the rare earth cations and DEHPA molecules to form a stiff gel. Prevention of the formation of this gel is a major consideration in the design of concentrated extraction systems using DEHPA. This gelation problem has been overcome successfully by Mason et al[55] by using Di-2-ethylhexyl monothiophosphoric acid instead of DEHPA. A 5-stage countercurrent extraction process employing 5 extractors in series with introduction of feed in the third extractor (2M HCl containing 50 mg/ml of each of rare earths) are involved. A 0.2 M hydrochloric acid solution is introduced in the first extractor as scrub solution.

It is well known that DEHPA is an efficient extractant for the metal separation of rare earths particularly with respect to the middle and heavy rare earths because of its high separation factor. Inspite of this, DEHPA has the disadvantage of diffficulty in back extraction. Very high acidities are required in the back extraction and hence poses problem in the commercial extraction systems using DEHPA. A change in the acidity of the extractant caused by the exchange of the alkoxyl groups by alkyl groups reflects their ability as extractants. This change can be demonstrated in the use of 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (henceforth EHEHPA, II)[56-59] in the place of DEHPA. EHEHPA



(II)

has a higher ability of back extraction at low acidities than DEHPA. EHEHPA is a cationic extractant and the simplified extraction mechanism of a trivalent rare earth metal ions with EHEHPA in aromatic diluent proceeds as follows:

$$Ln^{3+} + 3(\overline{HR})_2 \rightleftharpoons \overline{Ln(HR_2)_3} + 3\ H^+$$

where Ln stands for the rare earth element and $(HR)_2$ refers to the dimer of the extractant in the organic phase. The extraction constant can be written as

$$K_{ex} = \frac{[\overline{Ln(HR_2)_3}]\,[H^+]^3}{[Ln^{3+}]\,[(\overline{HR})_2]^3}$$

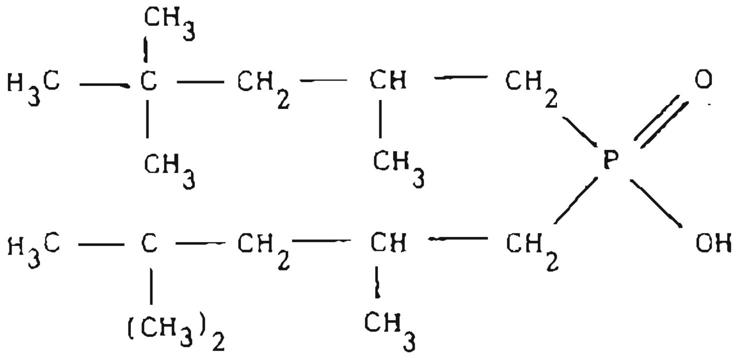
Several investigators have used EHEHPA for the extraction of rare earths from aqueous solutions and have established the usual cation exchange mechanisms as reported by Balint[60], Mori et al[61], Sato[62] and Santhi et al[63]. A process for the separation of neodymium and samarium using 1 M EHEHPA in kerosene on a commercial scale was developed by Fujimono and Miura[64]. A laboratory scale process for the preparation of high purity neodymium oxide from a mixed lanthanide chloride feed using 20% saponified EHEHPA (1 M) was developed by Thakur and Koppiker[65]. The process involves 6 stages of extraction followed by 18 stages of scrubbing with 0.3 M HCl and 6 stages of stripping using 1 M HCl. A 90% recovery of 98% Nd_2O_3 was obtained by the above process.

Zhong et al[66] have developed a countercurrent liquid-liquid reflux extraction based on refinery distillation theory, mechanism and behaviour of rare earths extraction with EHEHPA. The process involves 11 stages of extraction, 20 stages of scrubbing 60 stages of enrichment, 7 stages of hydrochloric acid stripping and 20 stages of water washing in mixer settlers. This process results in the production of 98% of 99.95% pure lutetium oxide and a raffinate containing ytterbium product of 92%.

A novel method using saponified organophosphonic acid was developed by Li et al[67] for the separation of rare earths by countercurrent extraction with three outlets. They have also given the calculation of dynamic equilibrium by computer simulation for the extraction of samarium, europium and gadolinium .

Li et al[68] have obtained the separation of rare earth elements by one step extraction in a multiple outlet involving the extraction of mixed rare earth chloride (CeO_2-5-10%, Pr_6O_{11} 12% Nd_2O_3 70%, Sm_2O_3 5% and other rare earths 2-5% in HCl) feed with saponified EHEHPA in kerosene (1.0-1.5 M) in 80-100 stage countercurrent extraction trough. Each rare earth ion containing solutions was collected from different outlets. The purities obtained were CeO_2 60%, Pr_6O_{11} 70-80%, Nd_2O_3 95-98% and Sm_2O_3 50%. Li et al[69] have also reported the separation of dysprosium by liquid-liquid extraction using ammoniated EHEHPA from an ion-adsorption type of rare earth ore.

Organophosphinic acids have also been used for the extraction and separation of rare earths. Cyanex 272 (III) is a phosphinic acid extractant viz. bis(2,4,4-trimethylpentyl) phosphinic acid[70-72] with a structural formula shown below:



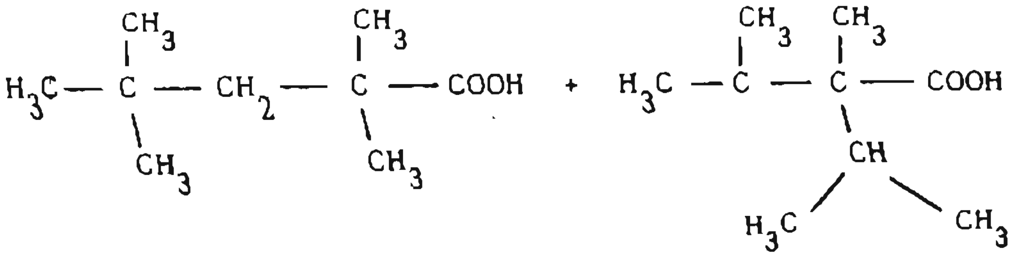
(III)

Levique[73] has developed a process for the separation of rare earths by using organophosphinic acid in a halogenated or carboxylic acid diluent.

Sabbot and Rollat[74] have prepared 99.3% pure ytterbium oxide using 1 M cyanex 272 in kerosene from nitrate solutions.

Carboxylic acids

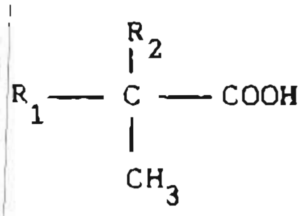
In this class of acidic extractants are the synthetically produced versatic acids and naphthenic acids obtained from the distillation of crude petroleum. Among the various versatic acids available, versatic 9 (IV)[75] and 911 (V) have been investigated the most. They are highly branched monocarboxylic acids. The other available versatic acids include versatic 10, 13, 1519 and SRS-100.



56%

27%

(IV)

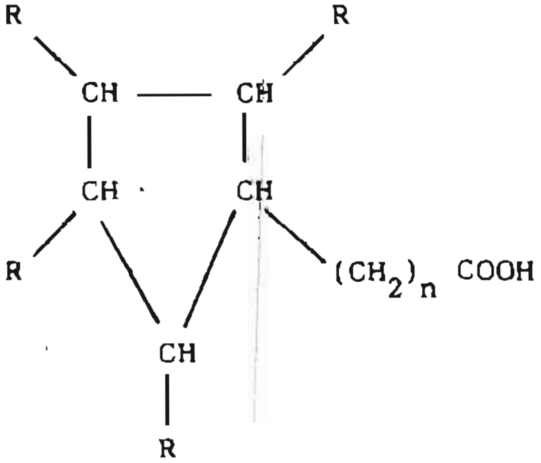


$$R_1 - \overset{\displaystyle R_2}{\underset{\displaystyle CH_3}{C}} - COOH$$

where R_1 R_2 = C_4 - C_5

(V)

Naphthenic acids (VI)[76-78] are a group of cyclic aliphatic mono-carboxylic acids and have the general structure.



(VI)

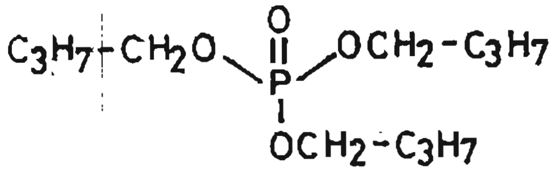
They are usually obtained from crude petroleum and having a molecular weight range of 170-330.

Versatic acid and naphthenic acid are shown to exist as dimeric form in non-polar solvents as proved by Zheng et al[79]. These authors have also used these carboxylic acids for the separation of yttrium from the heavy rare earths. Some of these carboxylic acids in xylene have been used for extraction of various metal cations by Preston[80]. The relationship between extraction behaviour and structure of carboxylic acid is also discussed. They have reported the relationships between the experimental $pH_{1/2}$ values and the characteristic properties of metal cations such as stability constants of carboxylate complexes and ionic radii. Mikhlin et al[81] have studied the extraction behaviour of neodymium using naphthenic acids. Various parameters such as nature of extracted species, degree of polymerisation of the extracted species in the organic phase and extraction constants were also determined. Zhenrong et al[82] have reported the recovery of high purity yttrium (99.9%) using naphthenic acid as extractant from acidic leach containing 50% yttrium oxide with an yield of 98%. Cai et al[83] have reported the separation of lanthanum oxide (99.95%) by naphthenic acid-tributyl phosphate (TBP) extraction system from the other rare earths. These extractants are economically viable and can replace the organophosphorus extractants which are expensive. Versatic acid has been used for the production of high purity yttrium by Trimble and Strott[84] from the heavy rare earths.

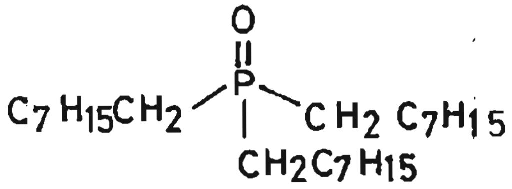
The selective extraction of yttrium using versatic 10 in kerosene as extractant from a solution containing ethylenediamine diacetic acid, yttrium and one or more rare earths was reported by Minagawa and Kaneto[51] . Brown and Sherrington[85] have used the total reflux method using versatic 911, TBP and DEHPA with respect to industrial solvent extraction of high purity La, Pr, Nd, Sm, Eu, Gd and Y oxides.

1.3.2 Neutral organophosphorus extractants

This group of solvent extraction systems is based on the solvation of neutral inorganic molecules or complexes by electron-donor containing extractants. There are two main groups of extractants in this area. Organic reagents containing oxygen bonded to carbon, such as ethers, esters, alcohols and ketones and those containing oxygen or sulphur bonded to phosphorus as in alkyl phosphates or alkyl thiophosphates. The most common of these extractants are tributylphosphate(TBP)[86-90] and tri-n-octyl phosphine oxide (TOPO)[91-94].



T B P



TOPO

Peppard and coworkers[95] have used TBP as an extractant in the extraction of trivalent rare earths from chloride and nitrate solutions. Nitrate system was more preferred over the chloride system. The average separation factor for adjacent rare earths was calculated to be 1.9. Further studies by the same authors give the mechanism of extraction. TBP extracts by coordinating with rare earth ion through phosphoryl group

$$Ln^{3+} + 3\ NO_3^- + \overline{3\ TBP} \rightleftharpoons \overline{Ln\ (NO_3)_3\ (TBP)_3}$$

The variation of D with nitric acid concentration do not follow simple pattern. To obtain reasonably high extraction and separation, the concentration of nitric acid used in the aqueous phase should be about 15 M as reported by Peppard et al[96]. A countercurrent extraction technique on York-Shiebel column was developed for production of 95% Gd_2O_3 by Weaver and coworkers[97] using TBP and HNO_3 as organic and aqueous phases respectively. A similar technique was again used by Weaver[98] for obtaining 98% pure samarium oxide. They have also developed a process for the preparation of high purity lanthanum, praseodymium and neodymium. Separation of rare earths by TBP was outlined by Callow[99]. The separation of rare earths by solvent extraction using TBP as an extractant from thiocyanate solutions was developed by Greinacher et al[100]. Many other authors have come out with schemes for the separation of individual rare earths from nitrate media using TBP viz. Sherrington and Kemp[101], Flett[102]. A process for the preparation of ultrapure yttrium oxide (99.999%) with an yield of 98.8% from a feed solution containing a mixture of rare earths was reported by Delloys and Sabbot[103]. The organic phase containing 75% cyanex 9233 in kerosene (60-40% mixture of $(C_6H_{13})_3PO$ and $(C_8H_{15})_3PO$) was used. These authors[104] have also reported a process for the preparation of high purity yttrium oxide using liquid-liquid extraction technique with bis(2-ethylhexyl) ethyl phosphine oxide as an extractant. The concentration of nitric acid used was in the range 1-10 M and extraction was carried out at 10-80 °C. They obtained 99.8% of yttrium oxide of 99.999% purity.

1.3.3 Basic extractants

Basic extractants are limited to amines and quaternary ammonium halides. Various extractants are available for the extraction of metal cations,

1. primary amines RNH_2,
2. secondary amines R_2NH,
3. tertiary amines R_3N
4. quaternary ammonium salts $R_4N^+X^-$

In these systems of extractants extraction involves ion-association. These extractants are anion exchangers. The quaternary ammonium salts are the most commonly employed extractants for rare earths. The mechanism of extraction with quaternary ammonium salts was reported by Kwang-Hsien et al[105].

The reaction proceeds as follows:

$$Ln^{3+} + 3\,L^- + X\ \overline{(R_4N^+L^-)_n} \rightleftharpoons \overline{LnL_3 .\ XnR_4N^+L^-}$$

where L^- is nitrate ion, $R_4N^+L^-$ is quaternary ammonium nitrate.

Liquid-liquid extraction process for the separation of yttrium from other rare earth elements was reported by Guadernack[106] using Aliquat 336 as an extractant. The separation is based on the different extraction behaviour of rare earths in nitrate and thiocyanate systems. It is based on the fact that yttrium behaves like a heavy rare earth in nitrate system and like a light rare earth in thiocyanate system. The extraction of light rare earth is possible in the nitrate process and heavy rare earths in thiocyanate process using quaternary ammonium nitrate and thiocyanate respectively. Separation of praseodymium and neodymium in high purity (99.9%) was reported by Kwang-Sien et al[105] using quaternary ammonium nitrate (0.65 M in xylene).

Hazen and Hadzeriga[107] have reported the process of double solvent extraction of rare earth elements. The process involves preferential extraction of lighter rare earth elements with amines such as trioctyl amine, primene JMT and dodecylamine and subsequent extraction of heavy rare earth elements with organophosphorus compounds like TBP, DEHPA leaving the middle rare earths in the aqueous raffinate.

The synthesis of suitable extractants for rare earths depends essentially on three factors: 1. Structure-reactivity relationships, 2. Hydrophobic nature of the extractant, 3. Steric hindrance of the extractant. The extraction of rare earths is essentially based on the formation of complexes by organic ligands. The extractive separation depends chiefly on the stability of metal complexes which are closely related both to the nature of metal ions and the structure of ligands. Being hard acids, the rare earths prefer to coordinate with hard bases according to HSAB principles. Hence the oxygen containing phosphorus based ligands are preferred. Steric factors consisting of shielding and strain effect can either assist or hinder the extraction process. In the structure-reactivity studies by dialkyl phenyl phosphonates[108] and dibutyl alkyl phosphonates[109], it was shown that the steric effect of alkyl group in the former is considerably greater than that in the latter, owing to the significant steric hindrance arised from two ester alkyl groups in the molecule of dialkyl phenyl phosphonates. Meanwhile the heavier rare earths are extracted better than the lighter ones when the structure effect of organic ligands is similar due to lanthanide contraction. A substantial steric effect of alkyl groups lie in the following sequence.

$n\ C_4H_9 > i\ C_4H_9 > s\ C_4H_9 > t\ C_4H_9\ ,\ n\ C_5H_{11} >$
$t\ C_5H_{15} > neo\ C_5H_{11},\quad n\ C_6H_{13} > cyc\ C_6H_{11}$ and
$n\ C_8H_{17} > i\ C_8H_{17} > s\ C_8H_{17}.$

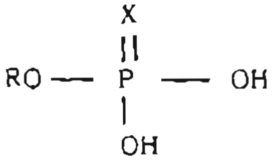
A bulky isopropyl directly linked to phosphorus atom affects extraction considerably. The size of the extractant appears to be of great importance in separating rare earth ions. The extraction constants are enhanced by the decreasing pK_a of the extractant. But in some cases pK_a values give no satisfactory explanation. Sterically hindered acidic organophosphorus compounds possessing smaller extraction constant usually have high selectivity in the rare earth extraction. Organic ligands used in the extraction of rare earths should be less soluble in water with more lipophilicity in order to keep more metal complexes in organic phase. For this purpose introduction of branched groups in the alkyl is usually necessary.

In view of the above, the synthesis of a few alkyl aryl and aryl phosphoric acid have been described for the extraction studies. It will not be out of place to give a brief review of the chemistry and synthesis of orthophosphate esters.

1.4 CHEMISTRY OF TETRA CO-ORDINATE PHOSPHORUS COMPOUNDS[110]

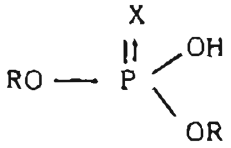
The development of the chemistry of phosphoric esters has been vast in last few decades. Besides a number of new methods, the number of definite chemical compounds in this field is also large. The first organic phosphorus compound to be identified was probably lecithin isolated from brain fat in 1811 by Vauquelin and characterised as a phosphorus containing lipid by Gobley in 1850. In 1820, the earliest laboratory synthesis of organic phosphorus compound nuclein was reported by Lassaigne who obtained crude alkyl phosphates by reacting alcohols with phosphoric acid. This was followed by the synthesis of phosphine derivatives by Thenard in 1840. The most notable pioneers in this field were Michaelis and Arbusov who are now regarded as the founders of organophosphorus chemistry. The intensive development of phosphorus compounds as insecticides and nerve gases were due to Schrader and Saunders who discovered the toxic properties of certain phosphate esters. By 1940, it had been clearly established that the highly polymerised phosphate ester known as nucleic acids were normal constituents of all cells. It is now well accepted that phosphorus compounds play a vital role in living process and are essential, not only for hereditary processes but for the growth, development and maintenance of all plants and animals.

The chemistry of tetra coordinate phosphorus compound possessing the phosphoryl (P = O) bond is described. All of these esters in principle may be considered as being derived from orthophosphoric acid. (a) By successive replacement of hydrogen atoms by organic groups, mono substituted dihydrogen phosphates (1, X = 0), disubstituted monohydrogen phosphates (2, x = 0) and finally phosphate triesters (3, X = 0) are obtained, (b) replacement of OH functions by halogen gives acid halides and replacement by nitrogen containing group gives, for example amides, (c) one or more oxygen atoms may be replaced by sulphur (eg. 1-3, X =S) or selenium (eg. 1-3, X = Se) to the form thio or seleno-phosphoric acid derivatives. Finally (d) the replacement of all the OH groups by organic groups leads successively to phosphonic acid (4, X = 0), phosphinic acid (5, X = 0) ultimately to tertiary phosphine oxide (6, X = 0).



$$RO-\overset{\overset{X}{\|}}{\underset{\underset{OH}{|}}{P}}-OH$$

(1)



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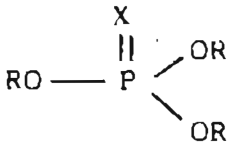

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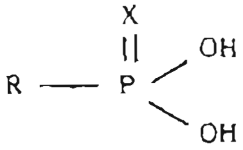

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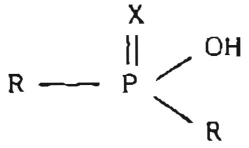
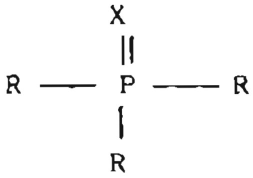


(5)



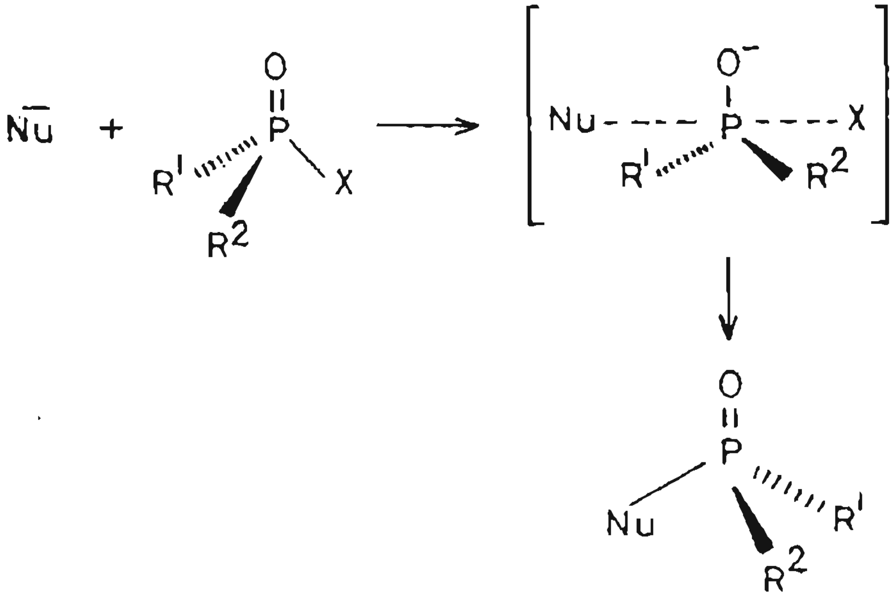
$$R-\overset{\overset{X}{\|}}{\underset{\underset{R}{|}}{P}}-R$$

(6)

A comparison of the phosphoryl and carbonyl bonds, superficially may seem to resemble each other. Both bonds are highly polar in the sense $M^{\delta+} - O^{\delta-}$ (M is C or P) and the very strong electron withdrawing ability of each bond confers a high degree of mobility on the hydrogen attached to adjacement atoms. In some of the phosphonic, phosphinic acid derivatives and even in some phosphine oxides, the phosphoryl bond activates groups such as α CH groups very strongly particularly when situated between two phosphoryl groups or between phosphoryl and carbonyl or aryl groups. Hence, phosphoryl methylene compounds very often behave like conventional active methylene compounds.

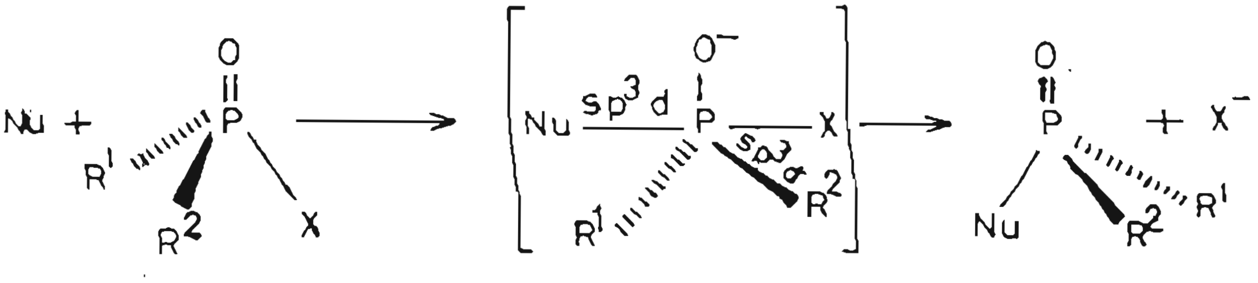
Both the carbonyl and phosphoryl bonds clearly detectable spectroscopically in the infra red region. The exact position of absorption being dependent upon the attached substituents in association with steric effects and electronic effects[111,112]. However there are difference in the hybridization in spite of the resemblance between phosphoryl P = 0 and carbonyl (C = 0) bond. The hybridisation at the carbonyl carbon is planar (sp^2) and phosphoryl phosphorus is tetrahedral (sp^3). The two bonds are affected by the total electronic effect of the attached groups to different extents, the carbonyl group by a combination of mesomeric and inductive effects and the phosphoryl by the inductive effect only. The molecular geometry around the two bonds differ markedly and hence differences in the degree of steric hindrance by the attached substituents also become apparent. The difference in the relative rates of hydrolysis of the carbonyl and phosphoryl chlorides with variation of the attached substituents provide a good evidence for difference in the combined steric and electronic effects at the two reactive sites[113-116].

Previously the phosphoryl bond was believed to be inert but now evidences are available to prove its participation in numerous chemical rections. Hence it can act as electron donor and as such can be protonated on oxygen. The ^1H and ^{31}P NMR spectroscopy[117] can be used to measure the relative basicities of a series of compounds. Electron acceptors like boron trifluoride and metallic salts complex with phosphoryl bond. The phosphoryl bond exhibits nucleophillic character. One example may be noted showing the involvement of phosphoryl group in reactions under particularly mild conditions. Thus the oxidation of the phosphines by potassium permaganate in acid solution yields the spirophosphoranes probably via the phosphine oxide[118]. In its tetracoordinate compounds, phosphorus becomes a centre of chirality through the presence of three different substituents in addition to phosphoryl group[119-122]. The optically active phosphate triesters have become relatively accessible for eg. O, S, dimethyl O-ethyl phosphorodithioate, ethyl isopropyl methyl phosphate (Hall et al, 1975). Phosphoryl compounds show mainly three group of reactions. (a) Reactions that are restricted to the actual phosphoryl group, (b) Displacement reactions at phosphorus which involve the breaking of bonds between phosphorus and oxygen, sulphur, nitrogen or halogens and sometimes phosphorus-carbon bonds as in the chemistry of tertiary phosphine oxides, (c) Reaction of substituents on phosphorus which do not involve with the fission of bonds between the substituents and the central phosphorus atom. It might be useful at this stage to review very briefly the mechanisms which have been proposed to account for the substitution reactions occurring at the phosphoryl phosphorus atom. Phosphorylation may proceed by bimolecular or unimolecular reaction. Individual examples of the mechanism will be examined more fully as the various classes of compound are considered (a) S_N2 (P) process (Scheme 1.1) named by analogy to the S_N2 displacement at saturated carbon involves simultaneous bond formation and bond fission within a transition state having two long pd bond and three shorter sp^2 bonds. Bimolecular kinetics coupled with isotope effects, stereochemical changes and failure to isolate intermediates all contribute to the evidence for the S_N2 (P) process. This mechanism is commonly encountered in displacement among both cyclic and acyclic phosphorohalidates, phosphoric, phosphonic and phosphinic acid derivatives with the notable exception of phosphate anions and phosphoramidates and related compounds possessing free NH bond.



Scheme 1.1

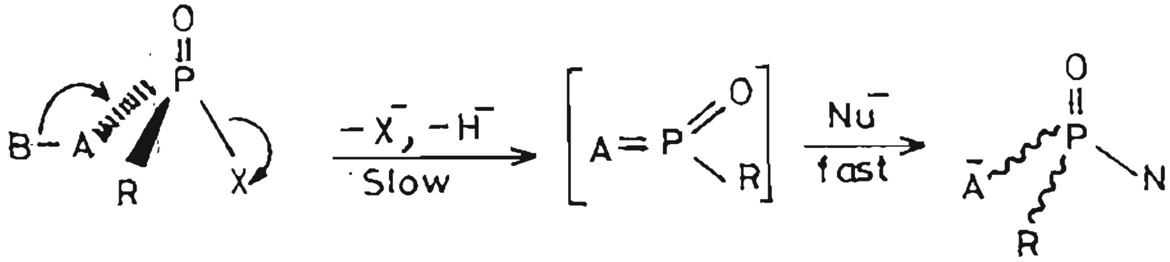
These reactions proceed with inversion of configuration. The mechanism of phosphorylation by phosphorus oxychloride in particular has been studied by Hudson[123]. (b) The addition-elimination (AE) mechanism (Scheme 1.2) involves the formation of a true penta coordinate intermediate generally thought to have trigonal bipyramidal geometry and constructed by apical approach



Scheme 1 .2

of the attacking nucleophile. With the removal of the displaced group at the opposite apex the outcome of this mechanism should be inversion of chirality at phosphorus, as in the case for the S_N2 (P) mechanism. In the case of the AE mechanism it is possible that as a result of stereotopic changes that evidently take place during the life time of the intermediate, the overall stereochemical course of the displacement can be retention or racemization[124-127]. The retention or racemeziation could well be the result of the formation or breakdown of the bipyramid by different processes i.e. apical entry, equatorial departure or vice versa or even of the formation of an intermediate of different geometry, eg. square pyramidal geometry.

The evidence for the formation of pentacoordinate intermediates has been indirect, being based on kinetics or optical measurements. Ramirez et al have provided more direct evidence based on the identity of products from combination of different starting materials, viz. for cyclic esters derived from catechol[128]. There is indirect evidence that AE mechanism is involved in the degradation of phosphine oxide under alkaline conditions and in the hydrolysis of five membered cyclic phosphate esters and related compounds, but failures to incorporate ^{18}O during the hydrolysis of acylic phosphoryl chlorides, and esters would seem to preclude the AE mechanism in these cases. (c) The elimination-addition (EA) mechanism (Scheme 1.3) involves the formation of transient metaphosphoric acid derivatives in a two stage process comprising a rate determining elimination followed by a rapid addition step. This mechanism is seen in the alkaline hydrolysis of phosphate anions and also many phosphoryl amide compounds. This is otherwise called unimolecular phosphorylation



Scheme 1.3

The EA mechanism has often been referred to as S_N1 (P) or ElcB. The former seems to be less appropriate since it draws the idea of planar phosphinyl cation (by analogy to the S_N1

process in carbon chemistry) as far as can be ascertained the intermediate is planar (like the carbocation),but may be non-ionic. This mechanism dealing with phosphinyl cation have been particularly applicable when good leaving groups for eg. benzoyloxy and 2,4-nitrophenoxy are involved. The observed experimental results can be explained by the acceptance of the ideas of the AE mechanisms[129].

Displacements at the phosphoryl centre can undergo the general acid or base catalysis distinguishable by kinetic isotope effects. Catalysis by electrophilic reagents also, eg. metal ions (through coordination to the phosphoryl oxygen or to the leaving group) or by nucleophiles as in the catalysis of alcoholysis of phosphoric acid derivatives (primary or secondary esters) or pyrophosphates) by aromatic amines have all been widely observed[130]. The high reactivity exhibited at a pH of about 4 by monoalkyl phosphates may be due to a mechanism of this kind.

1.5 GENERAL METHOD OF PREPARATION OF PHOSPHORIC ACID ESTERS[131-138]

The direct esterification of orthophosphoric acid or acid functions of polyphosphoric acids is an extraordinarily slow reaction which is practically not applicable for the preparation of phosphoric esters. For instance the direct phosphorylations by orthophosphoric acid to obtain uridine 2'(3')-phosphate with uridine took place at 160° C. In the esterification of phenols by phosphoric acid much higher temperatures i.e. of the order of 280 to 300 °C were required. Hence the general methods applied can be divided into two groups, (a) use of reactive derivatives of phosphoric acid (anhydrides, halides etc.), (b) use of phosphorus acids with coordinatively unsaturated P (mostly phosphorus acid) and which therefore are capable of direct esterification by alcohols followed by transformation of the organic derivatives into molecules with tetra coordinated phosphorus.

1.5.1 Anhydrides (complete or partial) of orthophosphoric acid

The reaction of phosphorus pentoxide with hydroxy compound is one of the oldest and cheapest methods for the synthesis of a mixture of primary and secondary phosphates[139-141].

$$3\ ROH + P_2O_5 \longrightarrow (RO)\,PO_3\,H_2 + (RO)_2\,PO_2\,H$$

Phosphorus pentoxide (P_2O_5) is not a monomeric molecule, but it has the structural unit of at least P_4O_{10} which consists of a closely knit network of phosphorus to oxygen to phosphorus bonds between the phosphoryl groups arranged approximately in a tetrahedron. The attack of the alcohol on such a structure proceeds by the progressive cleavage of the anhydride bonds. When all the anhydride linkages in the pentoxide unit are cleaved, then primary and secondary esters are the predominant products. The reaction of four to five molar ratio of alcohol to pentoxide, gives pyrophosphates and polyphosphates which is quenched with water to obtain the individual primary and secondary ester which are separated by the fractional crystallization of their metallic salts.

1.5.2 Use of haloderivatives of pentavalent phosphorus

In this category derivatives with halogens or halogens and oxygenated functions (O, OR) are considered. In all these compounds the halogens react with hydroxy compounds yielding POR functions, as do acyl halides. Primary or secondary phosphoric esters containing one or more than one halogen atom are produced as intermediates which on hydrolysis yield mono or diesterified phosphoric acids.

Phosphorus pentahalides[142] and hydroxy compounnds

The reaction of phosphorus pentahalides with primary alcohols result in the formation of alkyl halophosphates. This reaction gives a spectrum of esters either from disproportionation or from non-homogeneity of the intermediate products. But in the case of secondary and tertiary alcohols, the formation of alkyl halides is more pronounced.

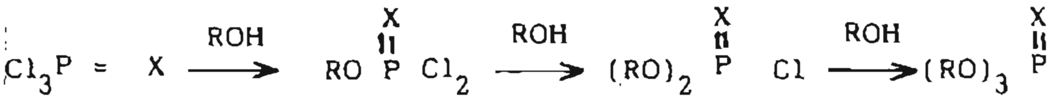
$$PCl_5 + ROH \longrightarrow (H_2O) \longrightarrow ROP(O)(OH)_2$$

$$PCl_5 + 3\ ROH \longrightarrow (H_2O) \longrightarrow (RO)_3PO$$

$$PCl_5 + 4\ ROH \longrightarrow (H_2O) \longrightarrow (RO)_3PO$$

Phosphoryl halides and hydroxy compounds

In a series of three S_N2 (P) displacement reaction which from the stoichiometric point of view, parallel those for the corresponding tervalent phosphorus halides, the phosphoryl halides $P(X) Y_3$ (X is O or S, Y is Cl or Br) react with hydroxylic compounds with the stepwise elimination of hydrogen halides.



$$Cl_3P = X \xrightarrow{ROH} RO\overset{X}{\overset{\|}{P}}Cl_2 \xrightarrow{ROH} (RO)_2\overset{X}{\overset{\|}{P}}Cl \xrightarrow{ROH} (RO)_3\overset{X}{\overset{\|}{P}}$$

With primary alcohol, phosphoryl chloride yields initially the phosphorodichloridates (X = 0) followed by phosphorochloridates (x = 0) in steps which do not require the presence of a scavenging agent to remove the hydrogen halide liberated. The third step resulting in the formation of the phosphate ester (X = 0) is greatly enhanced by the presence of acid binding agent such as pyridine or triethylamine or even inorganic base.

The reaction products with secondary and tertiary alcohols may be complicated with the formation of alkyl halides and alkenes. The reaction between phosphoryl chloride and phenols are slower and it may be advantageous to employ a metallic salt for eg. KCl or $MgCl_2$ as catalyst.

The hydrolysis of the dichloridates and chloridates yields the corresponding mono or diesterified phosphoric acid respectively.

Reaction with hydroxy compound

The halophosphates react as acid halides with hydroxy compounds or their metallic derivatives. Mixed tertiary phosphoric esters $(RO)_2$ (RO) PO where $R = C_2H_5$, n. C_3H_7, iso-C_3H_7 etc. can be prepared in this manner.

$$(RO)_2\ P(O)\ Cl + R'OH\ (R'\ OM) \longrightarrow (RO)_2\ (RO)\ PO + HCl\ MCl$$

Halophosphates can be used as further phosphorylating agent or it can be converted to phosphorylated hydroxy compound by boiling with $Ba(OH)_2$. The mixed tertiary esters obtained from halophosphates can be easily split off to furnish the secondary phosphates.

1.5.3 Use of anhydro acid derivatives

Pyrophosphates[143]

. Esters of pyrophosphoric acid can be used in two ways for the preparation of orthophosphoric esters (a) by controlled hydrolysis or (b) as phosphorylating agents of hydroxy compounds.

(a) Controlled hydrolysis of pyrophosphoric esters

Dialkyl phosphoric acids are obtained in high purity by treating tetra-alkyl pyrophosphates with water at moderately elevated temperatures. Similarly the partial esters of pyrophosphoric acid yield the corresponding phosphoric esters,

but evidently these esters are homogenous only when the original esters are symmetric pyrophosphoric esters.

(b) Pyrophosphoric esters as phosphorylating agents

The pyrophosphoric esters can be easily converted to the tertiary ester which will give the primary esters.

$$(RO)_2\ P(O)\ O\ P(O)\ (OR)_2\ +\ R\ OH \longrightarrow (RO)_2\ (RO)\ PO\ +\ (RO)_2\ PO_2H$$

By use of a group R which is easily split off, the tertiary ester $(RO)_2$ (RO) PO will give the primary ester RO PO_3H_2. This has been realised in particular with tetra-p-nitro phenyl pyrophosphate (prepared in situ from di-(p-nitrophenyl) phosphoric acid and dicyclohexyl carbodimide), the p-nitrophenyl ester function being easily hydrolyzed at room temperature in lithium hydroxide, which does not attack alcoholic ester functions under these conditions. The p-nitrophenyl residue may equally be removed by catalytic hydrogenolysis. This procedure has been applied to the phosphorylation of nucleosides.

1.5.4 Removal of ester groups

Partial splitting of secondary or tertiary phosphoric esters

In general, the stability of phosphoric esters decreases from primary to tertiary esters. Tertiary phosphates can be split readily to the secondary esters. The alkyl derivatives are attacked even at room temperature, provided that the substituents are moderately large; increased size rapidly increases hydrolysis resistance

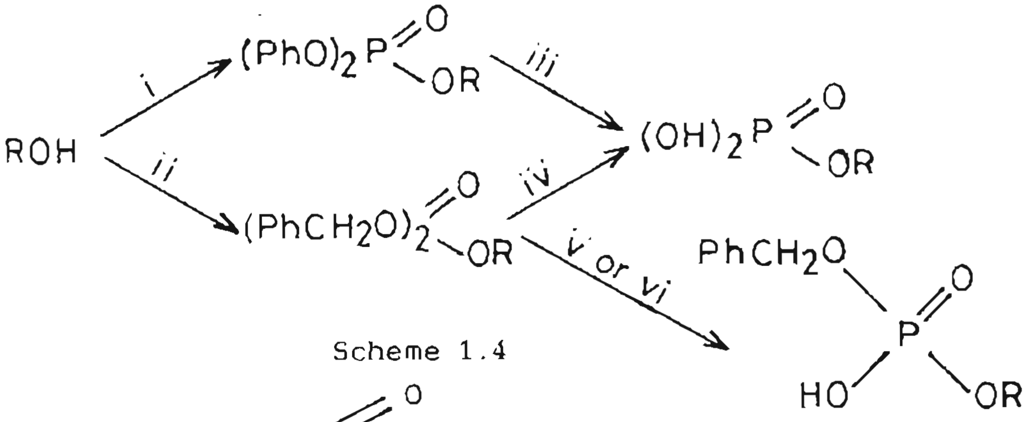
$$(RO)_3\ PO + NaOH \longrightarrow (RO)_2\ P(O)\ ONa + ROH$$

Acidic splitting is more difficult to control and progressive degradation products, down to phosphoric acid are formed. Tertiary phosphates containing two phenyl or benzyl groups may be hydrolysed by mild treatment with dilute mineral acid at moderately elevated temperature. Usually secondary esters are quite stable to alkaline splitting. In acid, the scission proceeds rather rapidly.

Hydrogenolytic removal of phenyl or benzyl groups[144,145]

The phenyl and the benzyl group can generallly be removed from the corresponding phosphates by catalytic hydrogenation. The tertiary esters $(XO)\ (RO)_2\ PO$ and $(XO)_2\ (RO)\ PO$ prepared from the corresponding dibenzyl or diphenyl or benzyl phenyl chlorophospnates $(RO)_2\ (RO)\ P\ (O)\ Cl$ or the dichloridates

(RO) $POCl_2$ (R = $C_6H_5CH_2$ or C_6H_5) respectively can be converted to primary and secondary esters $XOPO_3H_2$ and $(XO)_2PO_2H$. by this method of mild hydrogenolysis. The catalysts usually used are palladised carbon and platinum. Scheme 1.4 is shown below.



Scheme 1.4

i. $(PhO)_2-P(=O)Cl$, pyridine,

ii. $(PhCH_2O)_2-P(=O)Cl$, pyridine

iii. H_2, Pt (Adam's catalyst), iv. H_2/Pd,

v. H_2/Pd base, vi. I^-

Extensive study has indicated that use of ethanol or dioxane as the solvent, preferably in the presence of a little water and a trace of acid to be most favourable.

1.5.5 Exchange esterification of tertiary phosphates

Tertiary alkyl phosphates may be transesterified by heating with alcohols having bigger substituents than present in the ester. A mixture of mono and di-exchange products results when the reaction proceeds in the presence of sodium alkoxide.

$$(RO_3)PO + ROH + RONa \longrightarrow (RO)_2 (RO) PO + ROR$$

1.6 SPECTRAL PROPERTIES OF PHOSPHORIC ACID ESTERS

Considerable use of all types of spectroscopy is made in structural determination and in studies of reactions involving phosphorus[146]. Ultraviolet spectroscopy continues to be used extensively for the study of conjugative effects in phosphorus compounds[147].

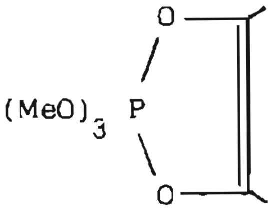
Infrared absorption stretching frequencies of most functional groups containing phosphorus have been determined and they are widely used in the structural investigation of unknown phosphorus compounds[148]. The infrared absorptions of some phosphorus bonds are shown in Table 1.1.

Table 1.1: Infra red absorption frequencies (cm^{-1}) of phosphorus bonds

P-OH	2750-2550 (broad and shallow)	P-F	985-710 (s)
P-H	2450-2240 (m)	P-P	510-390 (w)
P=N	1439-1120 (vs)	P-Cl	590-420 (s)
P=C	1230-1180 (m)	P-O-P	1060-850 (s)
P=O	1320-1200 (vs)	P=S	750-550 (s)
P-Ph	1450-1425 (s)	P-O-C	1060-90 (vs), 875-730 (s)

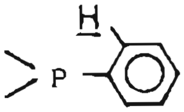
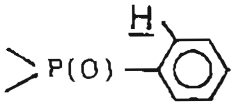
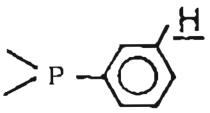
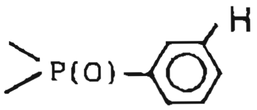
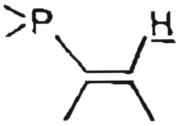
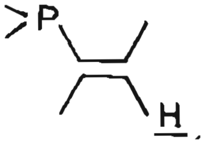
NMR spectroscopy provides the greatest source of structural information in phosphorus chemistry. Information can be obtained from ^{1}H and ^{13}C NMR, but further information particularly regarding the nature of phosphorus atom can be obtained from ^{31}P NMR spectra[149]. Limitations in the application of ^{31}P NMR have now been removed with the advent of fourier transform techniques. Some of the typical ^{31}P chemical shifts and coupling constants are shown in Tables 1.2 and 1.3 respectively.

Table 1.2: ^{31}P chemical shift of some organophosphorus compounds

P_4	+ 460	$MePO(OMe)_2$	-33
PH_3	+ 240	$(MeO)_3PO$	-1
Me_3P	+ 62	$(PNCl_2)_3$	-19
Ph_3P	+ 7	$Ph_3\overset{+}{P}MeBr^-$	-23
$(Me_2N)_2P$	-122	$Ph_3P=CH_2$	-4
$(MeO)_3P$	-140	PF_5	+35
PCl_3	-219		+49
Ph_3PO	- 25		
Cl_3PO	-3	$PhPF_5^-$ Et_2 NH_2^+	+136
$(Me_3N)_3PO$	- 24		
Me_2PO_2H	- 49		

Measured in ppm from 85% H_3PO_4 as standard

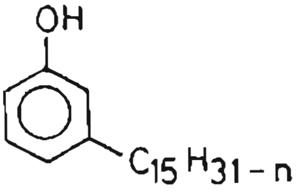
Table 1.3: Phosphorus-hydrogen coupling constant (Hz)

$>P\text{-}\underline{H}$	150-225		7-10
$>P(O)\ \underline{H}$	450-725		12 -14
$>P\text{-}\underline{H}$	450-600		1-2
$>P\text{-}C\underline{H}_3$	0-5		2-4
$>P(O)\underline{CH}_3$	8-18		
$>P\text{-}\overset{\mid}{\underset{\mid}{C}}\ \text{-}\ C\underline{H}_3$	10-30		
			12-15
$>PO\ CH\ C\underline{H}_3$	0-4		
$>P\text{-}O\ C\underline{H}_3$	7-15		28-32

The synthesis of reagents. for extraction has been very few. The most commonly used reagents for extraction on commercial scale have been DEHPA and EHEHPA. DEHPA can be synthesised by many procedures[150]. The most commonly adopted one is via dialkyl phosphite. The chlorination followed by hydrolysis of di-2-ethylhexyl phosphite yields DEHPA. EHEHPA is currently the more preferred extractant. It is again synthesised via. di-2-ethylhexyl phosphite[151]. The dialkyl phosphite is treated with sodium and alkyl halide to give the neutral phosphonate. The partial hydrolysis of the phosphonate gives the phosphonic acid EHEHPA.

In the present study, it was envisaged to synthesise some alkyl aryl phosphoric acids starting from CNSL. Cashew nut shell liquid (CNSL) is obtained as a by-product of cashew industry[152]. It is obtained as a reddish brown viscous liquid from the shell of cashewnut from the cashew tree Anacardium occidentale L[153,154]. It is a rich source of unsaturated long chain hydrocarbon phenols. The phenolic lipids present in CNSL are (1) Anacardic acid[155,156]; (2) cardanol[157], (3) cardol[158] and (4) 2-methyl cardol[159]. Natural CNSL contains anacardic acid as the major component which on decarboxylation gives technical CNSL containing cardanol as the major compound[153,160]. Cardanol was isolated from CNSL by Stadeler and structure assigned by Backer and Haack. B.G.K. Murthy et al[161] have separated cardanol into 4 components viz. saturated, mono, di- and tri-olefin using silver nitrate impregnated silica gel TLC and column chromatographic techniques.

Cardanol is a monohydric phenol with a C_{15} side chain in the meta position. It is obtained from technical CNSL by vacuum distillation at 3-4 mm Hg and the fraction distilling at 230-235°C was collected[162]. It is a mixture of four components differing in the degree of unsaturation in the side chain (Fig. 1.1). (1) 3-(pentadecyl phenol) 10%), (2) 3-(8-pentadecaenyl) phenol (52%), (3)3-(8,11-pentadecadienyl) phenol (20%), and (4) 3(8,11, 14-pentadecatrienyl) phenol (18%).



Cardanol

where

n = 0 $(CH_2)_{14}\ CH_3$

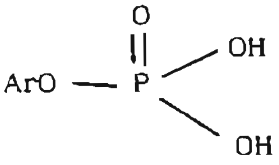
n = 2 $(CH_2)_7\ CH = CH\ (CH_2)_5\ CH_3$ 8' (Z)

n = 4 $(CH_2)_7\ CH = CHCH_2 - CH = CH\ (CH_2)_2\ CH_3$ 8' (Z), 11' (Z)

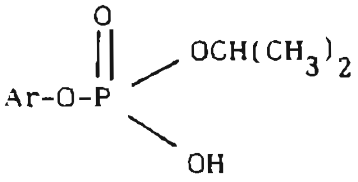
n = 6 $(CH_2)_7\ CH = CH - CH_2\ CH = CH\ CH_2\ CH = CH_2$ 8' (Z), 11' (Z), 14' (Z)

Cardanol was used as the starting material for the synthesis of a few alkyl aryl phosphoric acids. Cardanol was hydrogenated to obtain 3-pentadecyl phenol which is used for the synthesis of the following alkyl aryl phosphoric acid.

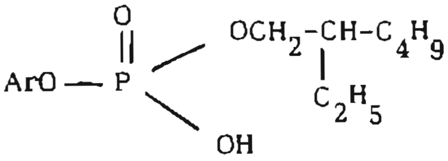
1.



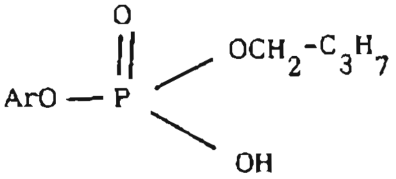
2.



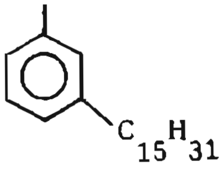
3.



4.



where Ar -



These compounds were used for the extraction of rare earths.

CHAPTER II

SYNTHESIS OF ALKYL ARYL PHOSPHORIC ACIDS

2.1 INTRODUCTION

The synthesis of phosphoric esters, particularly orthophosphate esters has been reported in very early times. The development of chemistry of phosphoric acid in different disciplines of chemistry has been extraordinarily vast. In contrast to the behaviour of most carboxylic and minerals acids, the direct esterification of orthophosphoric acid is an extremely slow reaction which practically is not appropriate for the preparation of phosphoric esters. Bliznyuk et al patented the preparation of monoaryl oxyethyl phosphoric acids by heating the corresponding alcohol with 85% phosphoric acid in an organic solvent with azeotropic distillation of water.

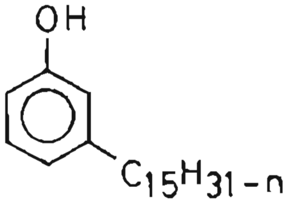
Phosphate esters find enormous importance in biochemistry and in many technological applications. The neutral esters find wider applications as solvents and plasticizers. In addition to the plasticizing action, the esters confer a degree of flame retardation to the formulations. Some of the sulphur derivatives of these esters have been used rather extensively as ore flotation agents and lubricating oil additives. The neutral tertiary ester and sulphur analogues have been used widely as pesticides and insecticides. Some of the phosphoric esters and phosphonic esters have been used in solvent extraction for the isolation and purification of various metal cations.

One of cheapest methods used even today for the synthesis of primary and secondary phosphates is the use of phosphorus pentoxide[139-141] . The polyphosphates obtained are hydrolysed to obtain the primary and secondary esters. Such procedures fail with larger substituents and the separations become extremely laborious if very pure products are desired.

The use of phosphorus halides like phosphorus pentahalides, oxyhalides, trihalides as phosphorylating agents for alcohols and phenols has been the main methods for the synthesis of a variety of organophosphorus compounds. The reaction of phosphorus halides[163] and oxyhalide[164] with an alcohol or phenol proceeds in the presence of an organic base. The hydrolysis of halides of primary or secondary phosphoric acid may be effected by water at room temperature or slightly above it. The halophosphates can be used as further phosphorylating agents. They can also be used for the synthesis of tertiary mixed esters. Secondary esters can be obtained by the partial splitting of tertiary esters. Especially in the aliphatic series, such reactions can be used for synthetic purpose in alkaline solutions. Increased size of the substituent rapidly increases hydrolysis resistance. Acidic splitting is more difficult to control and generally results in various degradation products. The need for purer products has resulted in the method of hydrogenolysis[145] .

The benzyl derivative of the alkyl, aryl or mixed phosphoric ester is synthesised and is easily purified by column chromatography. The pure benzyl esters are converted to the corresponding phosphoric acids by catalytic hydrogenation.

The synthesis of newer reagents for the isolation and separation of rare earths has been only very few. In the present work it was envisaged to synthesise some phosphoric acid esters from regionally available and naturally occurring sources like cashew nut shell liquid (CNSL). Cardanol (I) is the major component of CNSL.

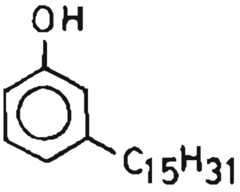


where n = 0, 2, 4, 6.

I

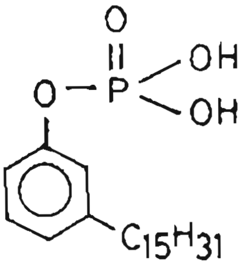
Cardanol was obtained by the double distillation of CNSL at 3-4 mm Hg and fraction which distilled at 230–235°C gave a refractive index of 1.509 and Brookfield viscosity of 420-520 Cps at 30°C as reported for pure cardanol. Cardanol is a mixture of four components varying in the degree of unsaturation in the side chain.

The IR spectrum of the hydrogenated product showed a band at 3500 cm^{-1} for the phenolic hydroxyl group. It was devoid of any bands for the olefinic bonds. The ^{1}HNMR spectrum of the product did not show any olefinic protons indicating that the desired compound has been obtained.

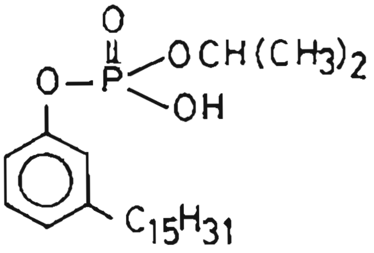


3-pentadecylphenol (II)

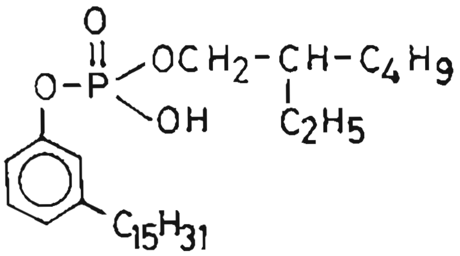
Since cardanol is a mixture of four compounds mentioned above, it became imperative to convert it to a single product viz. 3-pentadecylphenol (II). This was achieved by catalytic hydrogenation. The four compounds envisaged to be synthesised from 3-pentadecylphenol are given below (IV, VI, VIII, X).

1)


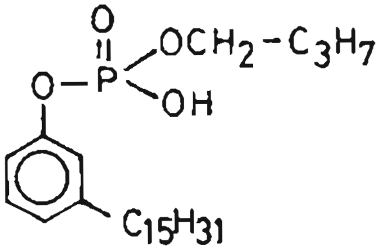
IV

2)


VI

3)


VIII

4)


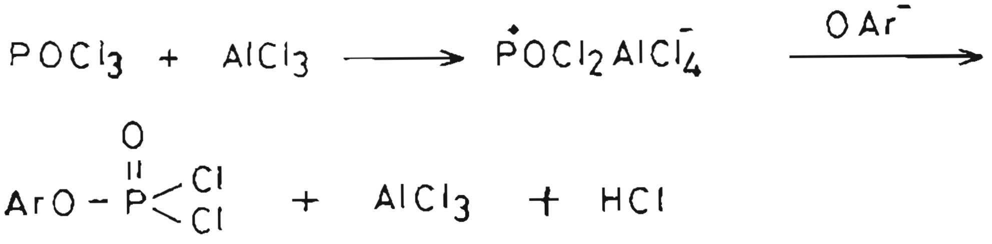
X

The methodology adopted for the synthesis of the above compounds involved the synthesis of the phosphorodichloridate followed by reaction with the respective alcohol and benzyl alcohol to give the corresponding triester. Hydrogenolysis of the purified benzyl ester gave the corresponding mixed alkyl 3-pentadecylphenyl phosphoric acids. Mono (3-pentadecylphenyl) phosphoric acid was prepared by hydrolysis of the dichloridate.

2.2 DISCUSSION

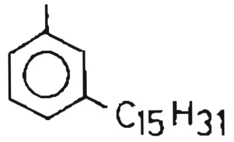
2.2.1 SYNTHESIS OF 3-PENTADECYLPHENYL PHOSPHODICHLORIDATE (III)

The synthesis of phosphorodichloridate was achieved by using anhydrous aluminium chloride as catalyst.



$$POCl_3 + AlCl_3 \longrightarrow \overset{+}{P}OCl_2AlCl_4^- \xrightarrow{OAr^-} ArO-\overset{O}{\overset{\|}{P}}<^{Cl}_{Cl} + AlCl_3 + HCl$$

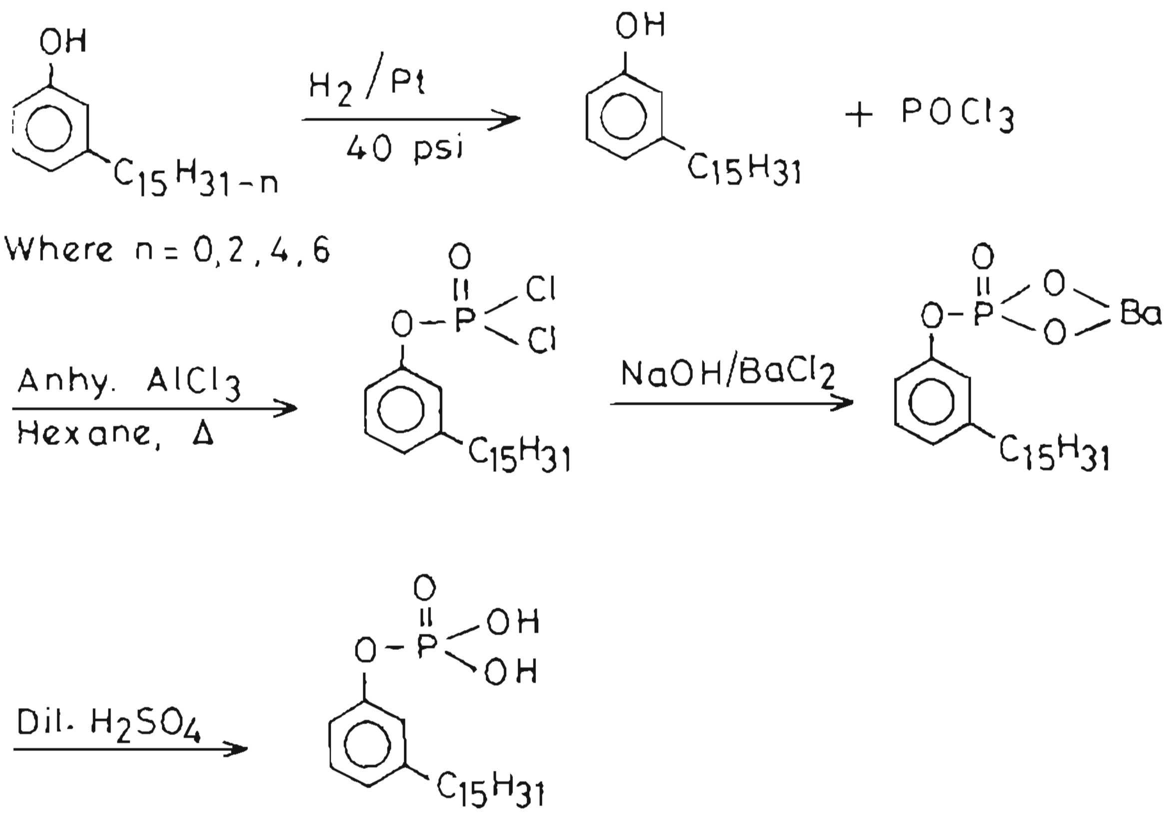
Where Ar –



The $AlCl_3$ was filtered and excess $POCl_3$ was distilled off. The ^{1}HNMR spectrum of 3-pentadecylphenyl phosphorodichloridate clearly indicates the absence of signal for the P-O<u>H</u> group. Since the phosphorodichloridate is highly sensitive to moisture, the next step of the synthesis was carried out immediately.

2.2.2 SYNTHESIS OF MONO(3-PENTADECYLPHENYL) PHOSPHORIC ACID (MPPA) (IV)

The title compound was synthesised as shown in Scheme 2.1.



Scheme 2.1

The hydrolysis of the 3-pentadecylphenyl phosphorodichloridate with excess water was found to give a product contaminated with pyrophosphates and polyphosphates. After a series of experiments it was found that the best method to get the title compound was to hydrolyse the 3-pentadecylphenyl phosphorodichloridate with dil. NaOH in the presence of $BaCl_2$ to precipitate as its barium salt. The barium salt was filtered, washed thoroughly with acetone and regenerated with acid and extracted with large amount of hexane to selectively extract the title compound. The compound which was a solid was recrystallised from hexane. It gave a melting point of 76^{o}C.

The IR spectrum (Fig. 2.1) of the compound showed strong absorptions for groups such as P = O, P-OH (broad and shallow), and P-O-C stretching vibrations at 1243, 2348 and 1020, 954 cm^{-1} respectively. The ^{1}HNMR (Fig. 2.2) of MPPA showed alkyl and aryl protons of 3-pentadecylphenyl group at δ 0.8 to 1.8 and δ 6.6 to 7.1. The peak at δ 2.3 to 2.6 corresponds to the Aryl-C$\underline{H}_2$ protons. The P-O$\underline{H}$ peak was not seen and it may be due to intramolecular hydrogen boonding.

The ^{31}P NMR of MPPA gave a signal at -5.7 ppm (Fig. 2.3) indicating its purity. A total of 100 gms of the compound was prepared in several batches.

The alternate route followed for the synthesis of MPPA was to prepare the dibenzyl ester from the phosphorodichloridate.

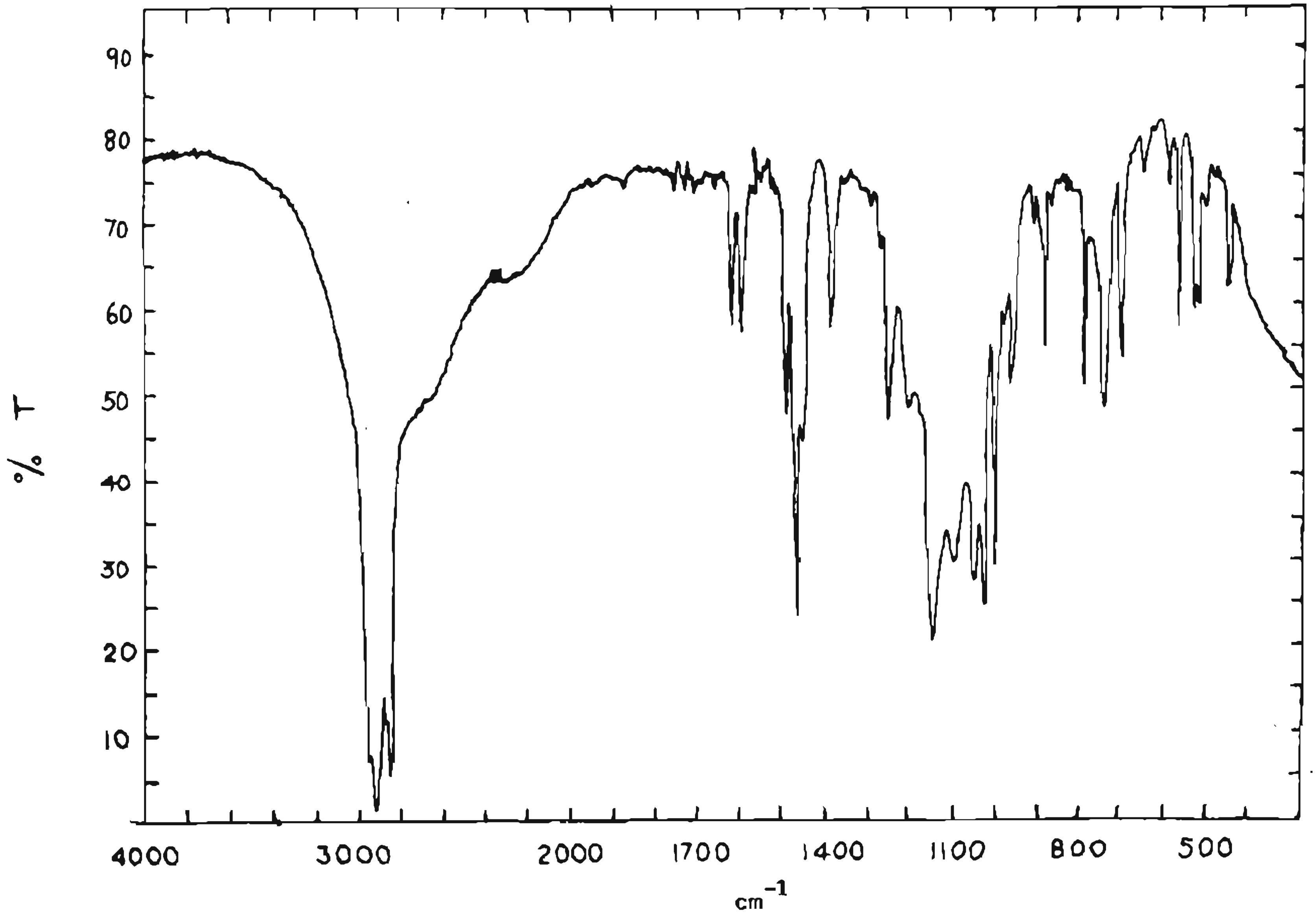


Fig. 2.1: IR spectrum of mono 3-pentadecylphenyl phosphoric acid (in nujol)

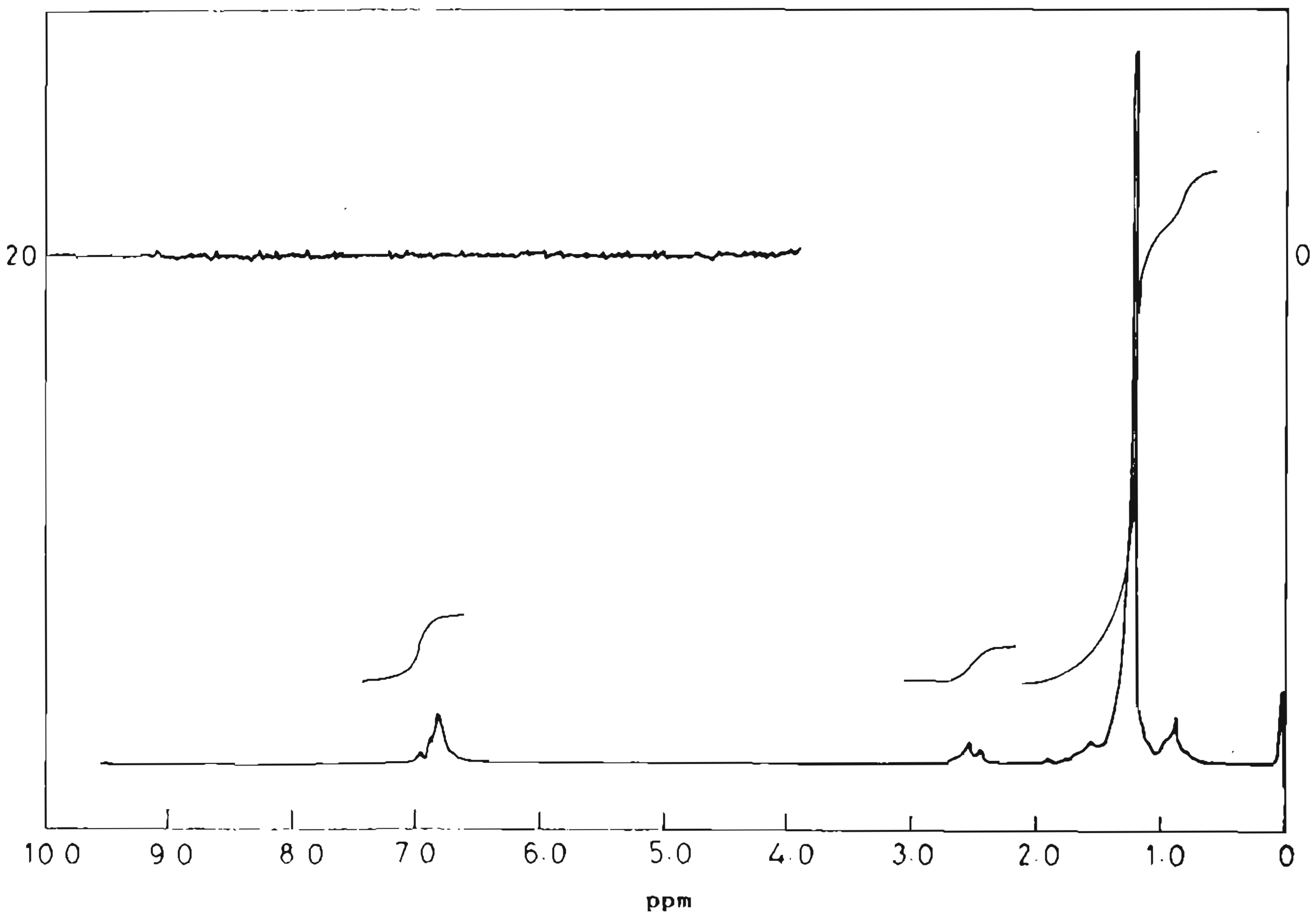


Fig. 2.2: ^{1}H NMR spectrum of mono(3-pentadecyl) phosphoric acid

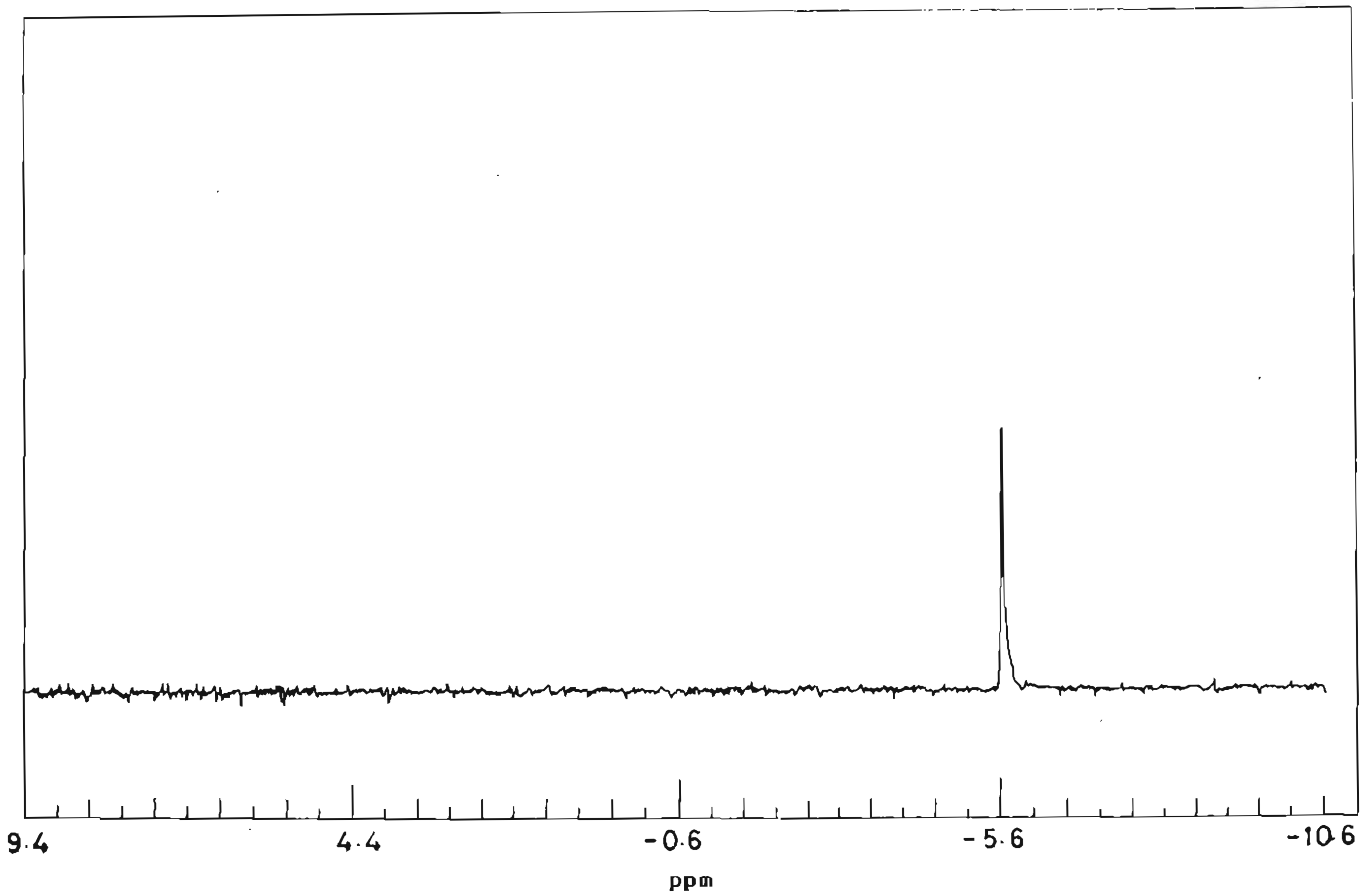
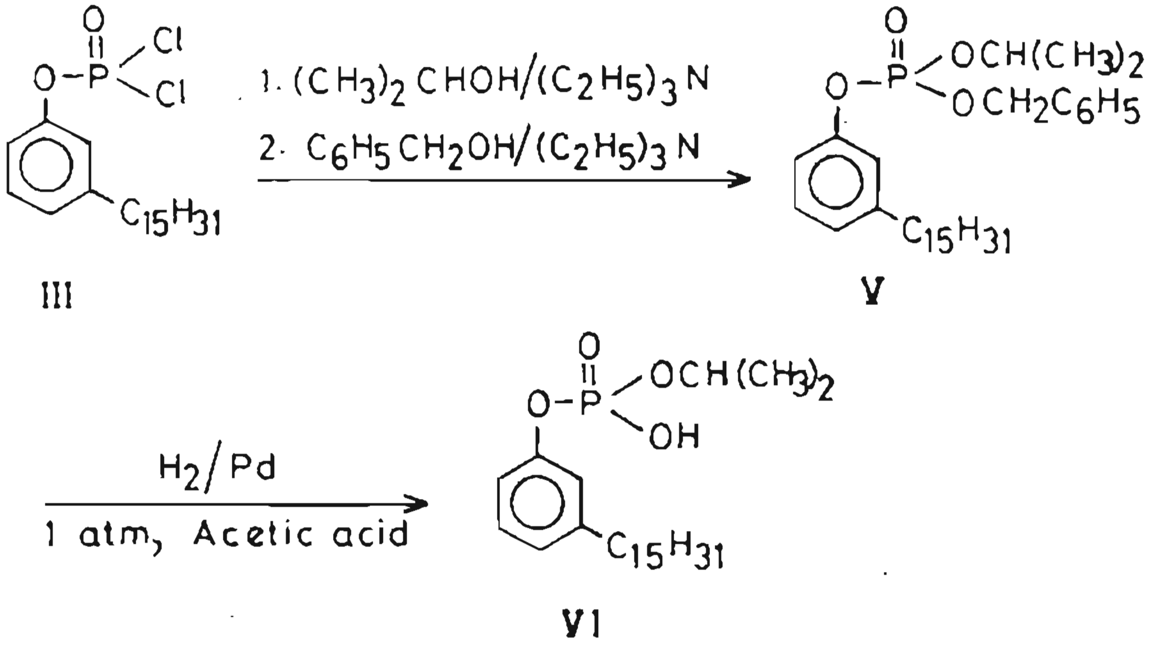


Fig. 2.3: ^{31}P NMR spectrum of mono 3-pentadecylphenyl phosphoric acid

It was observed that the yield of the dibenzyl ester was found to be poor and hence this route was not followed.

2.2.3 SYNTHESIS OF ISOPROPYL-3-PENTADECYLPHENYL PHOSPHORIC ACID (IPPA) (VI)

The above compound was synthesised as shown in Scheme 2.2.



III

V

VI

Scheme 2.2

Synthesis of isopropyl-benzyl-3-pentadecylphenyl phosphate(V)

The highly reactive phosphorodichloridate obtained in the above step was taken in toluene dried over sodium and mixture of stoichiometric amounts of isopropyl alcohol and triethylamine was added dropwise. The reaction was carried out at

20^{o} C for 1 hr. Then stoichiometric amounts of benzyl alcohol and triethylamine were added and the reaction allowed to continue for 24 hrs. By adopting this technique maximum yield of the desired product was achieved. The product was purified by elaborate column chromatography over silica gel to yield the title compound in high purity. Purification by vacuum distillation was not resorted to because of high molecular weight and boiling point. The chances of decomposition by pyrolysis at higher temperatures could also be avoided by not resorting to distillation. The ^{1}HNMR (Fig. 2.4) spectrum of the compound showed the alkyl and aryl protons of the 3-pentadecylphenyl group at δ 1.0 to 2.7 and δ 6.7 to 7.1 respectively.

The C-$\underline{H}$ proton of the isopropyl group gave a signal centered at δ 4.6 as a multiplet accounting for one proton. The $-CH_2$ of the benzyl group showed a geminal coupling of the methylene protons (J = 8 Hz). The nonequivalence of the two protons can be attributed to dissymmetry imparted to these by the phosphorus atom.

Synthesis of IPPA (VI)

The target compound (VI) was obtained by the hydrogenolysis of the triester (V) using 10% palladised charcoal as catalyst. The reaction was carried out in acetic acid at ambient temperature in a Parr hydrogenator. The hydrogen pressures of the order of 14 Psi was found to be enough to effect hydrogenolysis. It was observed that higher pressure resulted in the

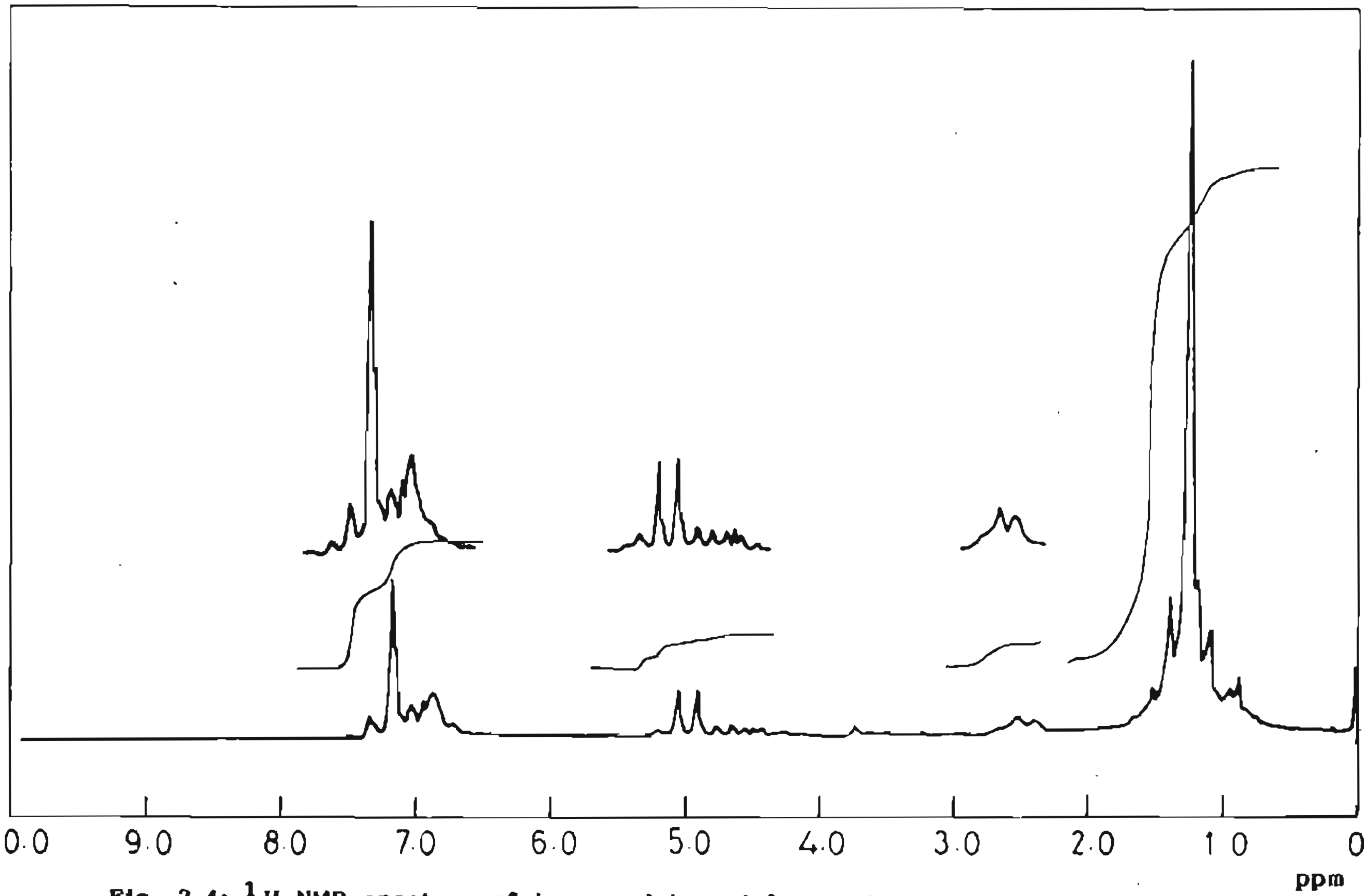


Fig. 2.4: ^{1}H NMR spectrum of isopropyl-benzyl-3-pentadecylphenyl phosphoric acid

splitting of the 3-pentadecylphenyl group also. The title compound was further purified by converting it into the barium salt.

The IR spectrum (Fig. 2.5) of the compound showed strong absorptions for groups such as P = O, P-OH (broad and shallow), P-O-C (aromatic) and P-O-C aliphatic stretching vibrations at 1250 cm^{-1}, 2700 cm^{-1}, 1180 cm^{-1} and 900 cm^{-1} respectively.

The ^1H NMR (Fig. 2.6) of the compound showed the alkyl and aryl protons of 3-pentadecylphenyl group at δ 0.9 to 2.2 and δ 6.7 to 7.1 respectively. The O-C<u>H</u> proton of the isopropyl group was seen as a multiplet centered at δ 4.4. The P-O<u>H</u> proton was seen as a broad signal at δ 11.5 confirming the structure of the compound. The methylene protons adjacent to the phenyl group in the 3-pentadecylphenyl moiety gave a signal as a triplet centered at δ 2.4.

The ^{31}P NMR of the compound (Fig. 2.7) showed a signal at δ —6.0 ppm with reference to phosphoric acid as standard. The value generally agrees with the chemical shift values for phosphoric acid diesters. The compound IPPA was made in the order of 100 gms by conducting reactions in batches of 5 gm, 50 and 100 gms.

2.2.4 SYNTHESIS OF 2-ETHYL HEXYL-3-PENTADECYLPHENYL PHOSPHORIC ACID (EPPA) (VIII)

The synthesis of the title compound was carried out as

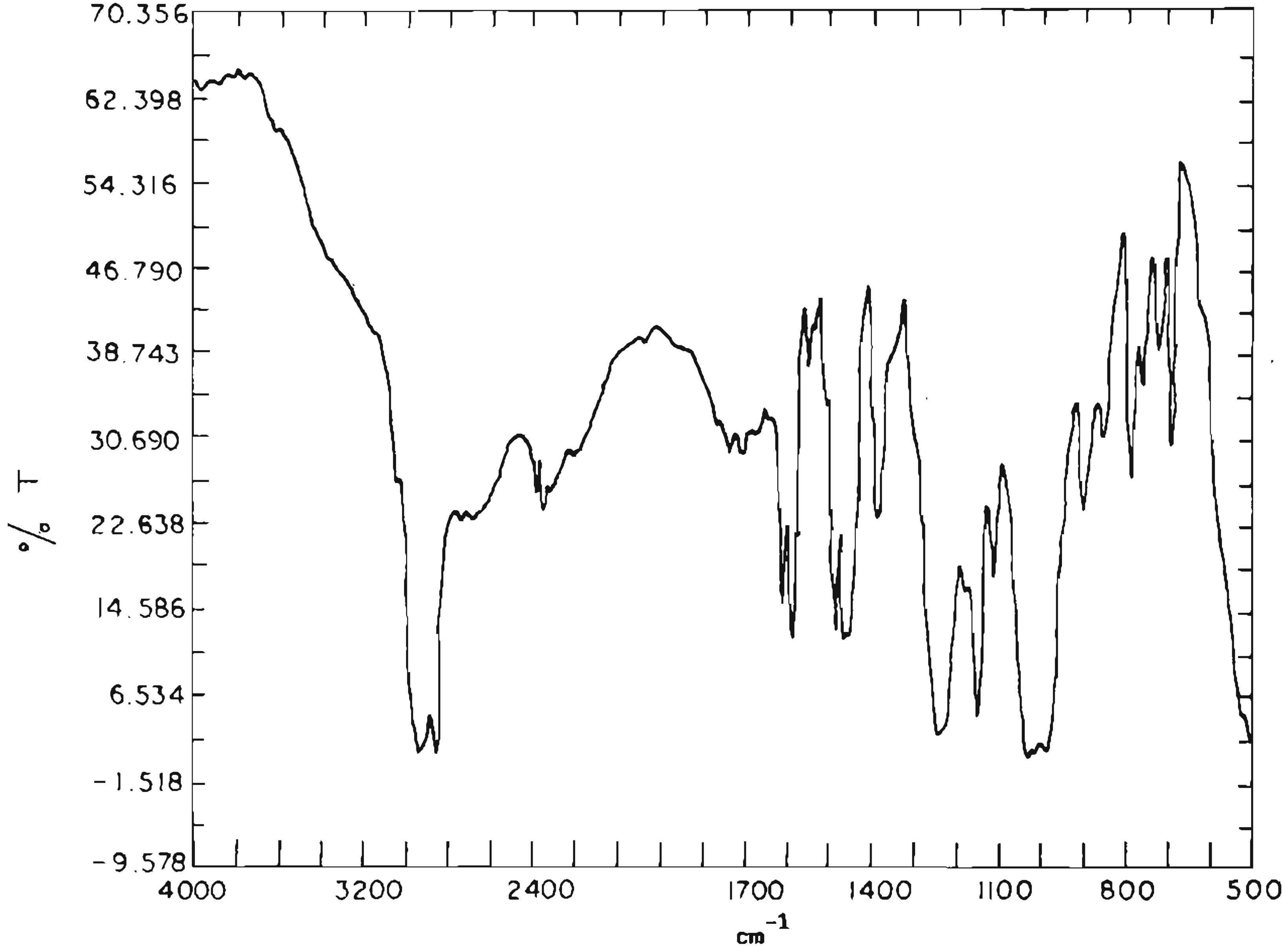


Fig. 2.5: IR spectrum of isopropyl-3-pentadecylphenyl phosphoric acid

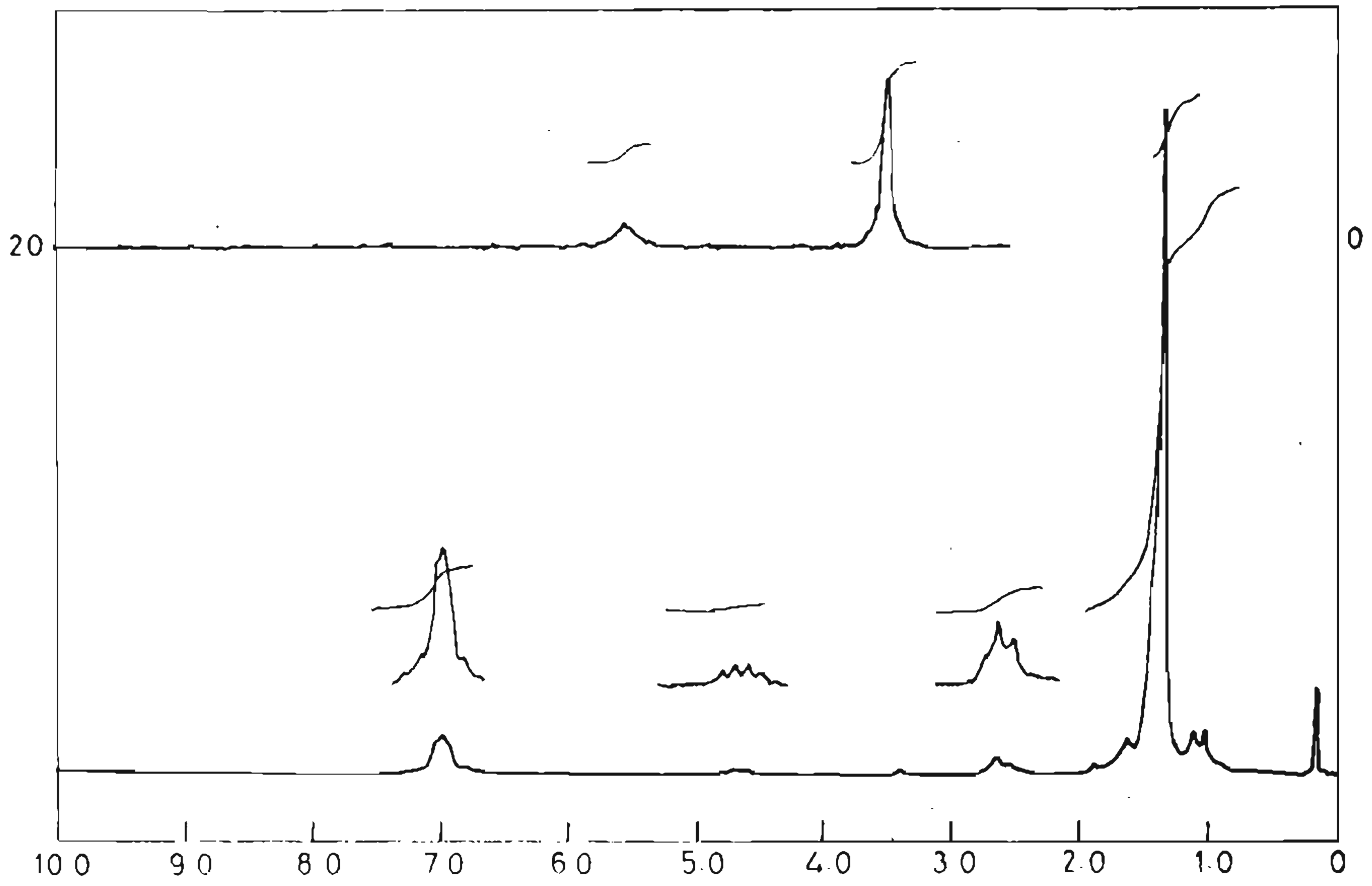


Fig. 2.6: ^{1}H NMR spectrum of isopropyl-3-pentadecylphenyl phosphoric acid

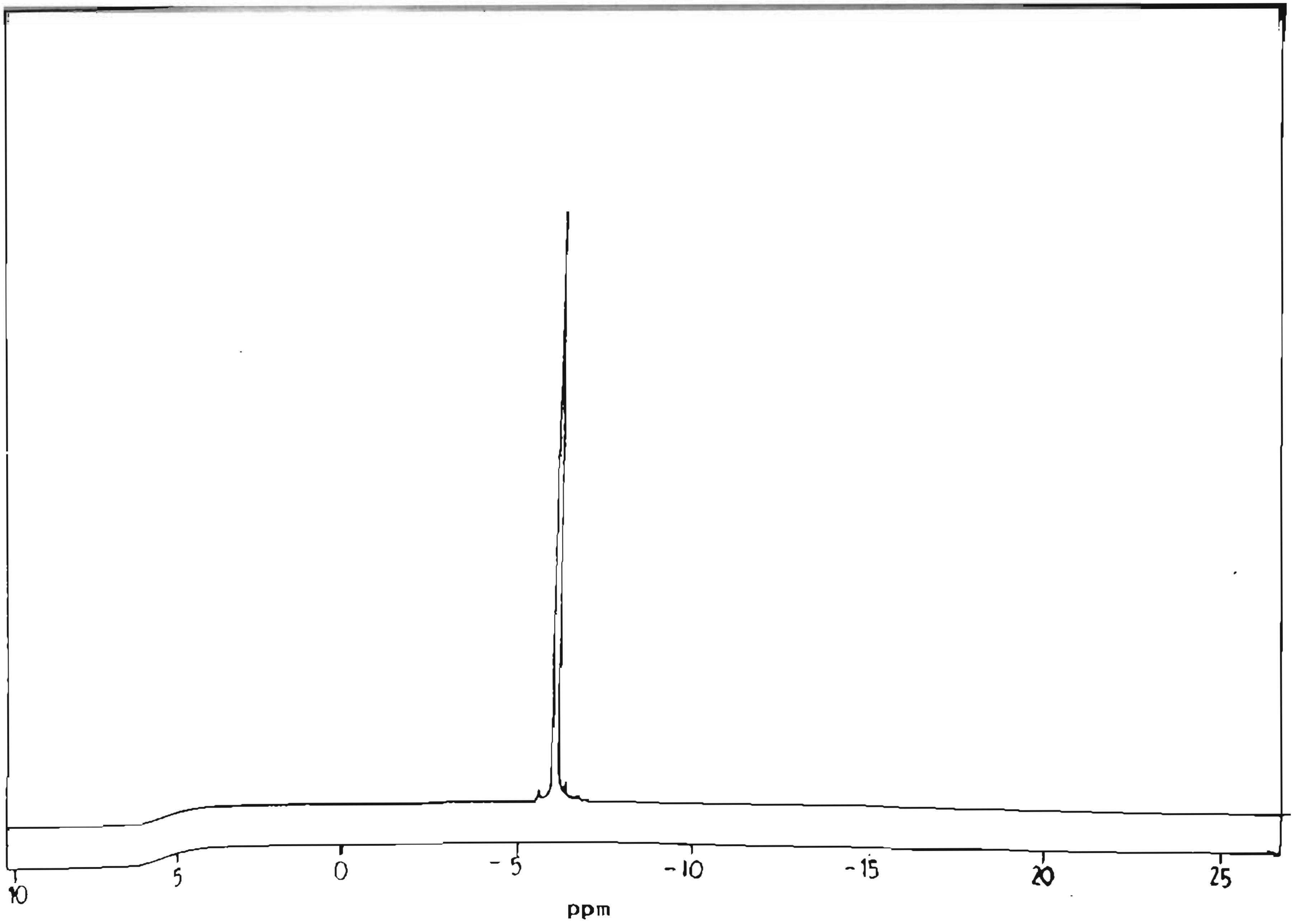
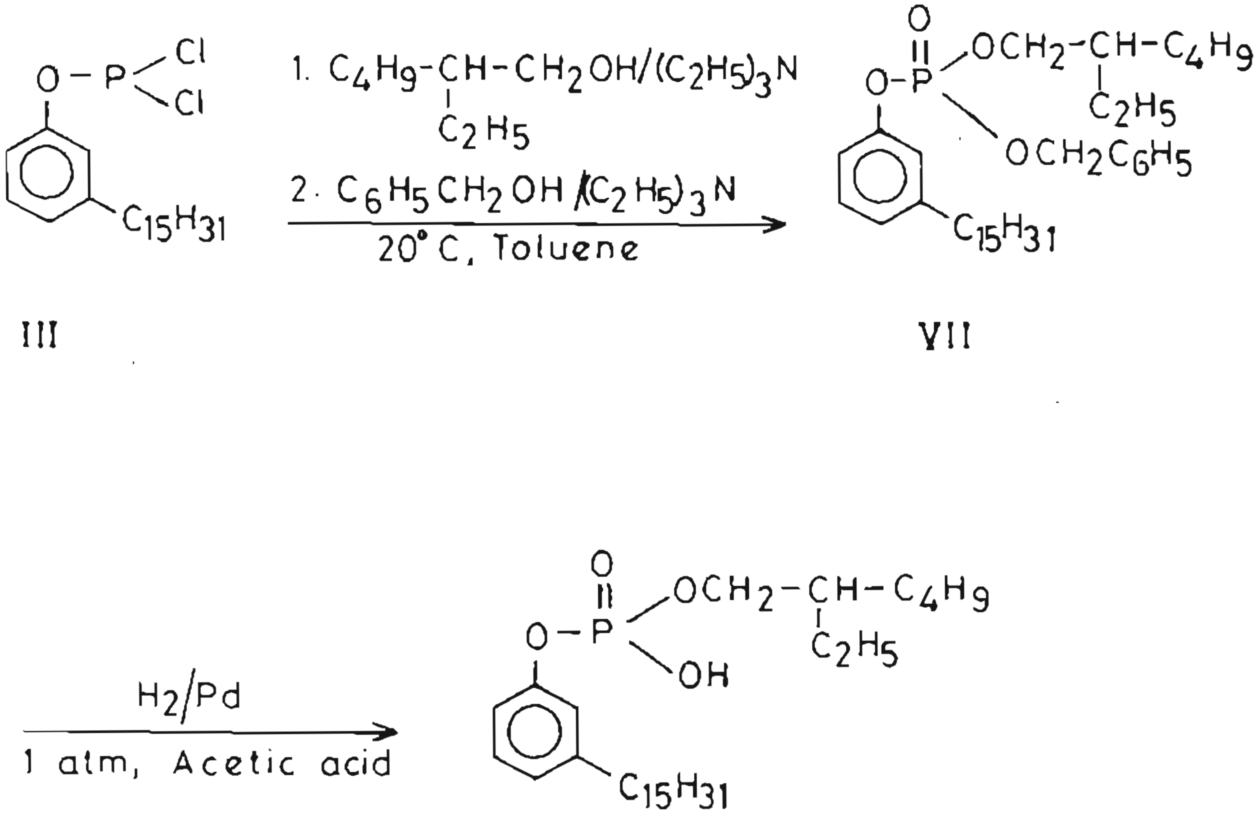


Fig. 2.7: ^{31}P NMR spectrum of Isopropyl-3-pentadecylphenyl phosphoric acid

shown in Scheme 2.3.



III

VII

VIII

Scheme 2.3

The 3-pentadecylphenyl phosphorodichloridate was synthesised freshly following the methods used for IPPA.

Synthesis of 2-ethylhexyl-benzyl-3-pentadecylphenyl phosphate (VII)

To the highly moisture sensitive 3-pentadecylphenyl phosphorodichloridate (III) in anhydrous toluene was added, stoichiometric amounts of 2-ethylhexanol and triethylamine and the reaction allowed to proceed for 1 hour. Further stoichiometric amounts of benzyl alcohol and triethylamine were added and the reaction continued for 24 hrs. The product was purified by elaborate column chromatography. The yield of the compound was 81%. As in the case of IPPA and MPPA, the $-CH_2$ protons of the benzyl group showed a geminal coupling (J = 10 Hz) (Fig. 2.8). A multiplet centered at δ 3.8 corresponded to $-OCH_2$ proton of 2-ethylhexyl group.

Synthesis of EPPA (VIII)

The title compound was prepared by the hydrogenolysis of 2-ethylhexyl - benzyl-3-pentadecylphenyl phosphate (VIII) using 10% palladised charcoal as catalyst in acetic acid. The compound was purified as its barium salt. The IR spectrum (Fig.2.9) of the compound gave a band around 2680 cm^{-1} corresponding to P-OH. The P=O, P-O-C alkyl, and P-O-C aryl bands came at 1230 cm^{-1} 980 cm^{-1} and 1150 cm^{-1} respectively. The ^{1}HNMR (Fig. 2.10) spectrum gave a signal at δ 12.1 corresponding to P-O<u>H</u>. The ^{31}P NMR (Fig. 2.11) of the compound showed a sharp singlet at -6.2 ppm indicating the purity of the compound.

2.2.5 SYNTHESIS OF BUTYL-3-PENTADECYLPHENYL PHOSPHORIC ACID (BPPA)

The methodology for synthesising the above compound was similar to the one adopted for IPPA. The scheme of synthesis is given in Scheme 2.4.

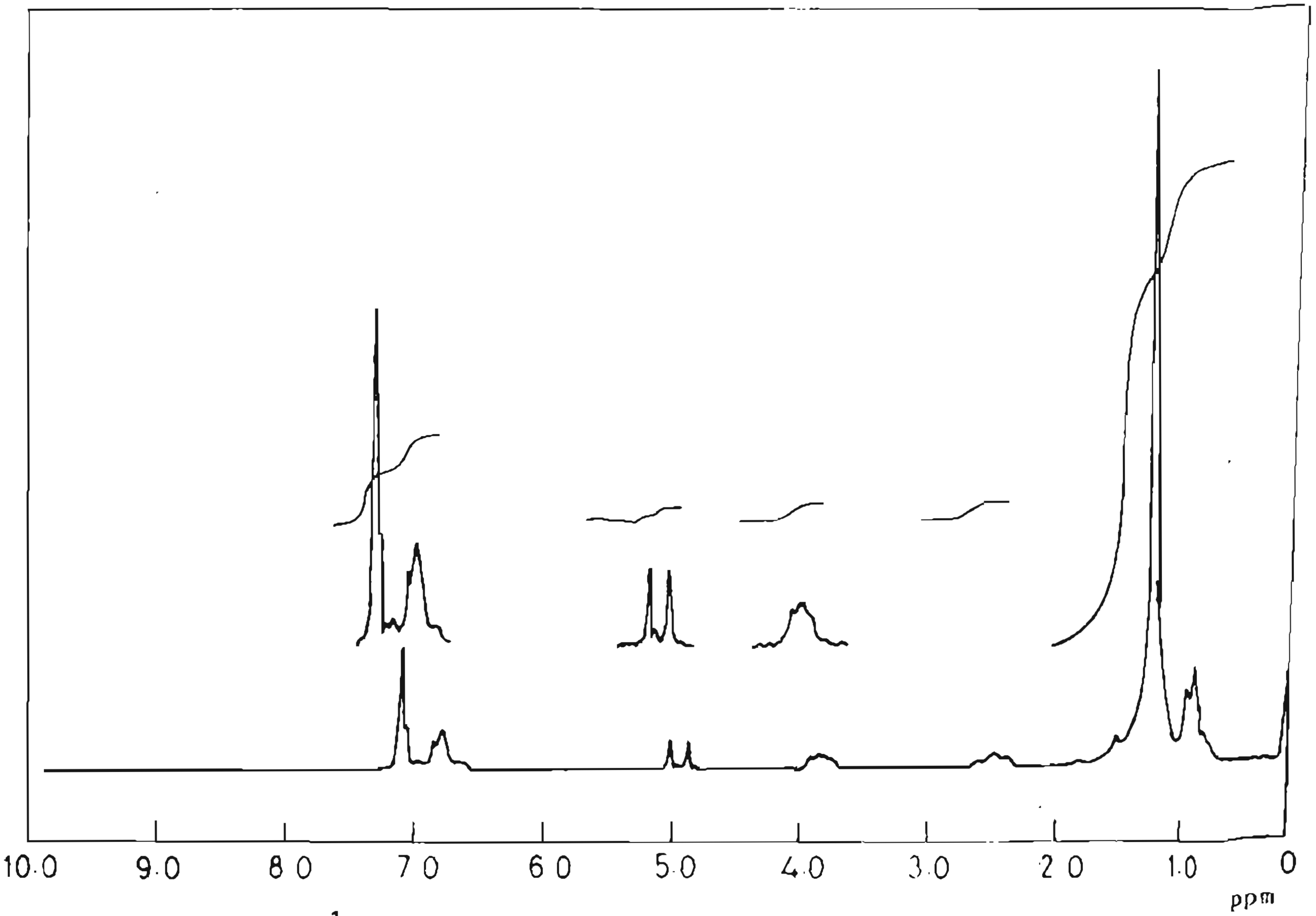


Fig. 2.8: ^{1}H NMR spectrum of benzyl-2- ethylhexyl-3-pentadecylphenyl phosphoric acid

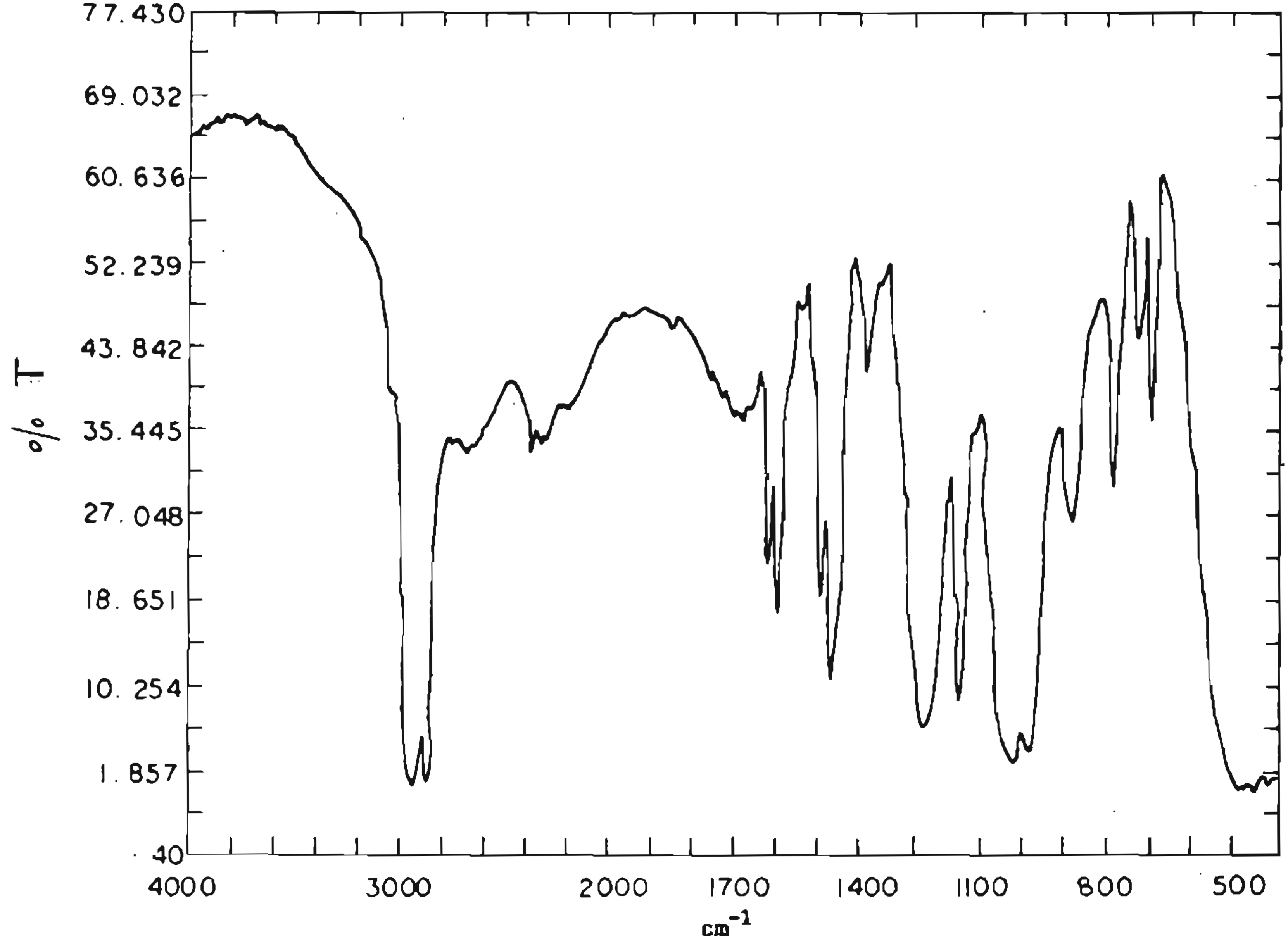


Fig. 2.9: IR spectrum of 2-ethylhexyl-3-pentadecylphenyl phosphoric acid

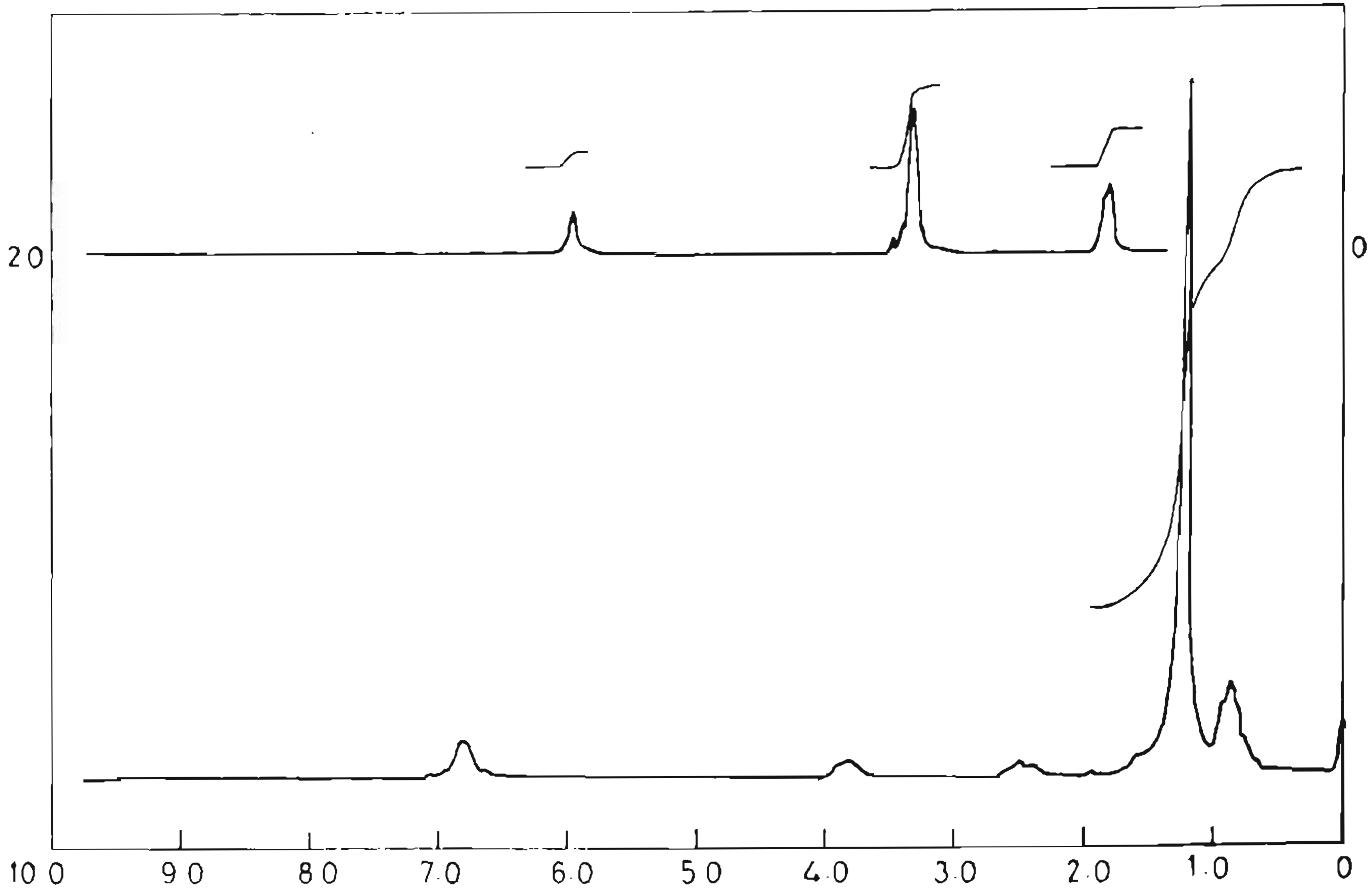


Fig. 2.10: ^{1}H NMR spectrum of 2-ethylhexyl-3-pentadecylphenyl phosphoric acid

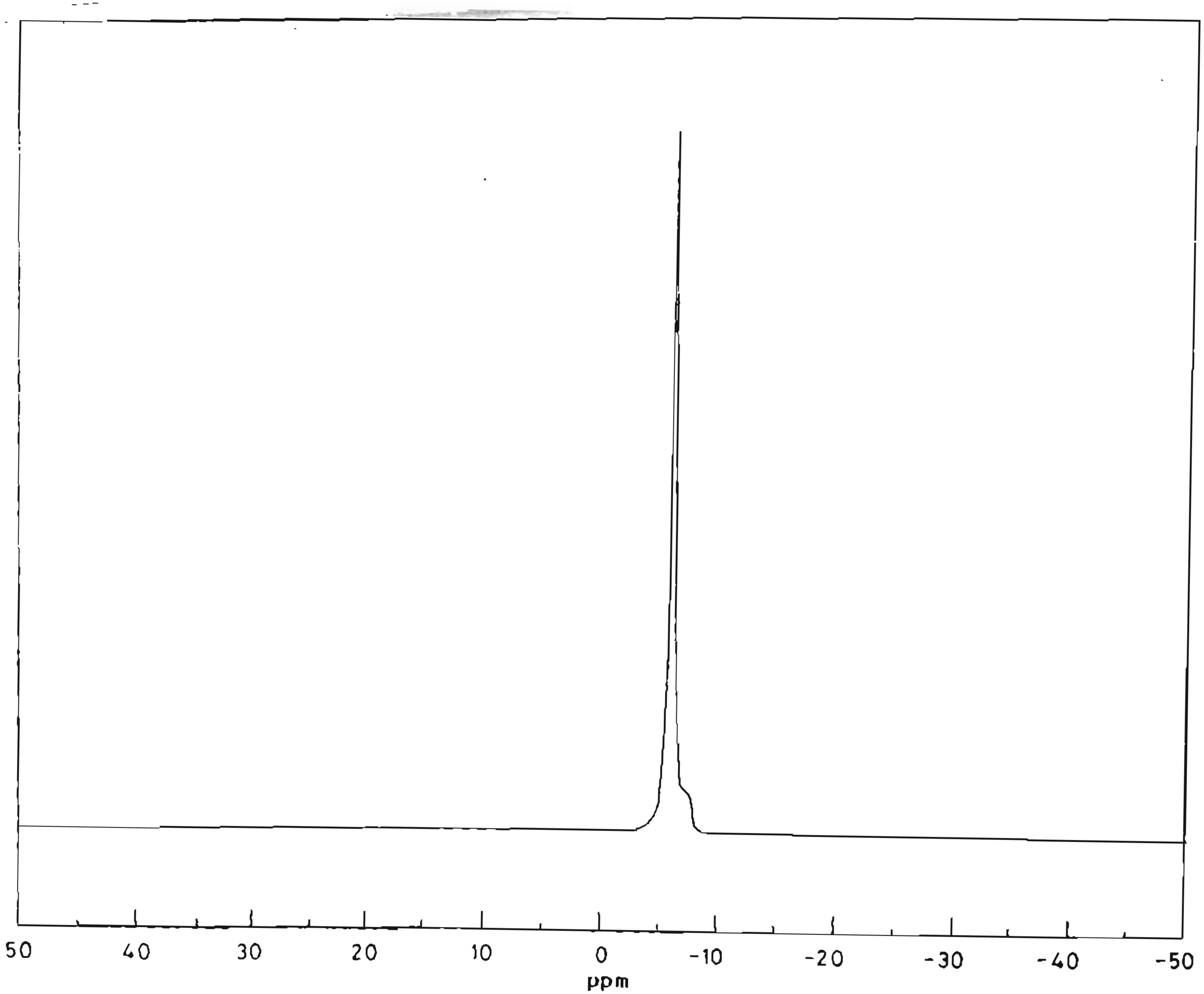
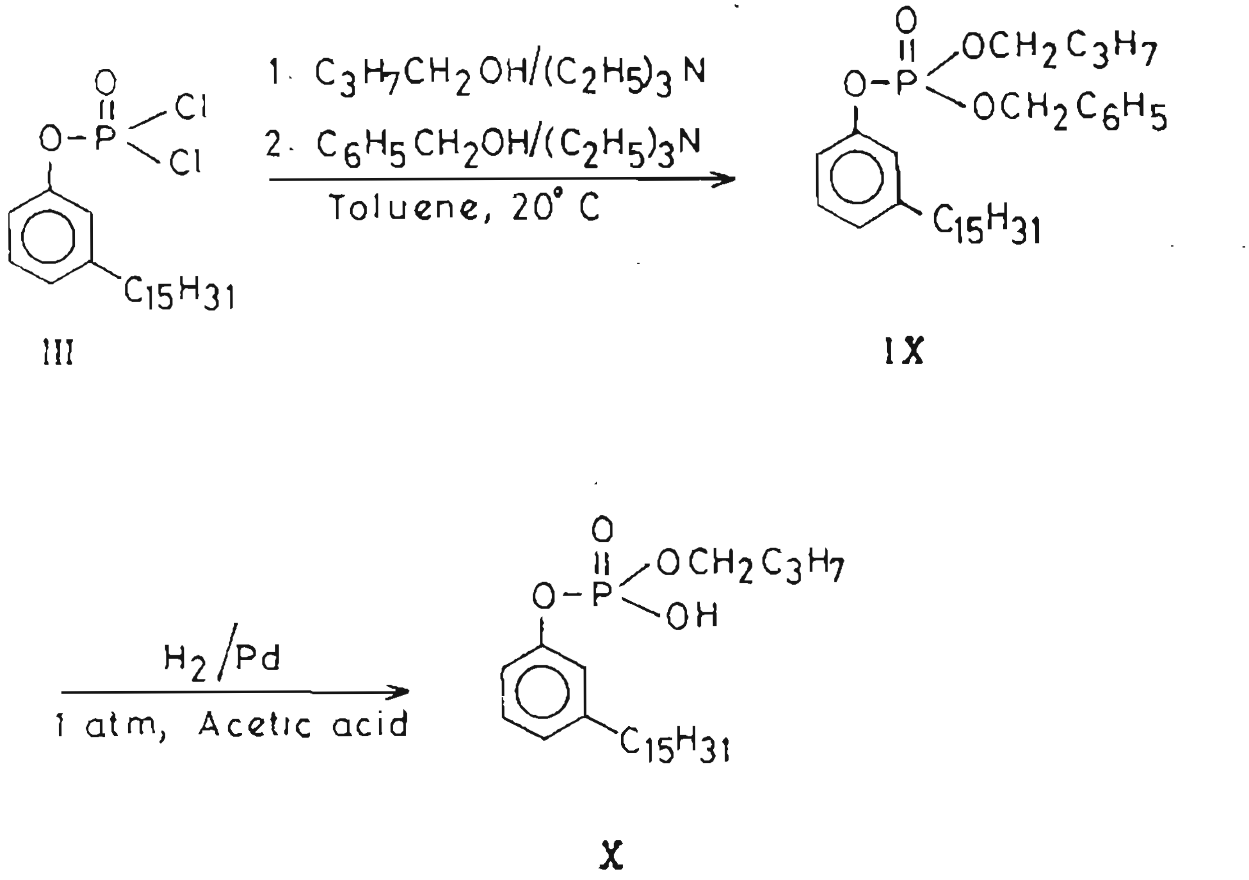


Fig. 2.11: ^{31}P NMR spectrum of 2-ethylhexyl-3-pentadecylphenyl phosphoric acid



Scheme 2.4

The 3-pentadecylphenyl phosphorodichloridate was synthesised as mentioned before (Scheme 2.1).

Synthesis of butyl-benzyl-3-pentadecylphenyl phosphate (IX)

Freshly prepared 3-pentadecylphenyl phosphorodichloridate (III) was taken in anhydrous toluene and a mixture of stoichiometric amounts of butyl alcohol and triethylamine were added and the reaction was allowed to run for 1 hr at 20°C.

Then stoichiometric amounts of benzyl alcohol and triethylamine were added to the rear mixture and the reaction continued for 24 hrs. The crude product was chromatographed over silica gel to obtain the title compound in the pure form. In similarity to EPPA ester, the butyl-benzyl-3-pentadecylphenyl phosphate also showed geminal coupling for $-CH_2$ of the benzyl group (J = 8 Hz) (see Fig. 2.12). The ^1H NMR spectrum did not show any P-O<u>H</u> confirming the compound to be a phosphate ester. The yield of the product was 80%.

Synthesis of BPPA (X)

The butyl-benzyl-3-pentadecyl phosphate was put to hydrogenolysis using palladised charcoal in acetic acid medium. The yield of product was quantitative. The product was purified as its barium salt. The IR spectrum (Fig. 2.13) of the compound showed P-OH stretching vibration (broad and shallow) around 2700 cm^{-1} confirming the complete hydrogenolysis of the benzyl group. The ^1H NMR spectrum (Fig. 2.14) showed a multiplet centered at δ 4.0 for $-OCH_2$ protons of the butyl group. The P-OH proton signal appeared at δ 12.05. The ^{31}P NMR (Fig. 2.15) of the compound showed a signal as a singlet at δ -6.1 indicating its purity. A total of 100 gms of BPPA was synthesised in three batches.

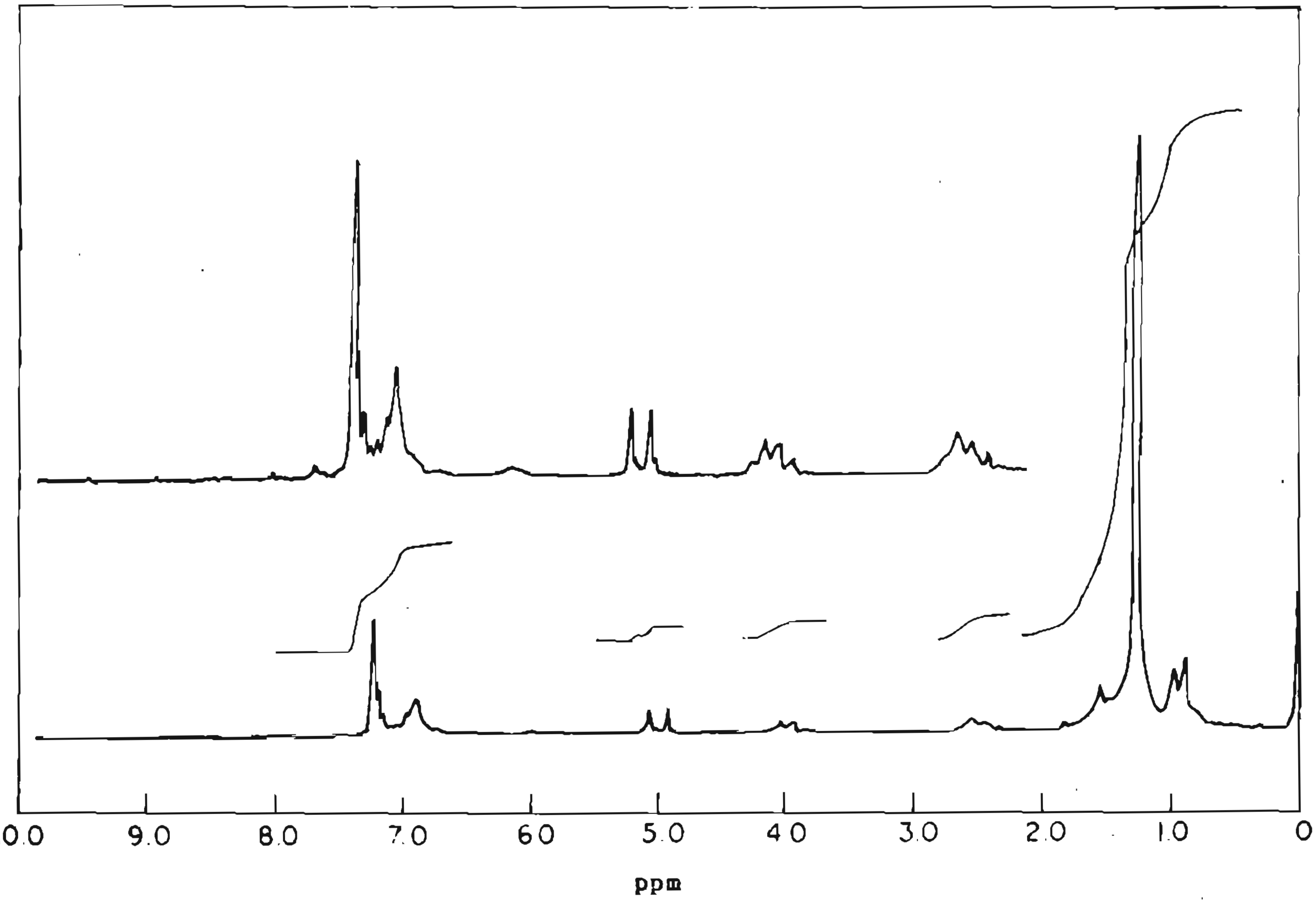


Fig. 2.12: ^{1}H NMR spectrum of butyl-benzyl-3-pentadecylphenyl phosphoric acid

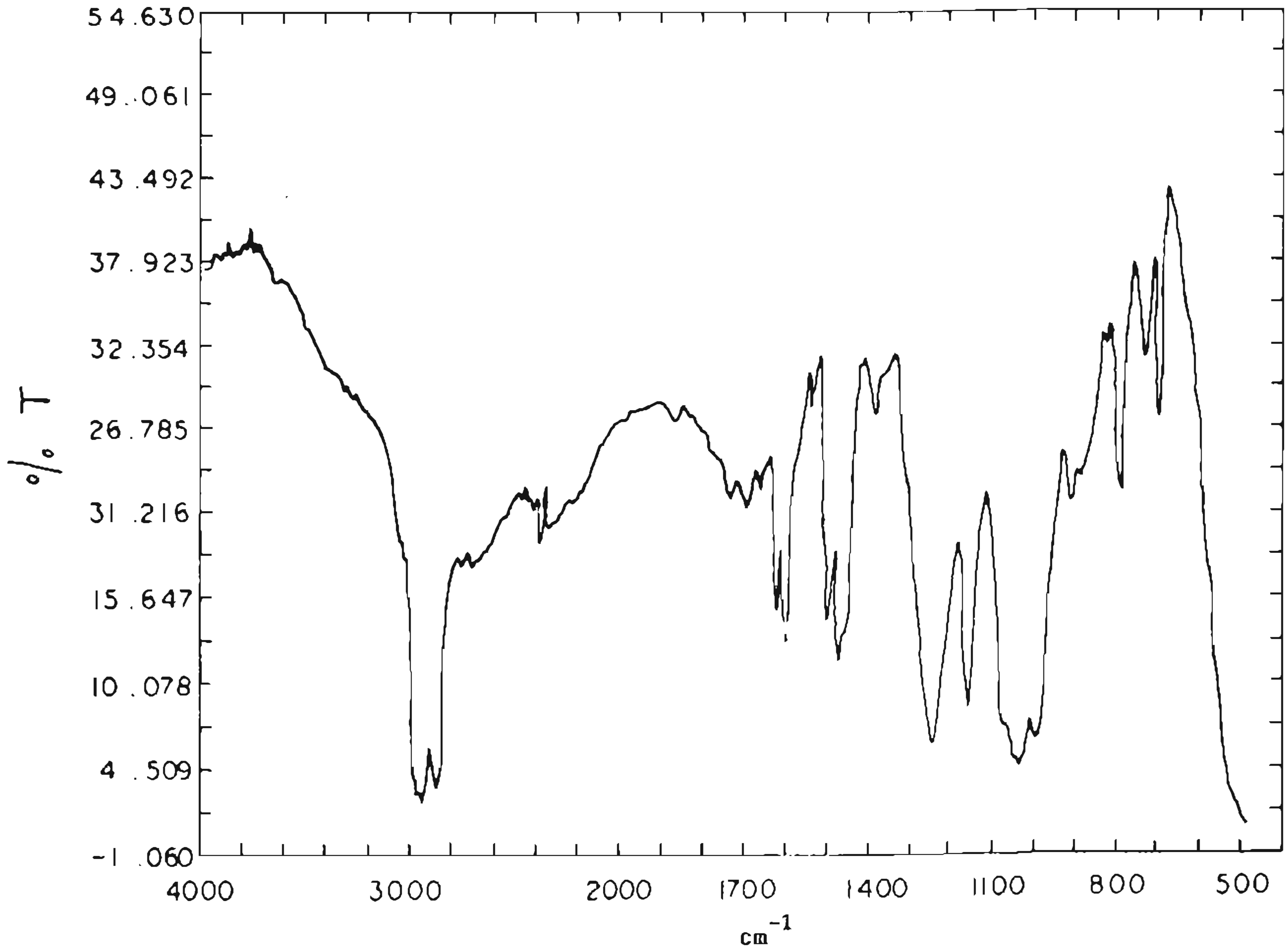


Fig. 2.13: IR spectrum of butyl-3-pentadecylphenyl phosphoric acid

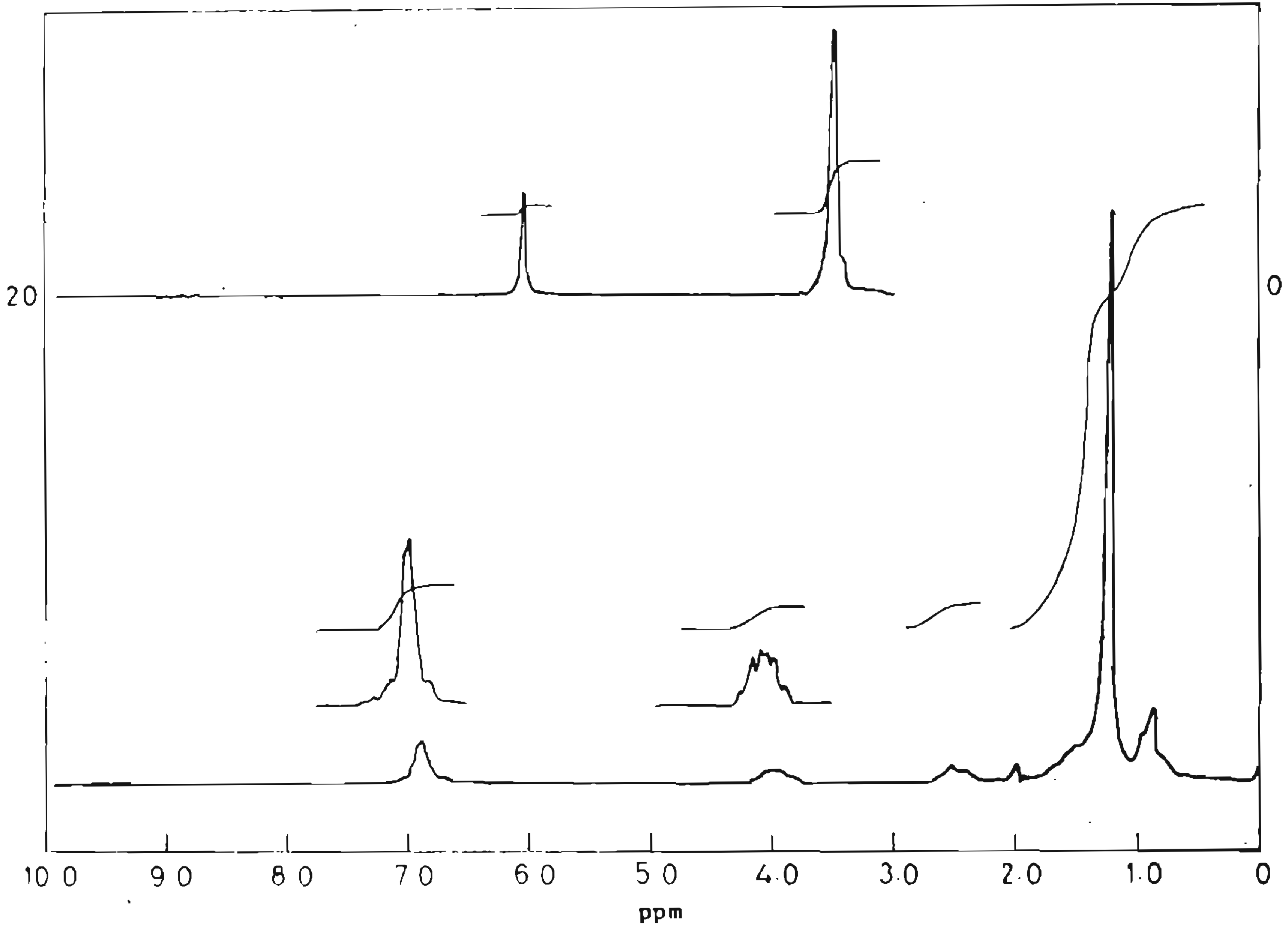


Fig. 2.14: ^{1}H NMR spectrum of butyl-3-pentadecylphenyl phosphoric acid

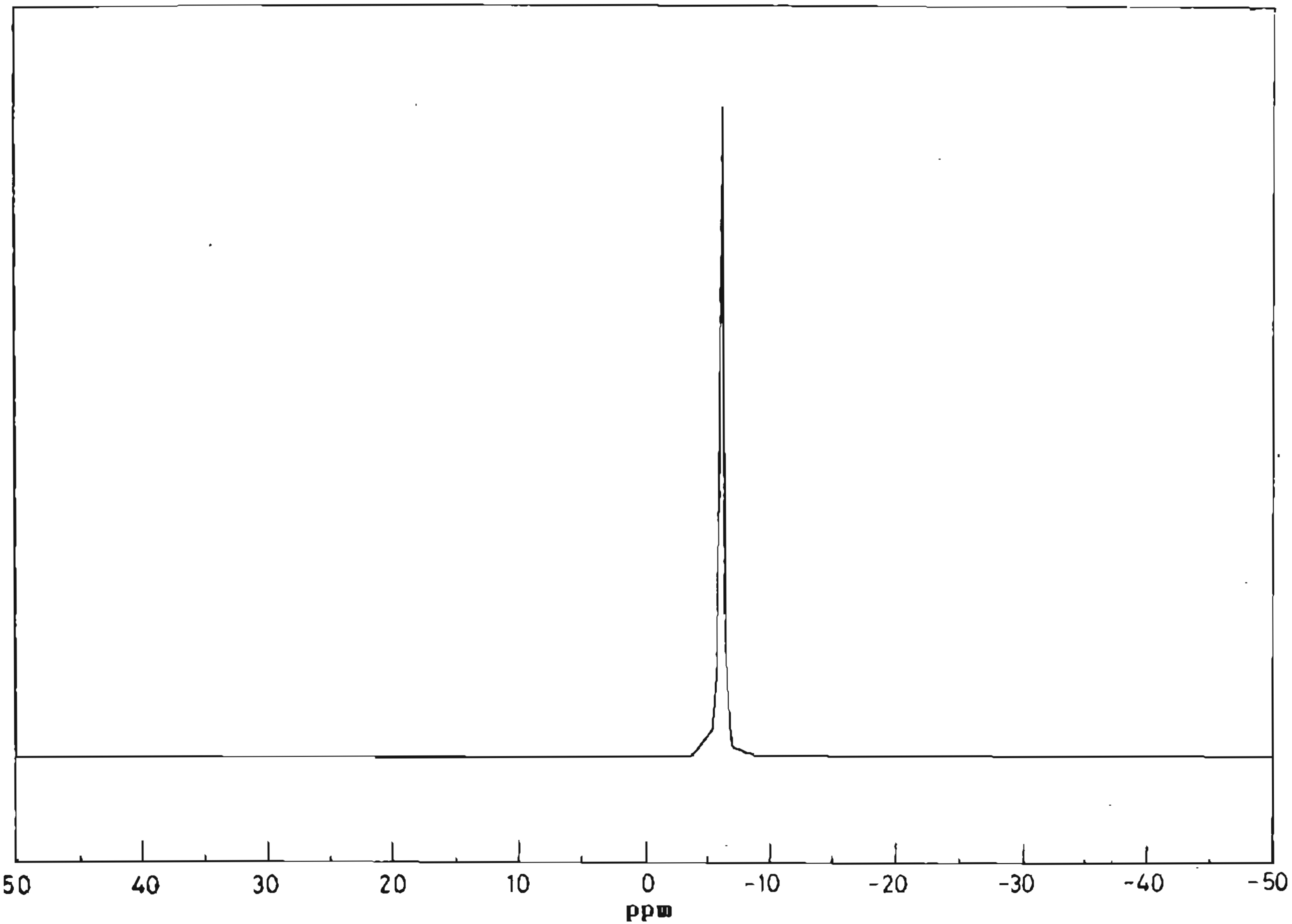


Fig. 2.15: ^{31}P NMR spectrum of butyl-3-pentadecylphenyl phosphoric acid

2.3 EXPERIMENTAL

2.3.1 HYDROGENATION OF CARDANOL TO 3-PENTADECYLPHENOL

Cardanol (100 g, 0.33 mol) in methanol (100 cm^3) was hydrogenated in a parr hydrogenator at 40 psi using platinum oxide (Adam's catalyst) (50 mg) at ambient temperature. The hydrogenation was complete in 2 hrs. The methanolic solution was filtered to remove the catalyst and methanol stripped off. The crude 3-pentadecylphenol was distilled under vacuum (4 mm of Hg). The fraction which distilled at 200^{o} C to 210^{o} C was collected. The white solid obtained was recrystallised from hexane twice to obtain pure 3-pentadecylphenol (m.p. 51^{o}C).

2.3.2 SYNTHESIS OF 3-PENTADECYLPHENYL PHOSPHORIDICHLORIDATE

A mixture of $AlCl_3$ (0.44 g, 0.01 mol) and phosphoryl chloride (60.0 g, 0.39 mol) in dry hexane was heated to reflux and 3-pentadecylphenol (100 g, 0.33 mol) dissolved in dry hexane was added dropwise with stirring over a period of 30 minutes. The hydrogen chloride evolved was absorbed in water. The $AlCl_3$ was filtered off. Hexane and excess phosphoryl chhloride was removed at $35-60^{o}$C initially at 100 mm and finally at 3 mm of Hg. The 3-pentadecylphenyl phosphorodichloridate so obtained was used as such for the subsequent reactions. The product was characterised by ^{1}H NMR.

^1H NMR values (δ):

0.7 to 1.0 (t, 3 H-CH_3), 1.2 (S, 26 H, (CH_2)

2.3 to 2.7 (t, 2H, Ar-CH_2), 6.6 to 7.0 (m, 4H, Ar-H)

2.3.3 SYNTHESIS OF MONO(3-PENTADECYLPHENYL) PHOSPHORIC ACID

The 3-pentadecylphenyl phosphorodichloridate was hydrolysed with NaOH in presence of barium chloride. The insoluble barium salt is filtered and acidified with dil. H_2SO_4. The product was taken in hexane and washed several times with water to remove free acid. The crude product was recrystallised from hexane four to five times. The pure acid gave a m.p. of 76°C. The IR, ^1H NMR, ^{31}P NMR and CH analysis values are given below.

IR (Nujol mull) (cm^{-1})

2924, 2348, 1610, 1590, 1485, 1465, 1243, 1145, 1043, 1020, 954, 780, 731.

^1H NMR, CCl_4 (δ):

0.8 to 1.8 (m, 31 H, $(CH_2)_n$ -CH_3),

6.6 to 7.1 (m, 4 H, Ar-H)

2.3 to 2.6 (m, 2 H, Ar-CH_2)

^{31}P NMR (δ)

- 5.7

C-H analysis (%)

Found C - 65.63   H - 9.64

Requires C - 65.60   H - 9.70

2.3.4 SYNTHESIS OF ISOPROPYL-3-PENTADECYLPHENYL PHOSPHORIC ACID

Synthesis of isopropyl-benzyl-3-pentadecylphenyl phosphate

A mixture of isopropanol (14.1 g, 0.24 mol) and triethylamine (24 g, 0.24 mol) in dry toluene were added dropwise to a stirring solution of 3-pentadecylphenyl phosphorodichloridate (100 g, 0.24 mol) in dry toluene at 20°C followed by the addition of a mixture of benzyl alcohol (25.5 g, 0.24 mol) and triethylamine (24.0 g, 0.24 mol). The mixture was stirred for 24 hrs. The triethylamine hydrochloride was removed by washing with water three to four times. The organic layer was dried with anhydrous sodium sulphate and solvent removed. The benzyl ester was purified by column chromatography. The ratio of benzyl ester to activated silica gel (100-200 mesh) used was 1:15. The eluent used was hexane : methylene chloride 1:1. The yield of the benzyl ester was 75%. The ^{1}H NMR and C-H analysis are given below.

^1H NMR values (δ):

1.0 to 1.7 (t, 3 H, $-CH_3$), 2.3 to 2.7 (t, 2 H, $Ar-CH_2$)

4.4 to 4.8 (m, 1 H, CH of $C\underline{H}\ (CH_3)_2$

4.9 to 5.0 (d, 2 H, $Ar-C\underline{H_2}$ of benzyl group)

6.7 to 7.5 (m, 9 H, $Ar-\underline{H}$)

C-H analysis (%)

Found c - 71.98 H - 9.26

Requires C - 72.06 H - 9.56

Synthesis of isopropyl-3-pentadecylphenyl phosphoric acid

A mixture of the benzyl ester (100 g, 0.19 mol) and 10% palladium on activated charcoal (7.0 g) in acetic acid (100 cm^3) was hydrogenated at ambient temperature and atmospheric pressure for 1 hr. The catalyst was filtered off. The product was taken in hexane, then washed with waater several times to remove acetic acid. Hexane was removed to obtain isopropyl-3-pentadecylphenyl phosphoric acid. The yield of hydrogenation was 100%. The compound was characterised by IR, ^1H NMR, ^{31}P NMR and C-H analysis.

IR (neat) (cm^{-1})

2940, 2840, 2700, 1640, 1600, 1500, 1480, 1390, 1260, 1180, 1000, 900, 800, 700.

^{1}H NMR (TMS internal standard) CCl_4 solvent (δ):

0.9 to 1.5 (m, 35 H, $C_{15}H_{\underline{29}}$ and $C(C\underline{H_3})_2$ of isopropyl/gp)

[illegible] (t, 2 H, Ar-C$\underline{H}_2$)   4.4 (m, 1 H, C-$\underline{H}$) .

6.8 (m, 4 H, Ar-$\underline{H}$),   11.5 (S, 1 H, P-O$\underline{H}$)

^{31}P NMR ($CDCl_3$) (δ):

- 6.0

C-H analysis (%)

Found C - 67.11 H - 9.74

Requires C - 67.57 H - 10.16

2.3.5 SYNTHESIS OF 2-ETHYLHEXYL-3-PENTADECYLPHENYL PHOSPHORIC ACID

Synthesis of 2-ethylhexyl-benzyl-3-pentadecylphenyl phosphate

A mixture of dry 2-ethylhexanol (30 g , 0.24 mol) and triethylamine (24 g, 0.24 mol) in dry toluene was added dropwise to a stirring solution of 3-pentadecylphenyl phosphorodichloridate (100 g, 0.24 mol) in dry toluene at 20°C followed by the addition of a mixture of benzyl alcohol (25.5 g, 0.24 mol) and triethylamine (24.0 g, 0.24 mol). The mixture was stirred for 24 hrs. The organic layer was washed with water to remove hydrochloride, dried and solvent stripped off. The benzyl ester was purified by column chromatography (silica gel : compound) (15:1). The eluent used was hexane : methylene chloride (1:1). The yield of the benzyl ester–81%. The compound was characterised by ^{1}H NMR and C-H analysis.

^{1}H NMR, CCl_4, (δ):

0.7 to 1.8 (m, 44H, Alkyl-H) 2.3 to 2.7 (t, 2 H, Ar-$\underline{CH_2}$),

3.6 to 4.0 (m, 2 H, O-$\underline{CH_2}$), 4.8 to 5.1 (d, 2 H, Ar-$\underline{CH_2}$-O)

6.6 to 7.0 (m, 4 H, aryl protons of 3-pentadecylphenyl group),

7.0 to 7.2 (m, 5 H, aryl protons of benzyl group).

C-H analysis

Found C - 73.96 H - 9.63

Requires C - 74.21 H - 9.93

Synthesis of 2-ethyl hexyl-3-pentadecylphenyl phosphoric acid

A mixture of the benzyl ester (100 g, 0.17 mol) and 10% of palladium on activated charcoal (7.8 g) in acetic acid (100 cm^3) was hydrogenated at ambient temperature and atmospheric pressure for 1 hr. The catalyst was filtered, product taken in hexane and washed with water to remove acetic acid and solvent stripped off. The yield of hydrogenation was 100%. The product was characterised by IR, ^{1}H NMR and ^{31}P NMR and C-H analysis.

IR (neat), cm^{-1}

2940, 2680, 2880, 1620, 1590, 1500, 1460, 1390, 1230, 1150, 1020, 980, 880, 780, 720, 680

^{1}H NMR, CCl_4 (δ):

0.9 to 1.5 (m, 44 H, Alkyl-$\underline{H}$)

2.5 (t, 2 H, Ar-$CH_{\underline{2}}$), 3.8 (t, 2 H, -$OCH_{\underline{2}}$)

6.8 (m, 4 H, Ar-$\underline{H}$), 12.1 (S, 1 H, P-O$\underline{H}$)

^{31}P NMR δ

- 6.2

C-H analysis (%):

Found C - 69.93 H - 10.29

Requires c - 70.12 H - 10.76

2.3.6 SYNTHESIS OF BUTYL-3-PENTADECYLPHENYL PHOSPHORIC ACID

Synthesis of butyl-benzyl-3-pentadecylphenyl phosphate

A mixture of butanol (17.61 g, 0.24 mol) and triethylamine (24.0 g, 0.24 mol) in dry toluene was added drop-wise to a stirring solution of 3-pentadecylphenyl phosphorodichloridate (100 g, 0.24 mol) in dry toluene at 20^{o}C followed by the addition of a mixture of benzyl alcohol (25.5 g, 0.24 mol) and triethylamine (24.0 g, 0.24 mol). The mixture was stirred for 24 hrs. The triethylamine hydrochloride was removed by washing with water three to four times. The solvent stripped off and ester purified by column chromatography (Hexane : Methylene chloride 1:1). The yield of the benzyl ester was 74%. The IR, ^{1}H NMR values, and C-H analysis are given below.

^{1}H NMR (CCl_4), (δ):

0.90 to 1.8 (m, 36 H, Alkyl-$\underline{H}$)

2.40 to 2.80 (t, Ar-$C\underline{H_2}$) 3.9 to 4.2 (m, 2 H -$OC\underline{H_2}$),

4.9 to 5.1 (d, 2 H, $C\underline{H_2}$ of benzyl group)

6.8 to 7.1 (m, 4 H, Ar-$\underline{H}$), 7.2 to 7.3 (m, 5 H, Ar-$\underline{H}$ of benzyl group)

C-H analysis (%)

Found C - 72.01 H - 9.21

Requires C - 72.42 H - 9.69

Synthesis of n-butyl-3-pentadecylphenyl phosphoric acid

A mixture of the benzyl ester (100 g, 0.19 mol) and 10% palladium on activated charcoal (7.8 g) in acetic acid (100 cm^3) was hydrogenated at ambient temperature and atmospheric pressure for 1 hr. The catalyst was filtered off and the liquid was taken in hexane, washed with water, dried and hexane stripped off to obtain n-butyl-3-pentadecylphenyl phosphoric ac [illegible] 100%). The values of IR, ^{1}H NMR, and C-H analysis

IR (neat), cm^{-1}

2940, 2860, 2700, 1620, 1590, 1500,

990, 910, 780, 720, 690.

^{1}H NMR (CCl$_4$) (δ)

0.8 to 2.0(m, 36 H, Alkyl-$\underline{H}$)

2.3 to 2.7 (t, 2 H, ArCH$_{\underline{2}}$), 3.8 to 4.2 (m, 2 H, -OCH$_{\underline{2}}$),

6.7 to 7.1 (m, 4 H, Ar-$\underline{H}$), 12.05 (S, 1 H, P-O$\underline{H}$)

^{31}P NMR (δ) ppm:

- 6.1

C-H analysis (%)

Found C - 67.63 H - 9.89

Requires C - 68.15 H - 10.30

APPARATUS

IR spectra were recorded on a Perkin Elmer model 299 B IR spectrophotometer. The spectra were taken as KBr pellets or as neat film. The proton nuclear magnetic resonance spectra were recorded in a Hitachi 24 B model 60 MHz NMR spectrometer. The spectra were recorded in CCl$_4$ using TMS as internal standard. The chemical shifts were reported in δ(ppm). The phosphorus ^{31}P spectra were recorded on a Jeol FX-90 Q FT spectrometer using phosphoric acid as standard. The ^{31}P spectra were taken in CDCl$_3$.

REAGENTS

Methanol was distilled before use.

Phosphorus oxychloride was distilled before use.

Platinum oxide was used as such for hydrogenation.

Hexane was dried with anhydrous calcium chloride and then passed through activated silica gel (100-200 mesh) followed by distillation.

Isopropanol, n-butanol and 2-ethylhexanol were first dried with anhydrous calcium oxide and then with sodium followed by distillation.

Triethylamine was dried with KOH and then distilled.

Toluene was refluxed with sodium for 2 to 3 hrs and then distilled.

Methylene chloride was dried over anhydrous calcium chloride and then distilled.

Acetic acid was distilled and used.

Silica gel used was of 100-200 mesh size and it was activated by placing at 110°C for 15 hrs.

Palladised charcoal was used as such for hydrogenation.

All the above reagents were of AR grade.

CHAPTER III

LIQUID-LIQUID EXTRACTION STUDIES OF RARE EARTHS WITH MONO(3-PENTADECYLPHENYL) PHOSPHORIC ACID

3.1 INTRODUCTION

Acidic organophosphorus compounds have emerged as powerful extractants in the last three decades. Of these materials, the bulk of the work reports only on DEHPA (Di-2-ethylhexyl phosphoric acid[34-39]. Inspite of the potential of monoalkyl phosphoric acids as extractants, relatively less work has been reported on this class of extractants. Peppard and coworkers[42] used mono-2-ethylhexyl phosphoric acid (H_2 MEHP) for the extraction of lanthanides and actinides from urine samples. The same acid was used by Peppard et al[165] for the extraction of some lanthanides and actinides along with some other trivalent elements from aqueous perchloric and hydrochloric acid solutions in a toluene solution of H_2MEHP. Mixture of H_2MEHP and DEHPA has also been used for the extraction of some lanthanides[166] and titanium[167]. Synergistic effects of the addition of TBP (Tributyl phosphate) and Tri-n-octylphosphine oxide (TOPO) on the extraction of lanthanides and actinides by H_2 MEHP were investigated by Mason et al[168]. Some other monoalkyl phosphoric acids besides H_2MEHP have been used as extractants viz. monodecyl[169,170] mono-n-butyl, monoisoamyl phosphoric acids[171]. The high extraction of some lanthanides by these monoalkyl phosphoric acids has prompted us to systematically investigate the behaviour of mono(-3-pentadecylphenyl) phosphoric acid (MPPA) on the extraction of the rare earths.

This chapter deals with the extraction studies of rare earths using a newly synthesised reagent, Mono(3-pentadecylphenyl) phosphoric acid (MPPA) starting from 3-pentadecylphenol which is obtained by the hydrogenation of cardanol. The nature of extracted species was evaluated and the separation factors among the various rare earths were calculated.

3.2 RESULTS

3.2.1 Effect of mono(3-pentadecylphenyl phosphoric acid (MPPA) concentration

The dependence of the extraction of lanthanum(III), europium(III) and lutetium(III) from hydrochloric acid solution was investigated as a function of MPPA concentration. The concentration of MPPA used was 0.16 M to 0.3 M for lanthanum(III), 0.06 M to 0.15 M for europium(III) and 0.01 to 0.05 M for lutetium(III). The results obtained are shown in Fig. 3.1 from which it is clear that the extraction increases with increase in the MPPA concentration. The values of percent extraction range from 21.92 to 71.65 in the case of lanthanum(III), from 15.38 to 83.90 in the case of europium and from 21.06 to 87.71 in the case of lutetium(III). The plot of log D versus log [MPPA] is linear (Fig.3..2) with a slope nearly equal to three for all the three elements.

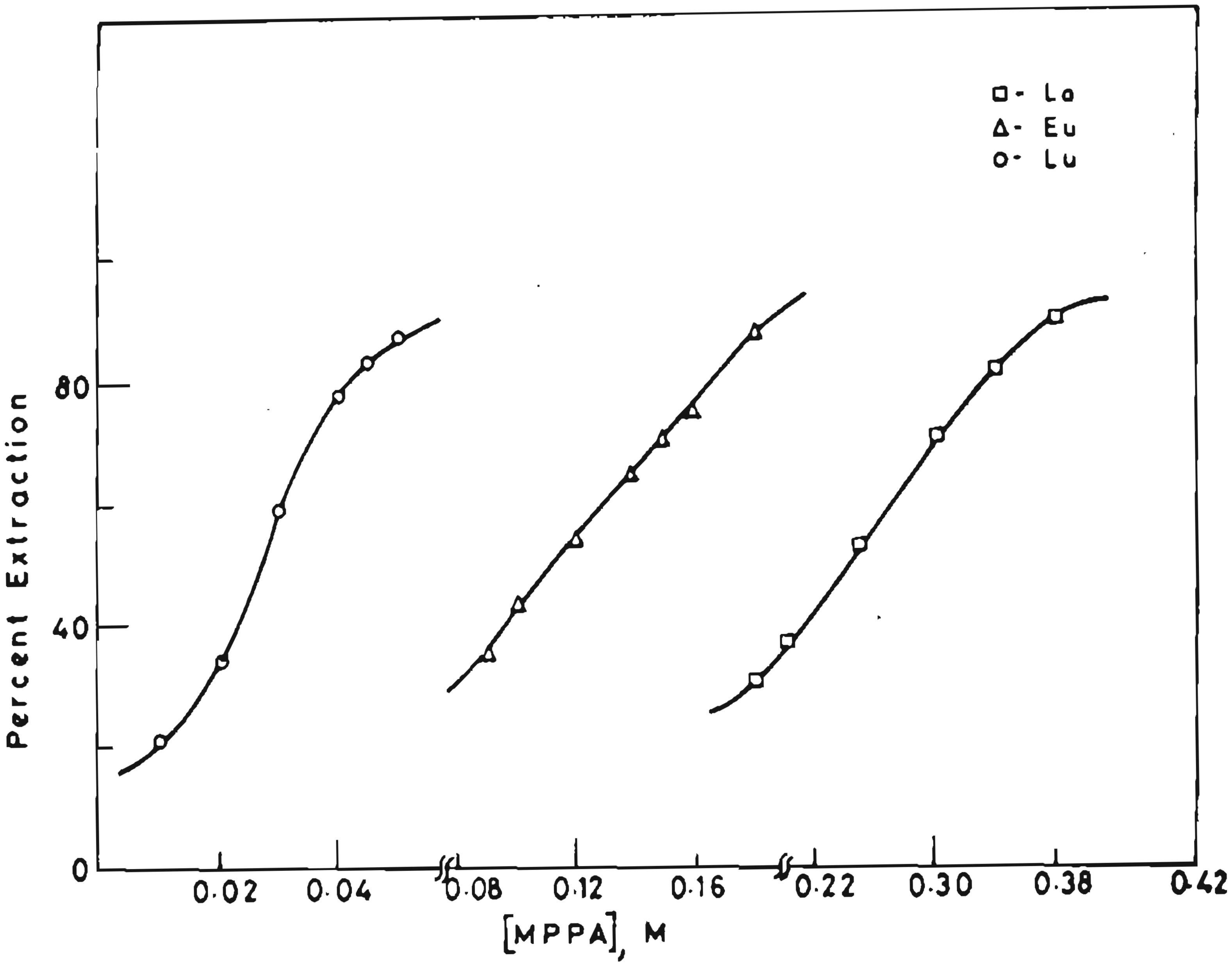


Fig. 3.1: Plot of percent extraction vs [MPPA] during the extraction of Lanthanum(III), Europium and Lutotium with 0.1 M HCl into MIBK

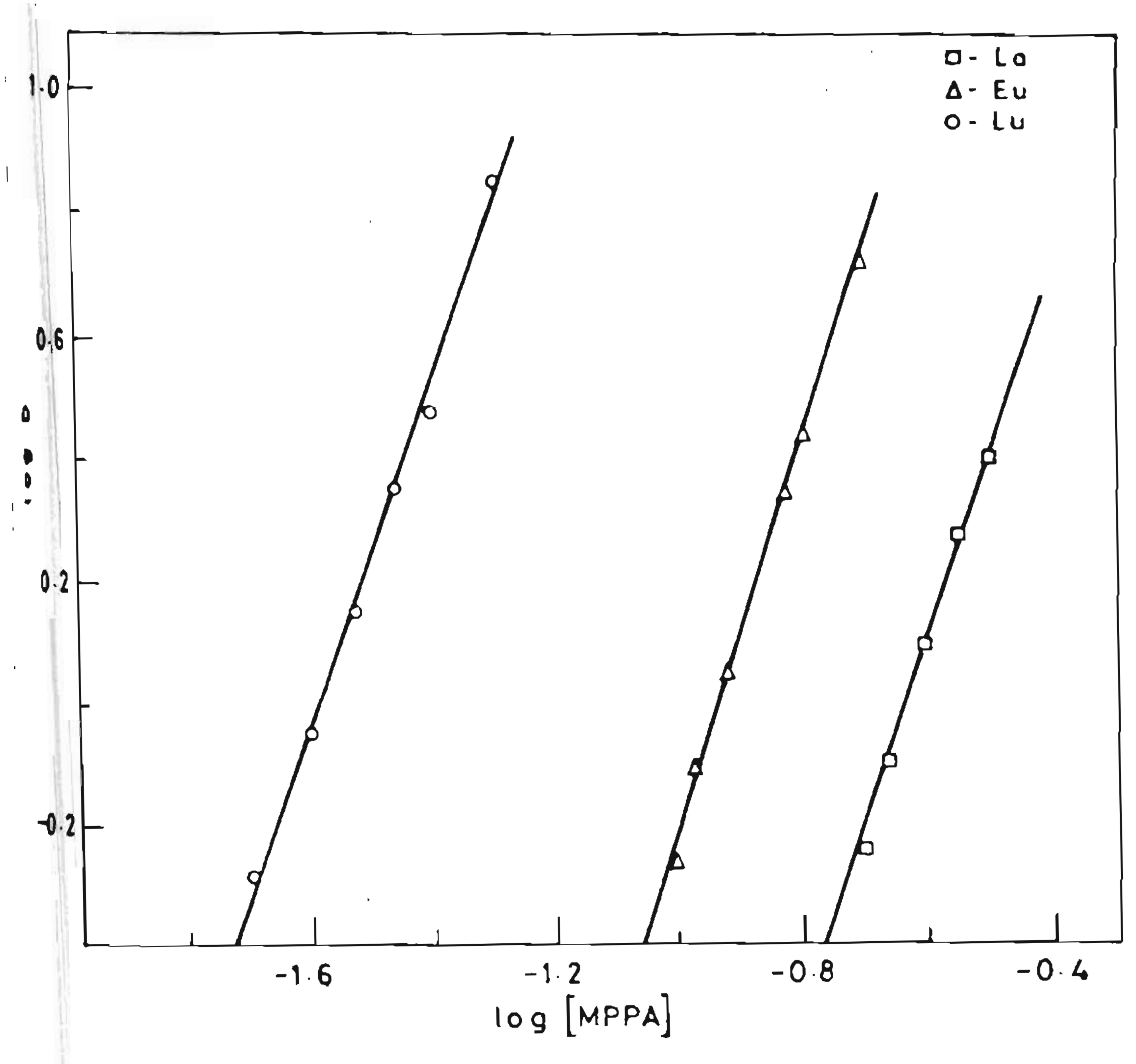


Fig. 3.2: Plot of log D vs log [MPPA] during the extraction of lanthanum, europium and lutetium with 0.1 M HCl into MIBK

3.2.2 Effect of acid concentration

Effect of hydrochloric acid

The effect of varying H^+ concentration over the range 0.05 M to 1 M of HCl was studied for lanthanum(III), europium(III) and lutetium(III) at a constant concentration of chloride. The concentration of MPPA used in these studies was 0.05 M for all the three elements. The extraction decreases drastically (Fig.3.3) with increase in H^+ concentration. A constant concentration of chloride was maintained using lithium chloride. The percent extraction values obtained were found to range from 8.62 to 1.00 for lanthanum(III), from 50.01 to 0.8 for europium(III) and from 96.49 to 3.50 for lutetium(III). The plot of log D vs log H^+ from hydrochloric acid medium for lutetium is shown in Fig. 3.4. The plot is linear with a slope of -3.

Effect of sulphuric acid

The extraction behaviour of lanthanum(III), europium(III) and lutetium(III) as a function of sulphuric acid concentration at a constant concentration of sulphate over the range 0.05 M to 1 M was studied. A constant concentration of sulphate was maintained using sodium sulphate. The concentration of MPPA in MIBK used in these studies was 0.05 M. The extraction decreases drastically with increase in H^+ concentration (see Fig.3.5). The percent extraction values obtained were found to range from 10.35 to 1.009 for lanthanum(III), from 26.16 to 0.2

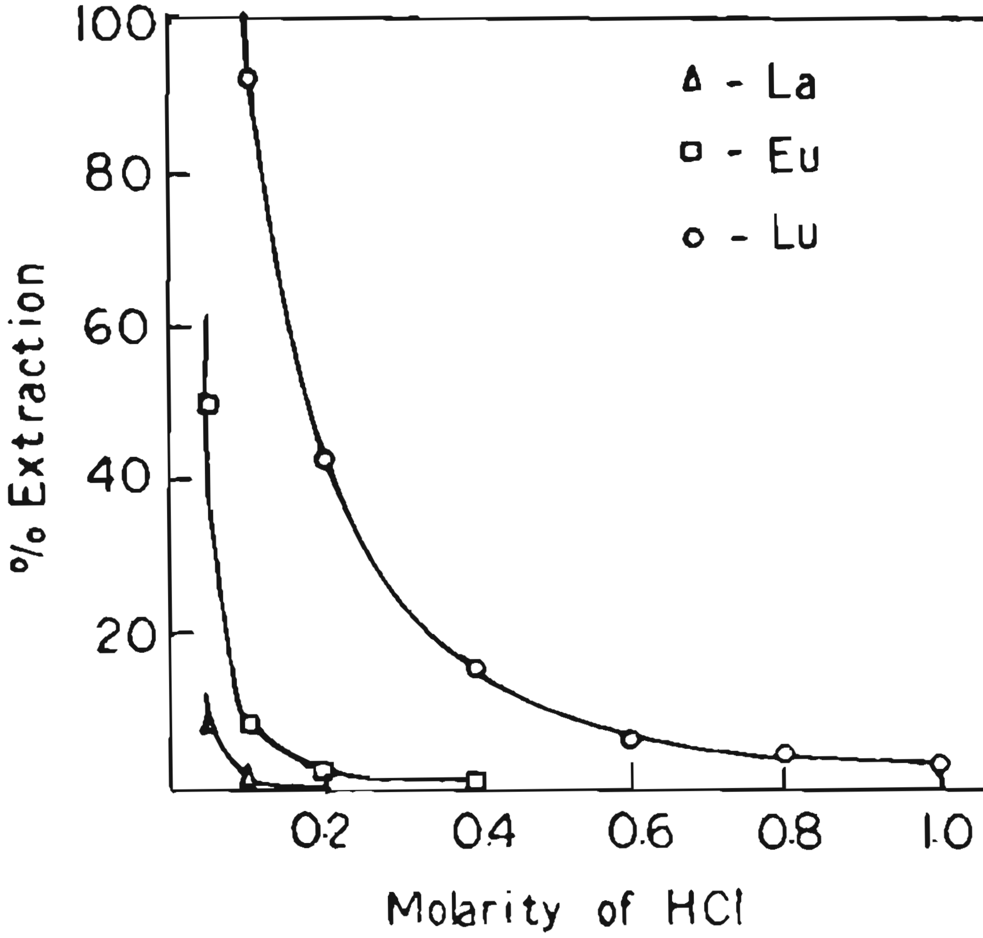


Fig. 3.3: Plot of percent extraction vs [HCl] during the extraction of lanthanum, europium and lutetium with 0.05 M MPPA in MIBK

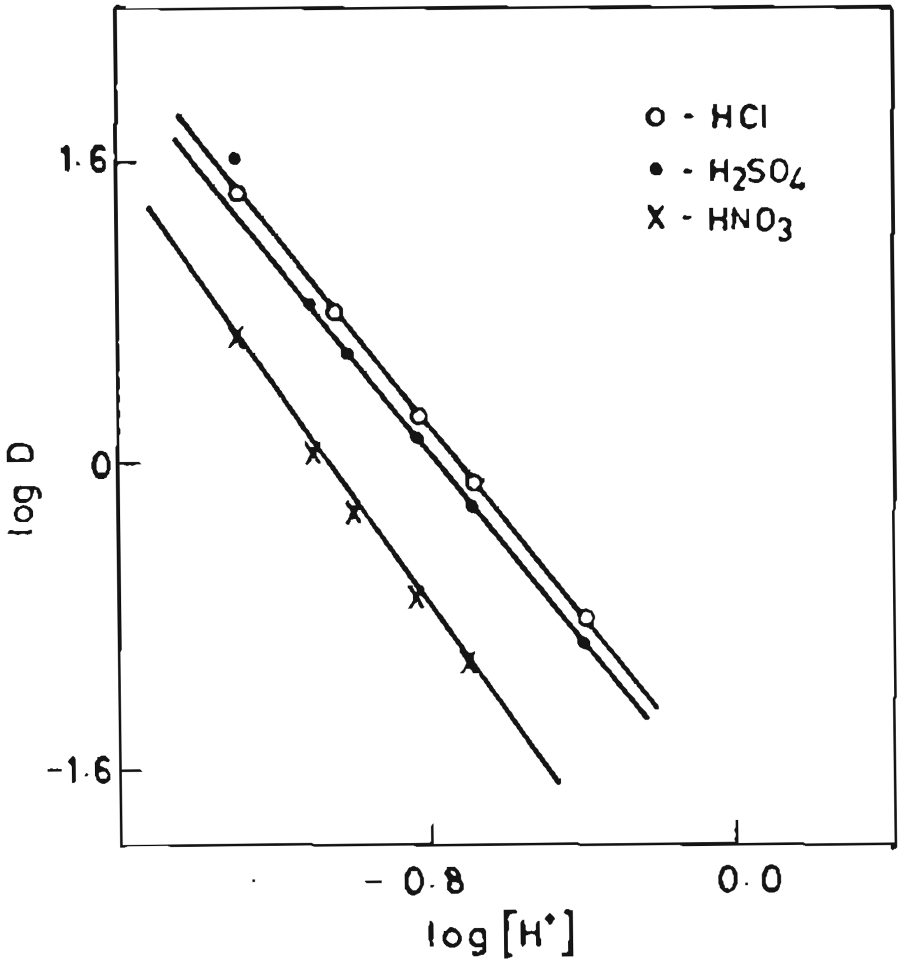


Fig.. 3.4 : Plot of log D vs log $[H^+]$ during the extraction of lutetium from HCl, H_2SO_4 and HNO_3 media with 0.05 M MPPA in MIBK

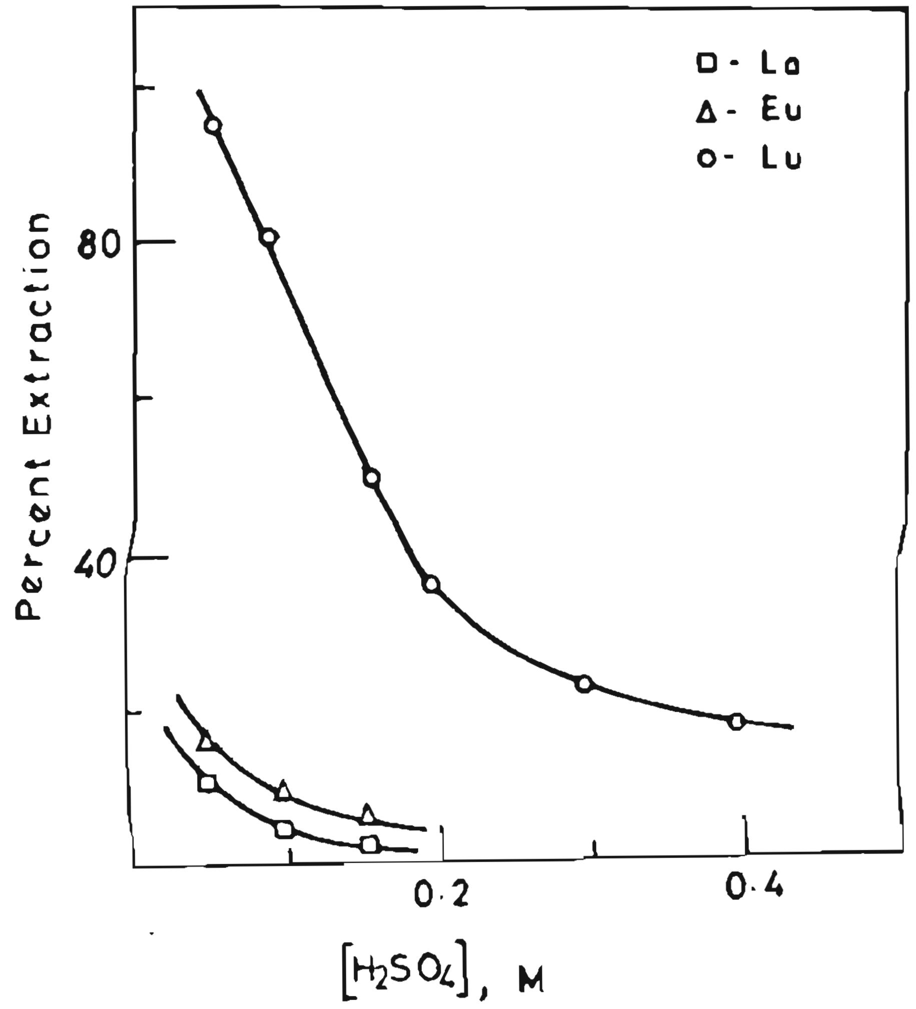


Fig. 3.5: Plot of percent extraction vs $[H_2SO_4]$ during the extraction of lanthanum, europium and lutetium with 0.05 M MPPA in MIBK

for europium(III) and from 95.10 to 17.6 for lutetium(III). The plot of log D vs log $[H^+]$ from sulphuric acid medium for lutetium is shown in Fig. 3.4. The plot is linear with a slope equal to -3.

Effect of nitric acid

The effect of H^+ concentration over the range 0.05 to 0.5 M at a constant concentration of nitrate for lanthanum(III), europium(III) and lutetium(III) was investigated. In these studies constant concentration of nitrate was maintained using sodium nitrate. The concentration of MPPA used was 0.05 M for all the three elements. The extraction decreases drastically (Fig. 3.6) with increase in H^+ concentration. The values of percentage extraction range from 3.53 to 0.1 in the case of lanthanum(III), from 20.12 to 0.19 in the case of europium(III) and from 78.07 to 3.51 in the case of lutetium(III). Fig. 3.4 shows the plot of log D against log $[H^+]$ which is linear with a slope equal to -3 for lutetium(III).

3.2.3 Effect of metal ion concentration

The effect of varying the metal ion concentration on the extraction of lanthanum(III), europium(III) and lutetium(III) from 0.1 M HCl using MPPA in MIBK was studied. The concentrations of MPPA used were 0.2 M for lanthanum(III), and europium(III) and 0.03 M for lutetium(III). The extraction decreases with increase in the initial metal ion concentration. The log-log plot (Fig.3.7)

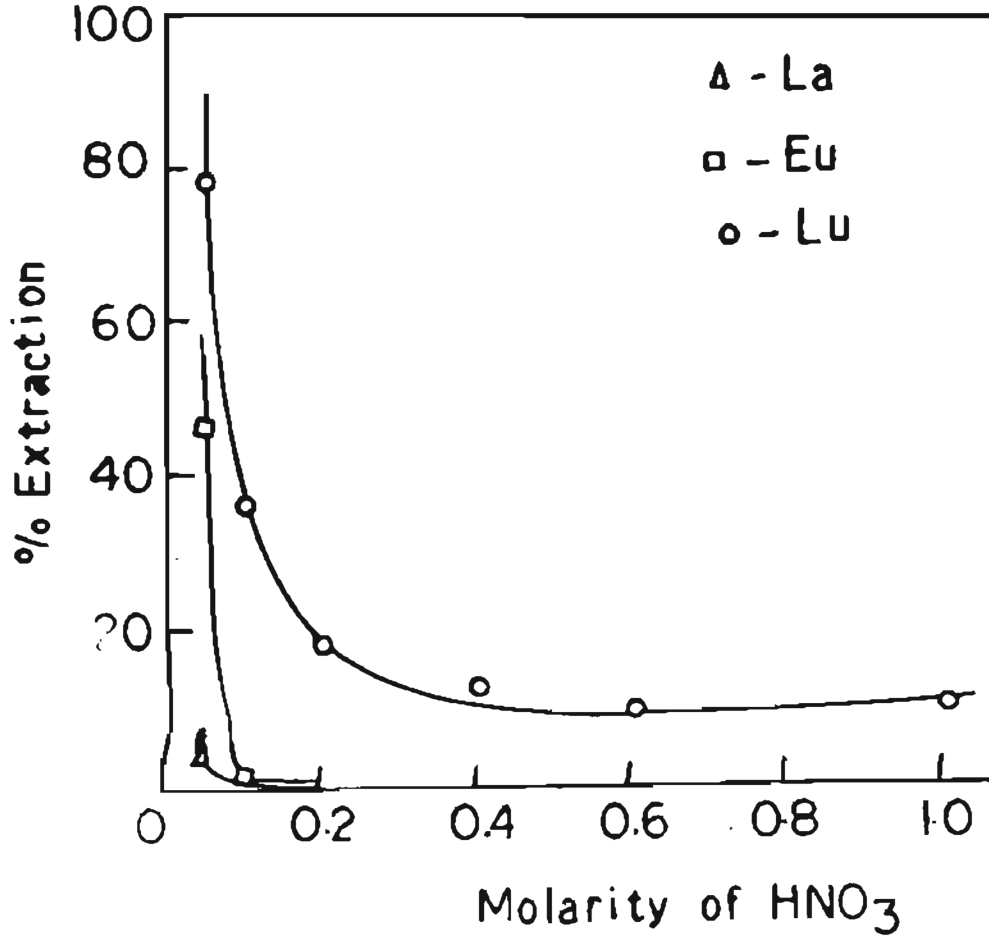


Fig. 3.6: Plot of percent extraction vs [HNO$_3$] during the extraction of lanthanum, europium and lutetium with 0.05 M MPPA in MIBK

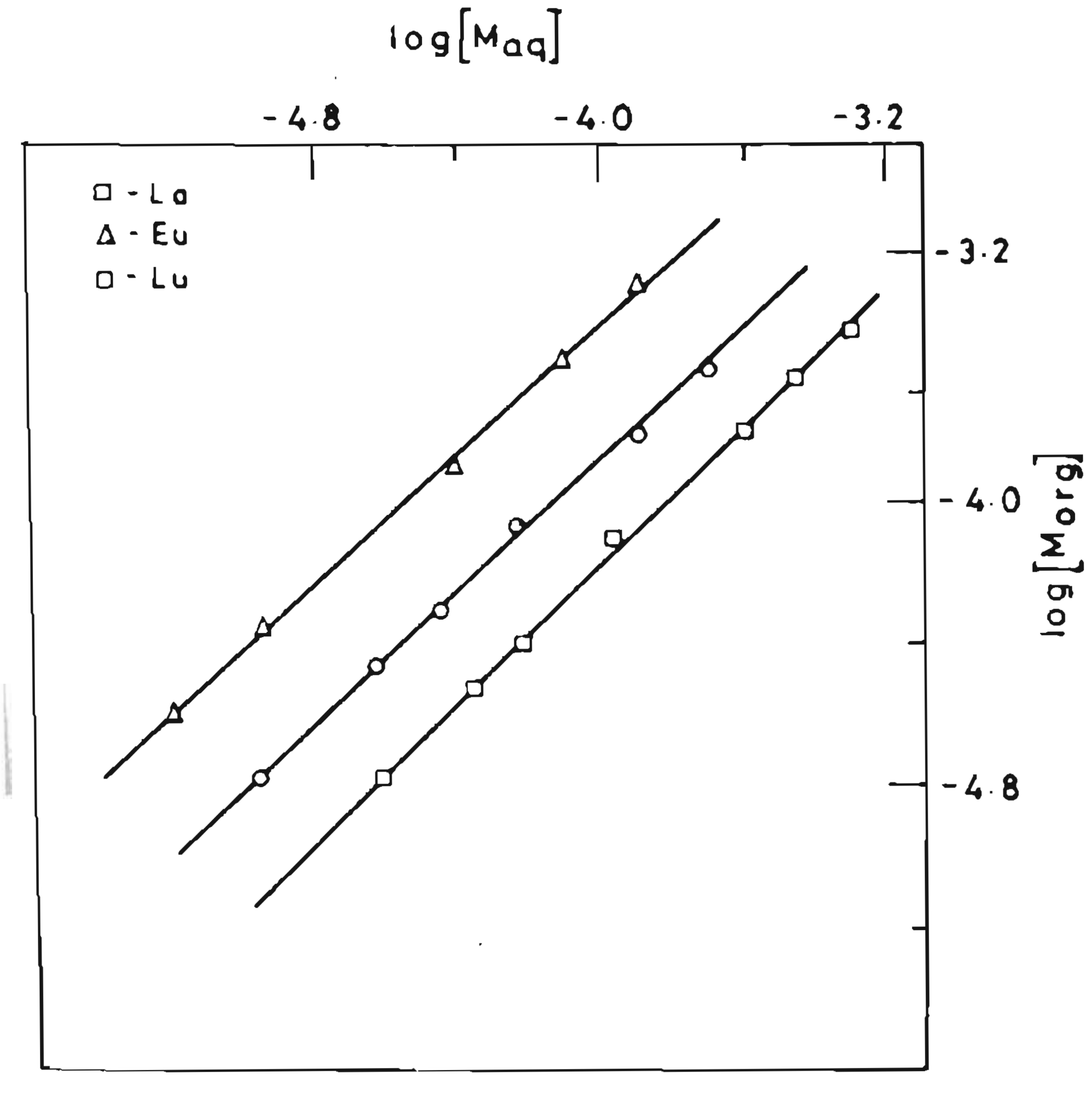


Fig. 3.7: Effect of metal ion concentration on the extraction of Lanthanum(III), Europium(III) and Lutetium(III) from 0.1 M HCl medium by MPPA (0.2 M for Lanthanum(III) and Europium(III) and 0.03 M for Lutetium(III) in MIBK

of the equilibrium organic phase metal concentration against the equilibrium aqueous phase metal concentration is linear with a slope nearly equal to unity.

3.2.4 Effect of time of equilibibrum

Studies on the rate of extraction of lanthanum(III), europium(III) and lutetium(III) from 0.1 M HCl by MPPA in MIBK were carried out. The results obtained are shown in Table 3.1. The concentrations of MPPA in MIBK used were 0.25 M for lanthanum(III), 0.12 M for europium(III) and 0.03 M for lutetium(III).

Table 3.1: Effect of time of equilibration on the extraction of lanthanum(III), europium(III) and lutetium(III) by MPPA in MIBK

Time of equilibration	Distribution coefficients		
	La	Eu	Lu
30 seconds	0.54	0.58	0.74
1 min	1.11	1.13	1.44
2 min	1.11	1.13	1.43
5 min	1.11	1.13	1.43

3.2.5 Extraction behaviour of other rare earths

The extraction behaviour of lanthanum(III), praseodymium(III), samarium(III), europium(III), gadolinium(III), holmium(III), ytterbium(III), lutetium(III) and yttrium by MPPA in MIBK has been studied. The extraction abilities were determined at 0.15 M MPPA in MIBK from 0.1 M HCl. The distribution coefficients calculated for Ln(III)-HCl-MPPA system are shown in Table 3.2.

The separation factors between the rare earths using Ln(III)-HCl-MPPA system are shown in Table 3.3.

Table 3.2: Distribution coefficients of rare earths using Ln(III)-HCl-MPPA system

Reagent	Distribution coefficients									
	La	Pr	Nd	Sm	Eu	Gd	Ho	Yb	Lu	Y
0.1 M HCl 0.15 M MPPA	0.38	1.20	1.31	2.14	2.30	4.51	6.73	*	*	7.89

* Quantitative extraction

3.3. DISCUSSION

3.3.1 Distribution of the acid

An attempt was made to ascertain the state of aggregation of the acid MPPA by IR absorption spectra. But clear cut evidence could not be drawn from this. The IR spectra is more or less similar to that reported by Peppard et al and Asha Jain et al. Hence MPPA was assumed to exist in the monomeric form as concluded by these workers.

Table 3.3: Separation factors between rare earths using Ln(III)-HCl-MPPA system (0.15 M MPPA, 0.1 M HCl)

	La	Pr	Nd	Sm	Eu	Gd	Ho	Yb	Lu	Y
La	-	3.16	3.45	5.63	6.05	11.87	17.71	∞	∞	2.08
Pr	0.32	-	1.09	1.78	1.92	3.76	5.61	∞	∞	6.58
Nd	0.29	0.92	-	1.63	1.76	3.44	5.14	∞	∞	6.02
Sm	0.18	0.56	0.61	-	1.07	2.11	3.14	∞	∞	3.69
Eu	0.17	0.52	0.57	0.93	-	1.96	2.93	∞	∞	3.43
Gd	0.08	0.27	0.29	0.48	0.51	-	1.49	∞	∞	1.75
Ho	0.06	0.18	0.20	0.32	0.34	0.67	-	∞	∞	1.17
Yb	∞	∞	∞	∞	∞	∞	∞	∞	∞	∞
Lu	∞	∞	∞	∞	∞	∞	∞	∞	∞	∞
Y	0.05	0.15	0.17	0.27	0.29	0.57	0.85	∞	∞	-

3.3.2 Extraction mechanism

The general mechanism of extraction of rare earth by an *acidic* organophosphorus extractant MPPA may be represented by the following general expression

$$Ln^{3+} + n(\overline{H_2R}) \rightleftharpoons \overline{Ln(HR)_n} + nH^+$$

where Ln stands for the rare earth element and $(\overline{H_2R})$ refers to the monomer of the extractant in the organic phase. The extractant constant K_{ex} for the extraction process may be written as

$$K_{ex} = \frac{D\,[H^+]^n}{[(\overline{H_2R})]^n}$$

Taking logarithms and rearranging, the above equation takes the form

$$\log D = \log K_{ex} + n \log [(\overline{H_2R})] - n \log [H^+]$$

By studying the distribution coefficient of the metal as a function of $[\overline{H_2R}]$ and $[H^+]$, the composition of the extracted species may be determined.

3.3.3 Effect of MPPA concentration

The extraction of lanthanum(III), europium(III) and lutetium(III) from 0.1 M HCl increases with increase of MPPA concentration. The linear plot of log D vs log [MPPA] has a slope of 3 indicating the association of three molecules of MPPA with each of the extracted metal species.

3.3.4 Effect of acid concentration

The extraction of lanthanum(III), europium(III) and lutetium(III) decreases with increase of H^+ concentration under the experimental conditions simplifies to

$$\log D \propto n \log [H^+]$$

The plot of log D vs log $[H^+]$ gives the number of H^+ ions released during the extraction of metal species. The resulting slope obtained is nearly -3 showing that during the extraction of each metal species there is a release of 3 H^+ ions. Hence the extraction with MPPA follows usual cation exchange mechanism .

The effect of the three acids namely HCl, H_2SO_4 and HNO_3 on the extraction of lanthanum(III), europium(III) and lutetium indicates that the extraction lies in the order $HCl > H_2SO_4 > HNO_3$. The extraction was very negligible beyond 1 M. The extraction of lanthanum(III) and europium(III) was very low and hence their log D vs log H^+ plot could *not be drawn.*

3.3.5 Effect of metal ion concentration

The extraction of lanthanum(III), europium(III) and lutetium(III) decreases with increase in the initial metal ion concentration from 0.1 M HCl. The slope of log D against log initial metal concentration is zero for all the three elements. These results show that the degree of polymerisation in the two phases is the same under the present experimental conditions. The log-log plot of equilibrium organic phase metal concentration against the equilibrium aqueous phase metal concentration is linear with slopes equal to one indicating the existence of mononuclear species $\overline{Ln(HR)_3}$.

3.3.6 Effect of time of equilibration

The extraction of lanthanum(III), europium(III) and lutetium(III) by MPPA in MIBK reaches equilibrium within 1 minute of shaking and remain same on further increase to 5 min. So it was decided to equilibrate the organic and aqueous phases for 5 minutes to ensure complete equilibrium.

3.3.7 Extraction behaviour of other rare earths

The extraction of rare earths increases with increase in atomic number from lanthanum(III) to lutetium(III). The reagent MPPA is very selective for the extraction of heavy rare earths particularly ytterbium and lutetium. From the separation factors, it is clear that more stabler complexes are formed for ytterbium(III) and lutetium(III) using MPPA and hence higher distribution coefficients.

3.4 EXPERIMENTAL

3.4.1 Apparatus

IR spectra were recorded on a Perkin Elmer Model 299 B IR spectrometer. IR of MPPA was taken in dilute solution of MIBK in demountable KBr cell of 0.25 mm thickness.

A Hitachi 220 double beams microprocessor controlled molecular absorption spectrophotometer was used for measuring the absorbances. An ELICO LI 120 digital pH meter was used for the pH measurements.

3.4.2 Reagents

Stock solutions of lanthanides were prepared from their oxides (Rare Earths Products, Cheshire, UK, 99.99%) by dissolving in 2 cm^3 of 1:1 hydrochloric acid and diluting to 100 cm^3.

Ammonium acetate buffer (pH 7.5) was prepared by dissolving 19.25 g in 250 cm^3 of water and adjusting the pH to 7.5 with HCl or NaOH.

Arzenazo I (Fluka, Switzerland) was prepared by dissolving 25 mg of the reagent in 250 cm^3 of water.

All the other chemicals were of analytical reagent grade and were used without further purification.

3.4.3 The extraction conditions

Solvent extraction measurements were made employing aqueous solution 0.05 to 1 M HCl. Except where stated otherwise, the initial concentration of La(III) was 7.20×10^{-5} M, that of Eu(III) 6.58×10^{-5} M and that of Lu(III) 5.82×10^{-5} M. Solutions of MPPA (0.01 to 0.3 M) in MIBK were used. In all systems the aqueous phase and organic phase were of equal volumes.

3.4.4 Extraction equilibrium procedure

Distribution coefficient were determined by shaking equal volumes of aqueous and organic phases (10 cm^3) for 5 minutes in 60 cm^3 separating funnel at 303 ± 1 K (extraction equilibrium was attained in 2 minutes). The distribution coefficient, D is given by

$$D = \frac{(\overline{Ln})}{(Ln)}$$

where $(\overline{Ln})$ and (Ln) are the concentration of the rare earth in the organic and aqueous phases respectively.

3.4.5 Method of estimation of rare earths

After extraction, the rare earth in the aqueous phase was estimated spectrophotometrically by complexing with Arzenazo I. After allowing the phases to settle, a 5 cm^3 aliquot of the aqueous phase was pipetted into a 25 cm^3 beaker and 1 cm^3 of ammonium acetate buffer and 5 cm^3 of Arzenazo I were added for the determination of metal ion. After adjusting the pH to 7.5 ± 0.1, the solutions were transferred to a 25 cm^3 volumetric flasks and made upto the mark.

The absorbance of the solutions was measured at 575 nm and the rare earth concentration was computed from the respective calibration graphs. The rare earth concentration in the organic phase was obtained by difference. These concentration values were used to obtain the distribution coefficient D. The percentage extraction was calculated from the distribution coefficient as follows:

$$\% E = \frac{100 D}{D + 1}$$

CHAPTER IV

LIQUID-LIQUID EXTRACTION STUDIES OF RARE EARTHS WITH ISO-PROPYL-3-PENTADECYLPHENYL PHOSPHORIC ACID

4.1 INTRODUCTION

The synthesis of a variety of reagents which enable the extraction efficiency and selectivity of the extractants for rare earths has been a topic of continuing interest. The search for more selective and versatile extractants has resulted in the evaluation of esters of orthophosphoric, phosphonic and phosphinic acids and similar compounds containing polyfunctional groups. Mono-acidic extractants such as diesters of phosphoric acid have been subject of several studies. Di(2-ethylhexyl phosphoric acid (DEHPA)[34-39], tributyl phosphate (TBP)[86-90] are commonly employed for the isolation of higher valent metal ions such as rare earths and actinides.

DEHPA has been extensively studied for the extractive separation of rare earth elements. The wider applications of DEHPA are however limited by some disadvantages arised from difficulty in stripping and comparatively higher acidity of aqueous phase required for extraction. Nowadays 2-ethylhexyl phosphonic acid -mono-2-ethylhexyl ester (EHEHPA)[56-59] is used for metal extraction due to lower acidities required for stripping.

The distribution ratios of metal ions in extraction is increased as the acidity of the compound is enhanced. Besides these, the steric effect plays an important role in the selectivity of reagents especially for the separation of rare earth elements with varying atomic radii.

The effect of organic substituents and structure of organophosphorus compound on the extraction abilities for uranium were reported by Nomura and Hara[172] . They have clearly indicated that among the phosphates, phosphonates, phosphinates and phosphine oxides, the relative order of the extracting abilities is tri-n-butyl phosphine oxide and n-butyldibutyl phosphinate > tricyclohexyl phosphate > diethylbutyl phosphonate>phosphates with branching alkyl groups > phosphates with normal alkyl groups > phosphates with aryl groups.

The structure-reactivity studies on the extraction of rare earths has been investigated by various group of workers. Early reports by Peppard et al [173] described the extraction of scandium(III), yttrium(III), lanthanum(III), actinium(III), promethium(III), thulium(III), americium(III) into solution of DEHPA, mono-2-ethylhexyl phosphoric acid (MEHPA), di(isooctylphenyl), mono(octylphenyl) esters of orthophosphoric acid where the octylphenyl group is specifically para (1,1,3,3-tetra methyl-1-butylphenyl) into toluene from aqueous mineral acid phases.

Later on Yuan Chengye et al[174] have reported the synthesis of acidic phosphates and phosphonates and their structure-reactivity studies on the extraction of neodymium, samarium, ytterbium and yttrium. The extraction of Nd, Sm, Y and Yb by dibasic phosphates or phosphonates is obviously greater than that of mono basic analogues. The extraction of lanthanum(III), praseodymium(III), europium(III), holmium(III) and ytterbium(III) into chloroform using dicyclohexyl phosphinic acid was studied by Ceconie and Freiser[175] in order to determine the effect of cyclic aliphatic substituents on the selectivity of phosphinic acid as chelating extractants.

Bifunctional and polyfunctional ligands are finding increasing application in metal ion extraction processes. The design and synthesis of several new families of polyfunctional organophosphonates ligand were reviewed by Paine et al[176] along with the studies on coordination chemistry of the ligands with lanthanide and uranyl ions. Even the use of polymeric materials for metal ion separation has been reported by Paine et al[177].

Recently Jain et al [33] have observed in their studies with mono(2-ethylhexyl) phosphoric acid that the extraction of rare earths is higher with alkyl aryl phosphoric acid compared to mono(2-ethylhexyl)) and di(2-ethylhexyl) phosphoric acids. It was felt to synthesise a variety of alkyl aryl phosphoric acids and study the extraction behaviour of rare earths. The alkyl aryl phosphoric acids were synthesised from easily available naturally occurring materials like cardanol as described in chapter 2.

This chapter discusses the extraction studies of rare earths from chloride and perchlorate media using a newly synthesised reagent isopropyl-3-pentadecylphenyl phosphoric acid (IPPA). The nature of extracting species was evaluatted and extractability of new reagent was compared with other commercially well known acidic organophosphorus acids like DEHPA and EHEHPA under identical conditions.

4.2 RESULTS

4.2.1 Effect of isopropyl-3-pentadecylphenyl phosphoric acid (IPPA) concentration

Hydrochloric acid medium

The dependence of the extraction of lanthanum(III), europium(III) and lutetium(IIII) (representative of light, middle and heavy rare earths) from 0.1 M hydrochloric acid solution was investigated as a function of IPPA concentration. The concentrations of IPPA used were 0.02 M to 0.1 M for lanthanum(III), 0.008-0.025 M for europium(III) and 0.001 to 0.002 M for lutetium(III) in toluene. The values of percent extraction range from 11.50 *to 92.50 in case* of lanthanum(III), *from 22.48 to 94.14* in the case of europium(III) and from 40.83 to 86.72 in the case of lutetium(III). Fig. 4.1 shows the plot of log D against log [IPPA] which is linear with a slope nearly equal to three for all the elements.

Perchloric acid medium

The dependence of extraction of lanthanum(III), europium(III) and lutetium(III) from 0.1 M perchloric acid was also investigated. The concentrations of IPPA used were 0.02 M to 0.1 M for lanthanum(III), 0.008-0.025 M for europium(III) and 0.001-0.002 M for lutetium(III) in toluene. The extraction increases with increase in concentration of IPPA for all the three elements. The percent extraction values range from 16.67 to 55.75

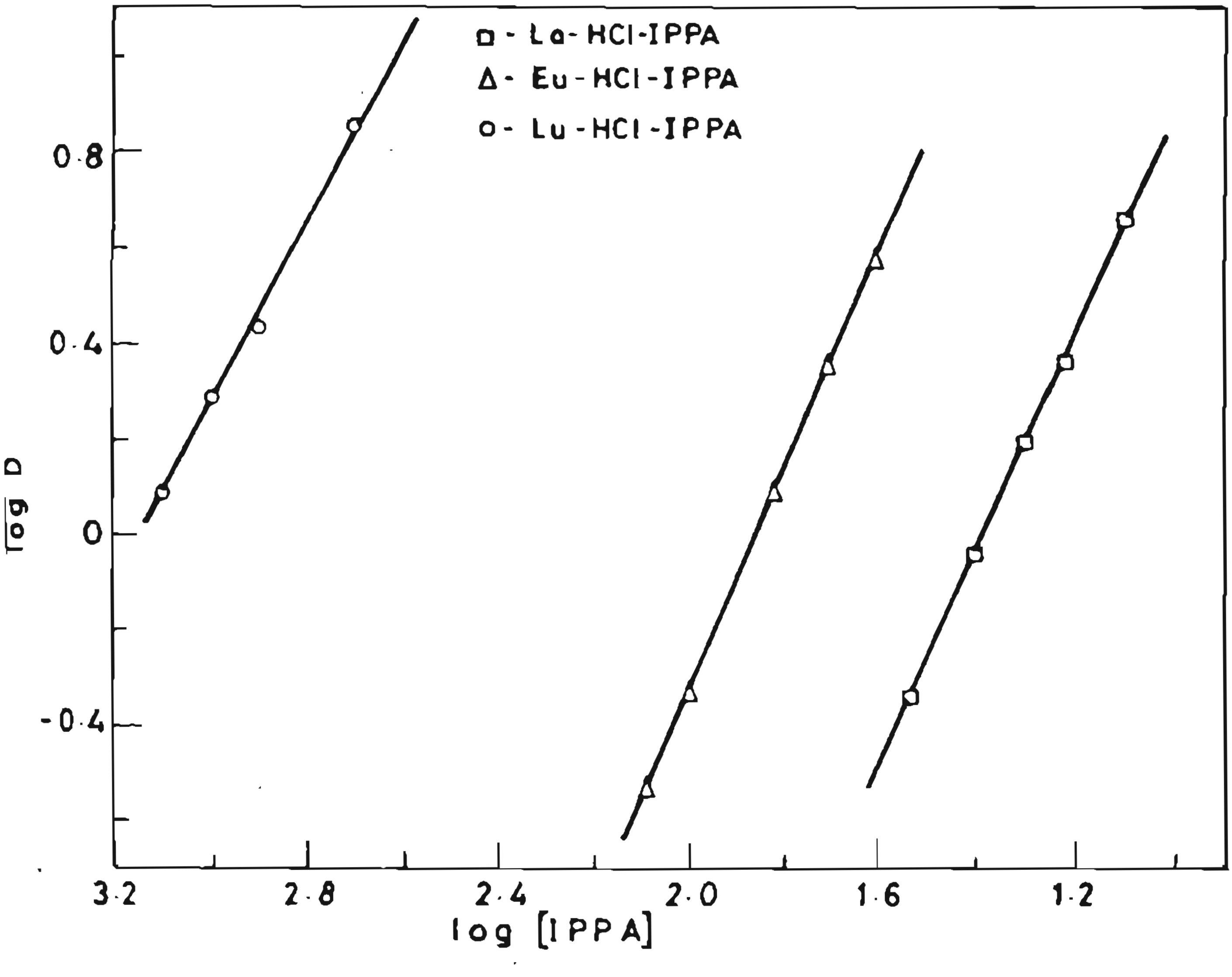


Fig. 4.1: Plot of log D vs log [IPPA] during the extraction of Lanthanum(III), Europium(III) and Lutetium(III) in the presence of 0.1 M HCl

for lanthanum(III), from 15.00 to 75.85 for europium(III) and from 35.90 to 91.84 for lutetium(III). The plot of log D vs log [IPPA] from perchloric acid is shown in Fig. 4.2. The plot is linear with a slope equal to 3 for all three elements.

4.2.2 Effect of acid concentration

Hydrochloric acid medium

The effect of H^+ concentration over the range 0.05 to 0.5 M at a constant concentration of chloride from a mixture of hydrochloric acid and lithium chloride was studied for lanthanum(III), europium(III) and lutetium(III). The concentrations of IPPA used in these studies were 0.08 M for lanthanum(III), 0.02 M for europium(III) and 0.01 M for lutetium(III). The extraction decreases drastically with increase in H^+ concentration and was negligible at about 0.5 M hydrochloric acid. The percent extraction values obtained were found to range from 91.67 to 4.21 for lanthanum(III), from 91.67 to 16.67 for europium(III) and from 86.74 to 47.92 for lutetium(III). The plot of log D versus log $[H^+]$ from hydrochloric acid medium is shown in Fig. 4.3. The plot is linear with a slope equal to -3 for all the three elements.

Perchloric acid medium

The effect of H^+ concentration over the range 0.05 M to 0.5 M at constant concentration of perchlorate from a mixture of perchloric acid and sodium perchlorate was studied for lanthanum(III), europium(III) and lutetium(III). The concentrations

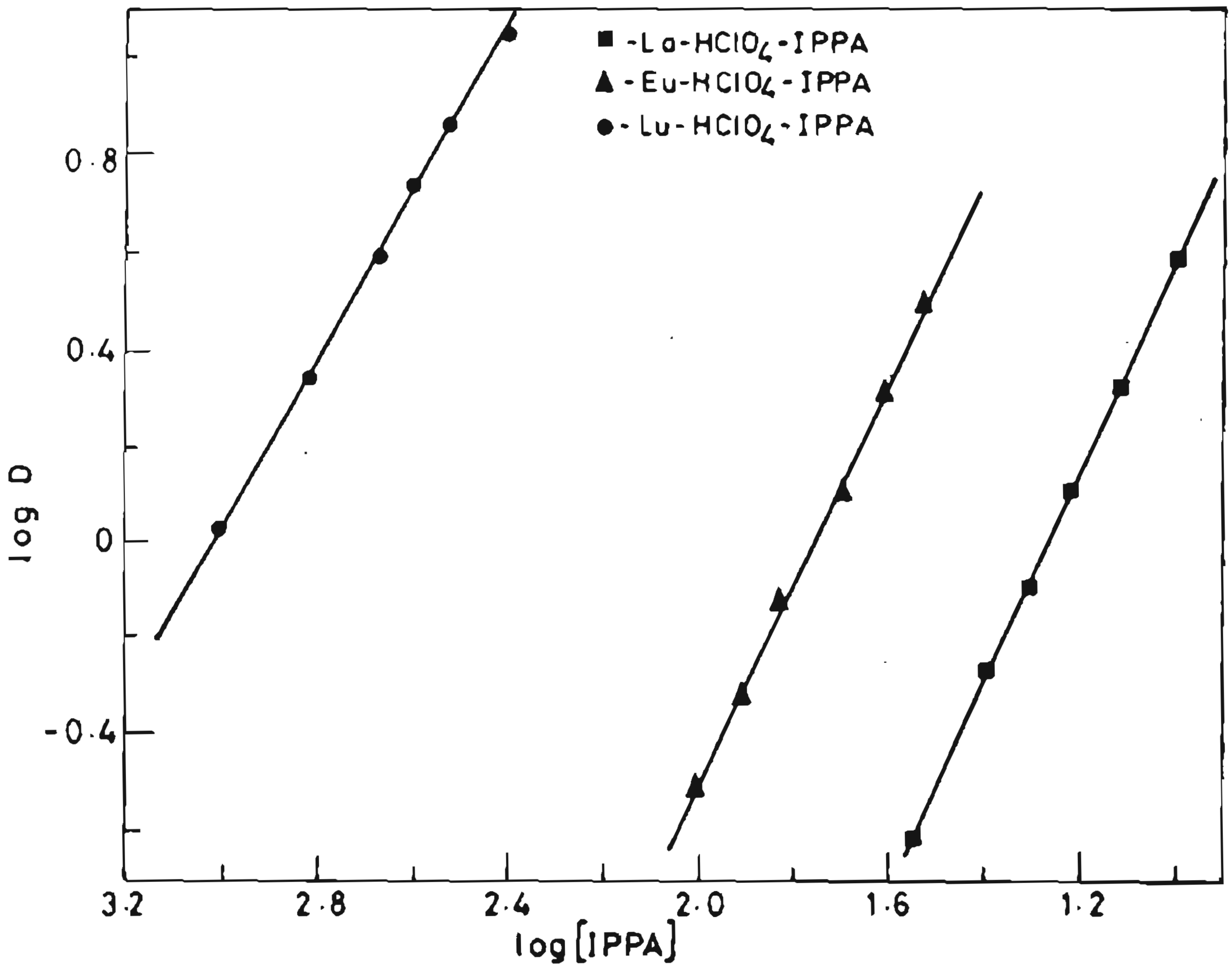


Fig. 4.2: Plot of log D vs log [IPPA] during the extraction of Lanthanum(III). Europium(III) and Lutetium(III) in the presence of 0.1 M $HClO_4$

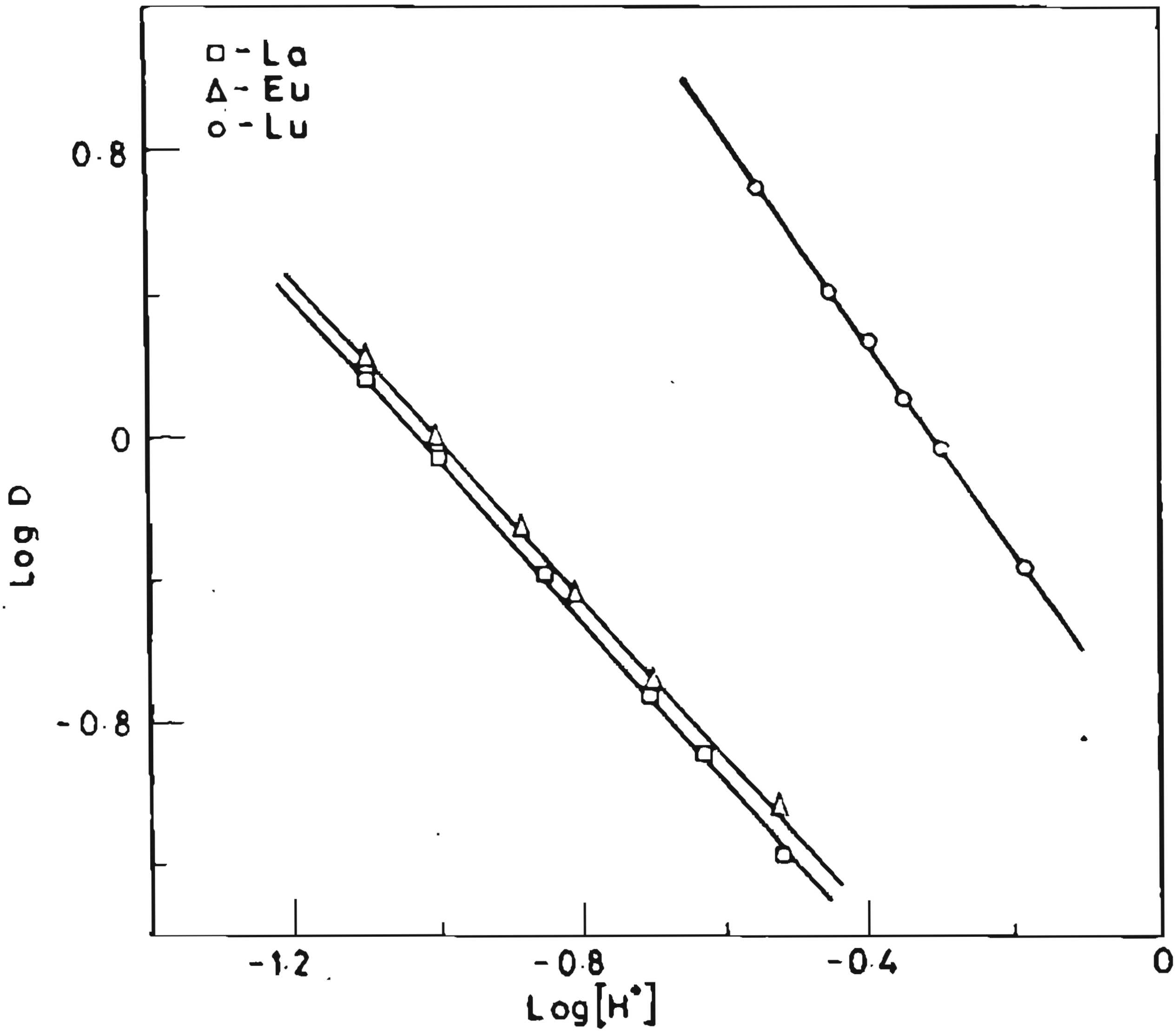


Fig. 4.3: Plot of log D vs log $[H^+]$ during extraction of Lanthanum(III), Europium(III) and Lutetium(III) with 0.08, 0.02 and 0.1 M IPPA respectively in toluene using HCl + LiCl mixtures

of IPPA used in these studies were 0.08 M for lanthanum(III), 0.02 M for europium(III) and 0.01 M for lutetium(III). The extraction decreases drastically with increase in H^+ concentration. Thus the values of percentage extraction ranges from 85.57 to 27.00 in case of lanthanum(III), from 89.16 to 35.90 in case of europium(III) and from 85.71 to 53.05 in case of lutetium(III). Fig. 4.4 shows the plot of log D against log $[H^+]$ which is linear with a slope nearly equal to -3 for all the three elements.

4.2.3 Effect of the metal ion concentration

Hydrochloric acid medium

The effect of varying the metal ion concentration on the extraction of lanthanum(III), europium(III) and lutetium(III) from 0.1 M HCl by using IPPA in toluene was studied. The concentrations of IPPA used were 0.05 M for lanthanum(III), 0.015 M for europium(III) and 0.0015 M for lutetium(III). The extraction decreases slightly with increase in the initial concentration of the metal ion. The slope of the log-log plot (Fig. 4.5) of the equilibrium organic phase metal concentration against the equilibrium aqueous phase metal concentration is linear with a slope nearly equal to unity.

Perchloric acid medium

The variation of metal ion concentration on the extraction of lanthanum(III), europium(III) and lutetium(III) from 0.1 M

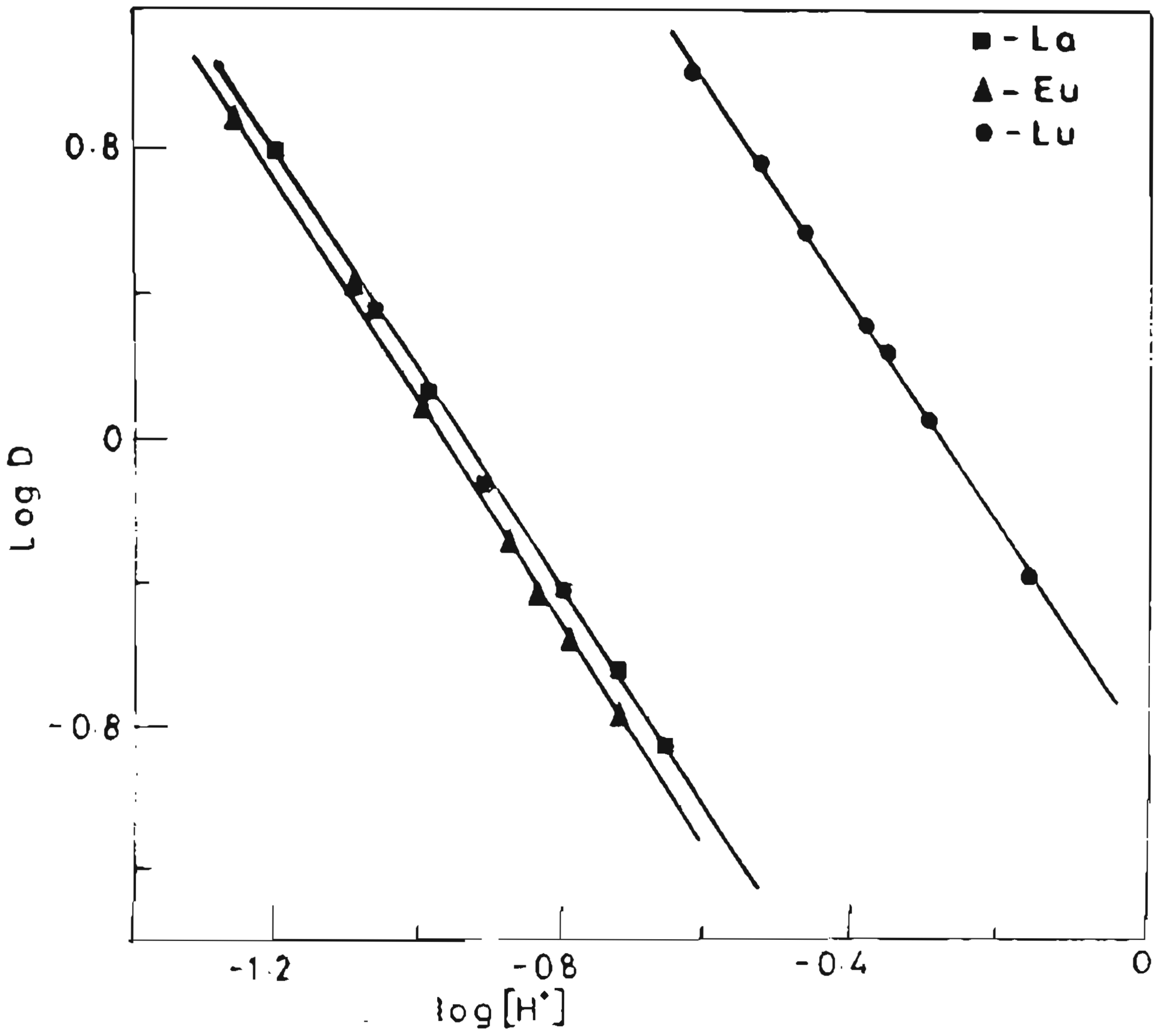


Fig. 4.4: Plot of log D vs log $[H^+]$ during the extraction of Lanthanum(III), Europium(III) and Lutetium(III) with 0.8, 0.02 and 0.1 M respectively IPPA in toluene using $HClO_4$ + $NaClO_4$ mixtures

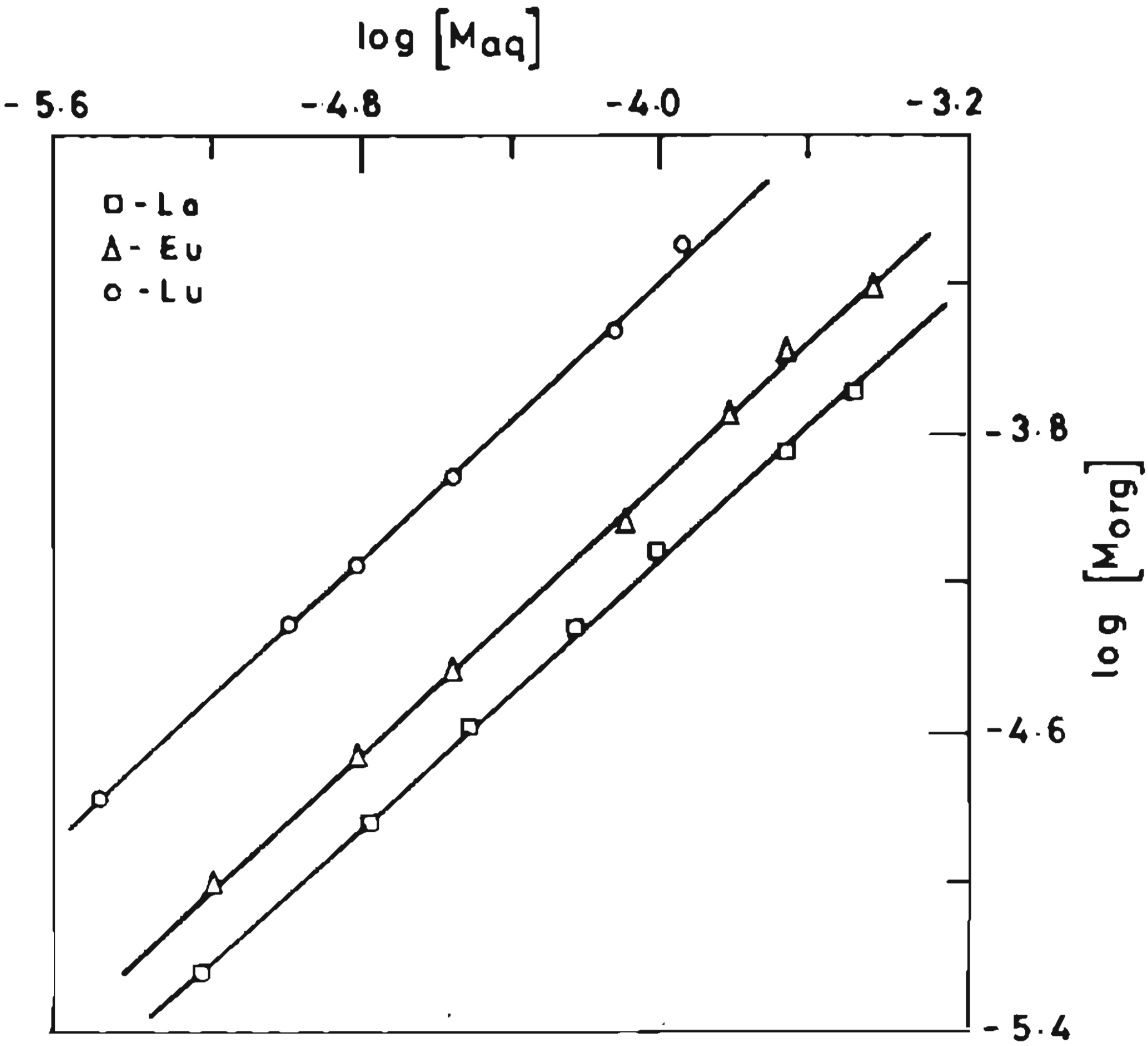


Fig. 4.5: Effecct of metal ion concentration on the extraction of Lanthanum(III), Europium(III) and Lutetium(III) from 0.1 M HCl medium by IPPA (0.05 M for Lanthanum(III), 0.015 M for Europium(III) and 0.0015 M for Lutetium(III) in toluene

perchloric acid by IPPA in toluene was studied. The concentrations of IPPA in toluene were 0.05 M for lanthanum(III), 0.015 M for europium(III) and 0.0015 M for lutetium(III). The extraction decreases slightly with increase in the initial concentration of the metal ion. The slope of the log equilibrium organic phase metal concentration against the log of equilibrium aqueous phase metal concentration (Fig. 4.6) is linear with slope equal to one.

4.2.4 Dependence of extraction on the nature of the solvent

Hydrochloric acid medium

The effect of various solvents on the extraction of lanthanum(III), europium(III), and lutetium(III) from 0.1 M hydrochloric acid using IPPA was studied. The concentrations of IPPA used in these studies were 0.05 M for lanthanum(III), 0.015 M for europium(III) and 0.001 M for lutetium(III) in various solvents. The results obtained are summarised in Table 4.1. The rare earths elements are not extracted by pure solvents under the present experimental conditions.

Perchloric acid medium

The effect of various solvents on the extraction of lanthanum(III), europium(III) and lutetium(III) from 0.1 M perchloric acid using IPPA was studied. The concentrations of IPPA used in these studies were 0.05 M for lanthanum(III), 0.015 M for europium(III) and 0.001 M for lutetium(III). The results obtained

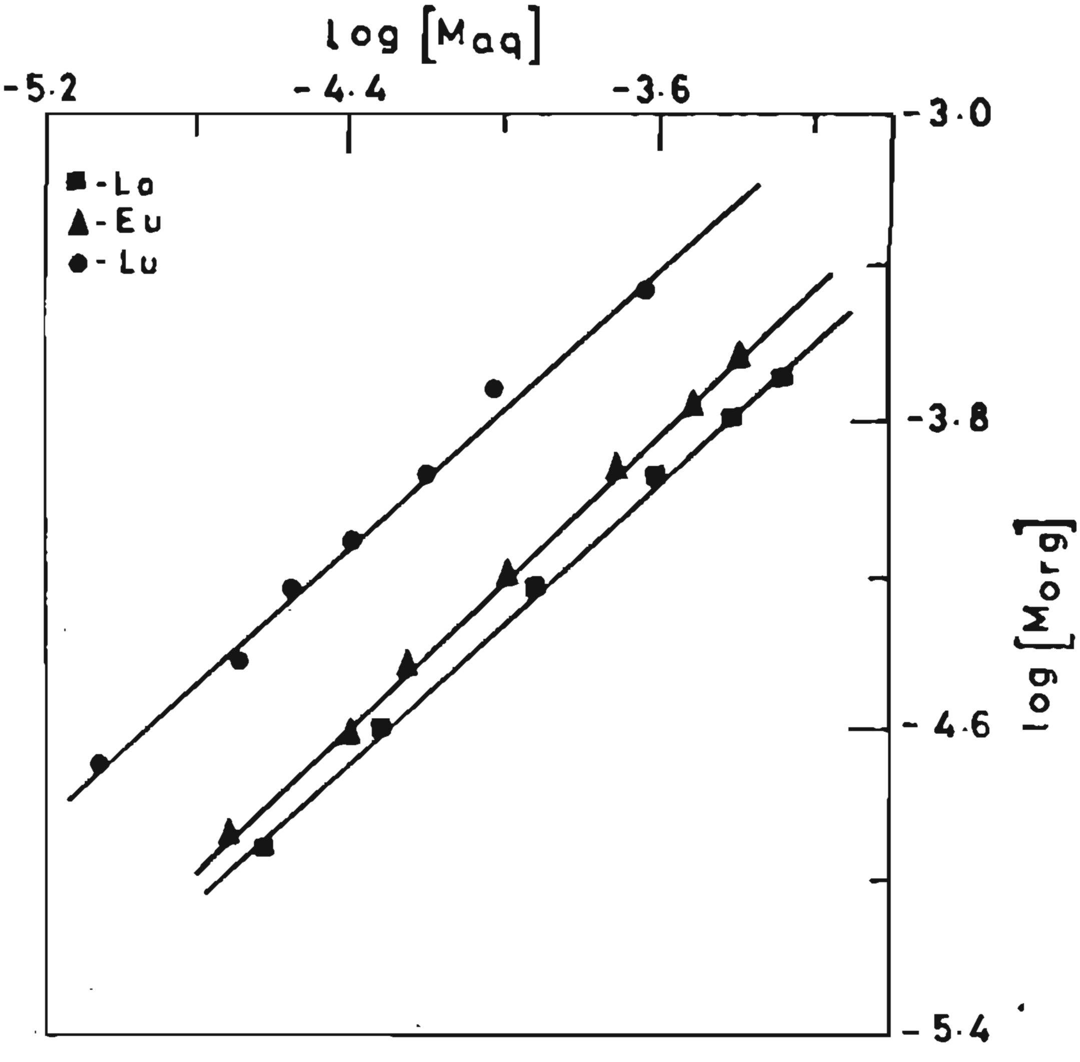


Fig. 4.6: Effect of metal ion concentration on the extraction of Lanthanum(III), Europium(III) and Lutetium(III) from 0.1 M $HClO_4$ medium by IPPA (0.05 M for Lanthanum(III), 0.015 M for Europium(III) and 0.0015 M for Lutetium(III)) in toluene

are summarised in Table 4.2. The rare earth elements are not extracted by pure solvents under the present experimental conditions.

Table 4.1: Extraction of lanthanum(III), europium(III) and lutetium(III) with IPPA in different diluents from 0.1 M HCl

Diluent	Dielectric constant	Distribution coefficient		
		La	Eu	Lu
Nitrobenzene	34.8	0.58	0.45	0.40
IBMK	13.11	0.04	0.11	0.08
Chloroform	4.61	0.39	0.21	0.13
Toluene	2.36	1.04	0.94	0.69
Xylene	2.35	2.15	1.45	1.04
Benzene	2.26	0.83	0.62	0.46
Carbon tetrachloride	2.22	*	9.91	5.00

* Quantitative extraction

Table 4.2: Effect of various solvents on the extraction of lanthanum(III), europium(III) and lutetium(III) using IPPA from 0.1 M $HClO_4$ medium

Diluents	Dielectric constant	Distribution coefficients		
		La	Eu	Lu
Nitrobenzene	34.8	0.82	0.19	0.20
IBMK	13.11	0.01	0.01	0.01
Chloroform	4.61	0.17	0.13	0.01
Toluene	2.36	0.55	0.74	0.56
Xylene	2.35	1.67	0.97	0.63
Benzene	2.26	0.47	0.36	0.17
Carbon tetrachloride	2.22	5.50	3.44	1.09

4.2.5 Effect of time of equilibration

Experiments were carried out to study the rate of the extraction of lanthanum(III), europium(III) and lutetium(III) from 0.1 M HCl/0.1 M $HClO_4$ media by IPPA in toluene. The concentrations of IPPA used were 0.05 M for lanthanum(III), 0.015 M for europium(III) and 0.001 M for lutetium(III). The results obtained are shown in Table 4.3.

Table 4.3: Effect of time of equilibration on the extraction of lanthanum(III), europium(III) and lutetium(III) by IPPA in toluene

Time of equilibration	Distribution coefficients					
	La		Eu		Lu	
	0.1 M HCl	0.1 M $HClO_4$	0.1 M HCl	0.1 M $HClO_4$	0.1 M HCl	0.1M $HClO_4$
30 seconds	0.68	0.36	0.48	0.35	0.31	0.24
1 min	1.31	0.76	0.94	0.74	0.69	0.56
3 min	1.31	0.76	0.94	0.74	0.69	0.56
5 min	1.32	0.76	0.94	0.74	0.69	0.56

4.2.6 Extraction behaviour of other rare earths

Hydrochloric medium

The extraction behaviour of lanthanum(III), praseodymium(III), neodymium(III), samarium(III), europium(III), gadolinium(III), holmium(III), ytterbium(III), lutetium(III) including yttrium(III) has been studied. The extraction abilities were determined at two different concentrations of IPPA namely 0.0015 M and 0.015 M in toluene from 0.1 M HCl. The distribution coefficients calculated for Ln(III)-HCl-IPPA system are shown in Table 4.4 .

The separation factors between the rare earths with Ln(III)-HCl-IPPA system in toluene are shown in Tables 4.5 and 4.6.

Table 4.4: Distribution coefficients of rare earths using Ln(III)-HCl-IPPA system

Medium	Distribution coefficients									
	La	Pr	Nd	Sm	Eu	Gd	Ho	Yb	Lu	Y
0.1 M HCl + 0.0015 M IPPA	< 0.01	< 0.01	< 0.01	0.07	0.08	0.06	0.12	0.94	2.38	0.10
0.1 M HCl + 0.015 M IPPA	0.02	0.25	0.32	0.53	0.69	0.93	22.59	> 99.99	> 99.99	35.63

Table 4.5: Separation factors of rare earths with Ln(III)-HCl-IPPA system in toluene (0.1 M HCl, 0.0015 M IPPA)

	La	Pr	Nd	Sm	Eu	Gd	Ho	Yb	Lu	Y
La	-	∞	∞	∞	∞	∞	∞	∞	∞	∞
Pr	∞	-	∞	∞	∞	∞	∞	∞	∞	∞
Nd	∞	∞	-	∞	∞	∞	∞	∞	∞	∞
Sm	0	0	0	-	1.14	0.86	1.71	13.43	34	1.43
Eu	0	0	0	0.88	-	0.75	1.5	11.75	29.75	1.25
Gd	0	0	0	1.17	1.33	-	2	15.67	39.67	1.67
Ho	0	0	0	0.58	0.67	0.50	-	7.83	19.83	0.83
Yb	0	0	0	0.07	0.09	0.06	0.13	-	2.53	0.11
Lu	0	0	0	0.03	0.03	0.03	0.05	0.39	-	0.04
Y	0	0	0	0.7	0.8	0.6	1.2	9.4	23.8	-

Table 4.6: Separation factor values for rare earths using Ln(III)-HCl-IPPA system in toluene (0.1 M HCl, 0.015 M IPPA)

	La	Pr	Nd	Sm	Eu	Gd	Ho	Yb	Lu	Y
La	-	12.5	16.0	26.5	34.5	46.5	1129.5	∞	∞	1781.5
Pr	0.08	-	1.28	2.13	2.76	3.72	90.36	∞	∞	142.52
Nd	0.06	0.78	-	1.66	2.16	2.91	70.59	∞	∞	111.34
Sm	0.04	0.47	0.60	-	1.30	1.76	42.62	∞	∞	67.23
Eu	0.03	0.36	0.46	0.77	-	1.35	32.74	∞	∞	51.64
Gd	0.02	0.27	0.34	0.57	0.74	-	24.29	∞	∞	38.31
Ho	0.001	0.01	0.01	0.02	0.03	0.04	-	∞	∞	1.58
Yb	∞	∞	∞	∞	∞	∞	∞	-	∞	∞
Lu	∞	∞	∞	∞	∞	∞	∞	∞	-	∞
Y	0.001	0.01	0.01	0.02	0.02	0.03	0.63	∞	∞	-

Perchloric acid medium

The extraction behaviour of La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Ho(III), Yb(III), Lu(III) and Y(III) has been studied from $HClO_4$ medium. The extraction abilities were determined at two different concentrations of IPPA namely 0.0015 M and 0.015 M in toluene from 0.1 M $HClO_4$ solutions. The distribution coefficients obtained for the Ln(III)-IPPA-$HClO_4$ system is shown in Table 4.7.

The separation factors using IPPA between various rare earth elements from 0.1 M $HClO_4$ are shown in Tables 4.8 and 4.9.

4.2.7 Comparison with other organophosphorus acids

Hydrochloric acid

The extraction efficiency of IPPA on the extraction of lanthanum(III), europium(III) and lutetium(III) from hydrochloric acid medium has been compard with other commercial acidic organophosphorus extractants like Di(2-ethylhexyl) phosphoric acid ((DEHPA) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA). The comparisons were done at two different reagent concentrations 0.0015 M and 0.015 M in toluene from 0.1 M HCl. The results obtained are presented in Table 4.10.

Table 4.7: Distribution coefficients of rare earths with $Ln(III)-HClO_4$-IPPA system

Medium	Distribution coefficients									
	La	Pr	Nd	Sm	Eu	Gd	Ho	Yb	Lu	Y
0.1 M $HClO_4$ + 0.0015 M IPPA	$<$0.01	$<$0.01	$<$0.01	0.05	0.03	0.09	0.06	0.97	1.72	0.06
0.1 M $HClO_4$ + 0.015 M IPPA	0.05	0.05	0.05	0.32	0.69	0.93	22.59	44.25	$>$99.99	26.47

Table 4.8: Separation factors of lanthanides obtained with Ln(III)-$HClO_4$-IPPA in toluene

(0.1 M $HClO_4$, 0.0015 M IPPA)

	La	Pr	Nd	Sm	Eu	Gd	Ho	Yb	Lu	Y
La	-	∞	∞	∞	∞	∞	∞	∞	∞	∞
Pr	∞	-	∞	∞	∞	∞	∞	∞	∞	∞
Nd	∞	∞	-	∞	∞	∞	∞	∞	∞	∞
Sm	0	0	0	-	0.6	1.8	1.2	19.4	34.4	1.2
Eu	0	0	0	1.67	-	3.00	2.00	32.33	57.33	2.00
Gd	0	0	0	0.56	0.33	-	0.67	10.78	19.11	0.67
Ho	0	0	0	0.83	0.5	1.50	-	16.17	28.67	1
Yb	0	0	0	0.05	0.03	0.09	0.06	-	1.77	0.06
Lu	0	0	0	0.03	0.02	0.05	0.04	0.56	-	0.04
Y	0	0	0	0.83	0.50	1.50	1	16.17	28.67	-

Table 4.9: Separation factor values obtained with $Ln(III)-HClO_4-IPPA$ system
(0.1 M $HClO_4$, 0.015 M IPPA)

	La	Pr	Nd	Sm	Eu	Gd	Ho	Yb	Lu	Y
La	-	1.0	1.0	6.4	13.8	18.6	451.8	885	∞	529.40
Pr	1.0	-	1.0	6.4	13.8	18.6	451.8	885.00	∞	529.40
Nd	1.0	1.0	-	6.4	13.8	18.6	451.8	885.00	∞	529.40
Sm	0.16	0.16	0.16	-	2.16	2.91	70.59	138.28	∞	82.72
Eu	0.07	0.07	0.07	0.46	-	1.35	32.71	64.13	∞	38.36
Gd	0.05	0.05	0.05	0.34	0.74	-	24.29	47.58	∞	28.46
Ho	0.002	0.002	0.002	0.01	0.03	0.04	-	1.96	∞	1.17
Yb	0.001	0.001	0.001	0.01	0.02	0.02	0.51	-	∞	0.60
Lu	∞	∞	∞	∞	∞	∞	∞	∞	-	∞
Y	0.002	0.002	0.002	0.01	0.03	0.04	0.85	1.67	∞	-

Table 4.10: Comparison of extraction efficiency of IPPA with DEHPA and EHEHPA

Reagent 0.1 M HCl	Distribution coefficients					
	0.0015 M Reagent			0.015 M Reagent		
	La	Eu	Lu	La	Eu	Lu
IPPA	< 0.01	0.08	2.38	0.02	0.69	*
DEHPA	< 0.01	< 0.01	< 0.01	< 0.01	0.04	2.16
EHEHPA	< 0.01	< 0.01	< 0.01	< 0.01	0.05	0.09

* Quantitative extraction

Perchloric acid medium

The extraction efficiency of IPPA on the extraction of lanthanum(III), europium(III) and lutetium(III) has been compared with commercial acidic organophosphorus extractants like DEHPA and EHEHPA from perchloric acid medium. The comparison was done at two different reagent concentration i.e. at 0.0015 M and 0.015 M from 0.1 M $HClO_4$ medium.

The results obtained are shown in Table 4.11.

Table 4.11: Comparison of extraction efficiency of IPPA with DEHPA and EHEHPA

Reagent 0.1 M $HClO_4$	Distribution coefficients					
	0.0015 M Reagent			0.015 M Reagent		
	La	Eu	Lu	La	Eu	Lu
IPPA	< 0.01	0.03	1.72	0.05	0.69	*
DEHPA	< 0.01	< 0.01	< 0.01	< 0.01	0.04	2.38
EHEHPA	< 0.01	< 0.01	< 0.01	< 0.01	0.03	0.05

* Quantitative extraction

4.3 DISCUSSION

4.3.1 Distribution of acid in the organic phase

The dibasic phosphoric acids are known to be dimeric in nonpolar, aromatic and aliphatic solvents [178]. The state of aggregation of IPPA was ascertained by infra red absorption spectra. It was found that no band for the -OH in the vicinity of 2900-3500 cm^{-1} was observed. The absence of free -OH indicates hydrogen bonding which may be due to the association of IPPA molecules. From the ^{1}H NMR it was clear that the hydroxy group present at δ 11·5 exchanges for deuterium on D_2O exchange. This confirms the association of IPPA molecules in toluene layer.

The association of IPPA molecules was further confirmed by vapour pressure osmometry. The observed molecular weight of IPPA was found to be 854 by vapour pressure osmometric measurements which is very close to two times the molecular weight of IPPA. Hence it is clear that IPPA is dimerised in toluene as $(HR)_2$ where HR is a IPPA molecule.

4.3.2 Extraction mechanism

The general mechanism of extraction of rare earths by an acidic organophosphorus extractant IPPA may be represented by the following general expression

$$Ln^{3+} + n\,\overline{(HR)_2} \rightleftharpoons \overline{Ln\,R_n\,(HR)_n} + nH^{+}$$

where Ln stands for rare earth element and $(\overline{HR})_2$ refers to the dimer of the extractant in the organic phase. The extraction constant (K_{ex}) for the extraction process may be written

$$K_{ex} = \frac{D[H^+]^n}{[(\overline{HR})_2]^n}$$

Taking logarithm and rearranging, the above equation takes the form

$$\log D = \log K_{ex} + n \log [(\overline{HR})_2] - n \log [H^+]$$

By studying the distribution coefficients of a metal as a function of $[(\overline{HR})_2]$ and $[H^+]$, the composition of the extracted species may be determined.

4.3.3 Effect of IPPA concentration

The extraction of lanthanum(III), europium(III) and lutetium(III) from 0.1 M HCl increases with increase of IPPA concentration. The linear plot of log D against log [IPPA] has a slope of 3 indicating the association of three molecules of reagent with each of the extracted metal species. Similarly the extraction of lanthanum(III), europium(III) and lutetium(III) from 0.1 M $HClO_4$ solution increases with increase of IPPA concentration. Further, the linear plot of log D against log [IPPA] has a slope of three indicating the association of three molecules of the reagent with each of the extracted metal species.

4.3.4 Effect of H^+ concentration

The extraction of lanthanum(III), europium(III) and lutetium(III) decreases with increase of H^+ concentration at a given total chloride ion concentration and reagent concentration. Under the experimental conditions the above equation simplifies to

$$\log D \propto n \log [H^+]$$

The plot of log D against log $[H^+]$ gives the number of H^+ ion released during the extraction of metal species. The corresponding slope is nearly -3 showing that during the extraction of each metal species there is a release of 3 H^+ ions indicating that the extraction follows usual cation exchange mechanism. Similar results and conclusions can be drawn from the extraction studies of lanthanum(III), europium(III) and lutetium(III) from perchloric acid solutions.

4.3.5 Effect of metal concentration

The extraction of lanthanum(III), europium(III) and lutetium(III) decreases slightly with increase in the initial concentration of metal from 0.1 M HCl or 0.1 M $HClO_4$ media. The slope of log D against log of the initial metal concentration is zero for all the three elements. These results show that the degree of polymerisation in the two phases is the same under the present experimental conditions. The log-log plots of equilibrium organic phase metal concentration against the equilibrium aqueous phase metal concentration are linear with slopes equal to one indicating the existence of mono-nuclear species $\overline{Ln\ R_3(HR)_3}$.

4.3.6 Dependence on the nature of the solvent

The present results show that the extraction varies with the nature of the diluent. The difference in extractive properties of an extractant in various diluents are usually ascribed to a varying extent of non-ideality of the solutes, the free extractant and its metal complex in the diluent. A quantitative determination of these effects is hardly possible because of the lack of data on the physicochemical properties of the systems. At low metal loadings, the metal distribution ratio is generally higher in aromatic and aliphatic hydrocarbons than in ethers and ketones[179-182] Especially when chloroform is used as diluent, very small extractions have been observed. The non-polar species will be extracted into non-polar solvents like carbon tetrachloride than into polar one[183] . On the other hand Pushlenkov and coworkers[184-185] concluded that extraction is not related to any single property such as dielectric constant or dipole moment, but to several factors. An important advancement has been made by Taube[186] who pointed out that the extraction depends on electrostatic interactions between the complex and dipole of the solvent molecules and on the work needed to form a hole in the organic medium.

4.3.7 Effect of time of equilibration

The extraction of lanthanum(III), europium(III) and lutetium(III) by IPPA in toluene reaches equilibrium within 1 minute of shaking and remains same on further increase to 5 minutes. Hence it was decided to equilibrate the aqueous and organic phases for 5 minutes to ensure complete equilibrium.

4.3.8 Extraction behaviour of other rare earths

The extraction of rare earths increases with increase of atomic number from lanthanum to lutetium. On the other hand, yttrium behaves like heavy rare earths and lies between holmium & ytterbium during the extraction with IPPA in toluene from 0.1 M HCl and 0.1 M $HClO_4$ media. Further, it can be seen from Tables4.4 and 4.7 that IPPA is very selective for the extraction of heavy rare earths especially ytterbium(III) and lutetium(III) from 0.1 M HCl or 0.1 M $HClO_4$ media. The separation factors for ytterbium and lutetium are much higher compared to other rare earths (cf. Tables 4.5, 4.6, 4.8 and 4.9).

4.3.9 Comparison with other organophosphorus acids

The extraction of lanthanum(III), europium(III) and lutetium(III) by IPPA in toluene from 0.1 M HCl and 0.1 M $HClO_4$ media are compared with DEHPA and EHEHPA. It is clear from the Tables 4.10 and 4.11 that IPPA is a better extractant for heavy rare earths especially ytterbium(III) and lutetium(III) than DEHPA and EHEHPA.

4.4 EXPERIMENTAL

4.4.1 Apparatus

IR spectra were recorded on a Perkin Elmer model 299 B IR spectrophotometer. IR of IPPA was taken in dilute solution of toluene in demountable KBr cell of 0.25 mm thickness.

The molecular weight was determined using Knauer vapour pressure osmometer Nr II.

A Hitachi 220 double beam microprocessor controlled molecular absorption spectrophotometer was used for measuring the absorbances. An ELICO LI-120 digital pH meter was used for the pH measurements.

4.4.2 Reagents

Stock solutions of the lanthanides were prepared from their oxides (Rare Earth Products, Cheshire, UK, 99.99%) by dissolving in 2 cm^3 of 1:1 hydrochloric acid and diluting to 100 cm^3.

Ammonium acetate buffer (pH 7.5) was prepared by dissolving 19.25 g in 250 cm^3 of water and adjusting the pH to 7.5 with HCl/NaOH.

Arzenazo I (Fluka, Switzerland) was prepared by dissolving 25 mg of the reagent in 250 cm^3 of water.

All the other chemicals were of *analytical reagent grade and were used without further purification.*

4.4.3 The extraction conditions

Solvent extraction measurements were made employing aqueous solution of 0.05 to 1 M HCl or 0.05 to 0.1 M $HClO_4$. Except where stated otherwise, the initial concentration of lanthanum(III) was 7.20×10^{-5} M, that of europium(III) 6.58×10^{-5} M and that of lutetium(III) 5.82×10^{-5} M.

Solutions of IPPA used was varied from 0.0015 M to 0.1 M in toluene. In all extraction systems the aqueous and organic phases were of equal volumes.

4.4.4 Extraction equilibrium procedure

Distribution coefficients were determined by shaking equal volumes o queous and organic phase (10 cm^3) for 5 minutes in a 60 cm^3 parating funnel at 303 ± 1 K (extraction equilibrium was attain in 1 minute). The distribution coefficient D is given by

$$D = \frac{[\overline{Ln}]}{[Ln]}$$

Where $[\overline{Ln}]$ and $[Ln]$ are the concentration of the rare earth in the organic and aqueous phases respectively.

4.4.5 Method of estimation of rare earths

After extraction, the rare earth in the aqueous phase is estimated spectrophotometrically by complexing with Arzenazo I.

After allowing the phases to settle, a 5 cm^3 aliquot of the aqueous phase was pipetted into a 25 cm^3 beaker and 1 cm^3 of ammonium acetate buffer and 5 cm^3 of Arsenazo I were added for the determination of metal ion. After adjusting the pH to 7.5 ± 0.1 the solutions were transferred to 25 cm^3 volumetric flasks and made upto the mark.

The absorbances of the solutions were measured at 575 nm and the rare earth concentrations were computed from the respective calibration graphs. The rare earth concentration in the organic phase was obtained by difference. The concentration values were used to obtain the distribution coefficients, D. The percentage extraction was calculated from the distribution coefficient as follows:

$$\% E = \frac{100 D}{D + 1}$$

CHAPTER V

LIQUID-LIQUID EXTRACTION STUDIES OF RARE EARTHS WITH 2-ETHYLHEXYL-3-PENTADECYLPHENYL PHOSPHORIC ACID

5.1 INTRODUCTION

Synthesis of novel and specific organic complexing agents often leads to the development of new separation processes for aqueous metal ions. There are not many recent reports on the synthesis of newer reagents for the extraction of rare earths. Recently, studies on the synthesis of octyl phosphonic acid mono-octyl esters and their structure reactivity relationship in lanthanide extraction was investigated by Chengye et al[187]. The effect of the structure of the alkyl group in the molecule of alkyl phosphonic acid monoalkyl ester on the separation abilities of lanthanides, viz. lanthanum, europium and lutetium was studied. The steric effect and the influence of isomerization of ester alkyl group on the extraction ability were investigated. It was concluded that strengthening of the isomerization of the ester alkyl group results in lower extraction ability of the reagent.

Konde et al[188] have synthesised a new reagent didodecyl phosphoric acid and determined the extraction equilibrium constants for samarium, europium and gadolinium. The separation factors between these metals were also calculated to compare with other known extractants. Gastrone et al[189] have shown that the number of bridging carbons between the phosphoryl (P=O) group and carbamoyl group (C=O) influences the electron density of the two donor groups and thereby the metal ion extraction properties. Myaseodov et al[190] have examined the effect of alkylation upon the bridging carbon of the carbamoyl methyl phosphine oxide class of extractants. It was observed that there is decrease in extraction capacity with an increase in the hardness of the donor groups. Musikas[191] has reported that bridging carbon alkylation of diamide extractants improves the solubility compared to the parent extractant.

Asha Jain et al[33] have reported the extraction of lanthanides using mono-2-ethylhexyl phosphoric acid. They observed that alkyl aryl phosphoric acids possess better extraction characteristics compared to the mono and di-2-ethylhexyl phosphoric acids.

Most of the studies on solvent extraction utilize well known commercial acidic organophosphorus extractants like DEHPA[34-39] and EHEHPA[56-59]. The effect on extraction of the rare earths by the introduction of a 3-pentadecylphenyl group in DEHPA by replacing one of the 2-ethylhexyl groups was investigated. The retention of one 2-ethylhexyl group increases the solubility of the extractant. Such sterically hindered acidic organo phosphorus compound is expected to have high selectivity in rare earth extraction. So one of this type of compounds viz. 2-ethylhexyl -3-pentadecylphenyl phosphoric acid (EPPA) was synthesised as described in chapter 2.

This chapter deals with the extraction studies of rare earths using the newly synthesised reagent EPPA (2-ethylhexyl-3-pentadecylphenyl phosphoric acid) in toluene and MIBK as diluents. The nature of extracting species was evaluated and extraction capabilities of the new reagent EPPA was compared with other commercially well known acidic organophosphorus acids like DEHPA and EHEHPA under identical conditions.

5.2 RESULTS

5.2.1 Effect of 2-ethylhexyl-3-pentadecylphenyl phosphoric acid (EPPA) concentration

Toluene as diluent

The dependence of the extraction of lanthanum(III), europium(III) and lutetium(III) (representative of light, middle and heavy rare earths) from 0.1 M hydrochloric acid solution was investigated as a function of EPPA concentration. The concentration of EPPA used was 0.03-0.08 M for lanthanum(III), 0.01-0.03 M for europium(III) and 0.0015-0.002 M for lutetium(III) in toluene. The values of percent extraction ranges from 23.08 to 78.82 in the case of lanthanum(III), from 16.67 to 91.67 in the case of europium(III) and from 28.57 to 90.96 in the case of lutetium(III). Fig. 5.1 shows the plot of log D against log (EPPA) which is linear with a slope nearly equal to 3 for all the elements.

MIBK as diluent

The dependence of extraction of lanthanum(III), europium(III) and lutetium(III) from 0.1 M hydrochloric acid was

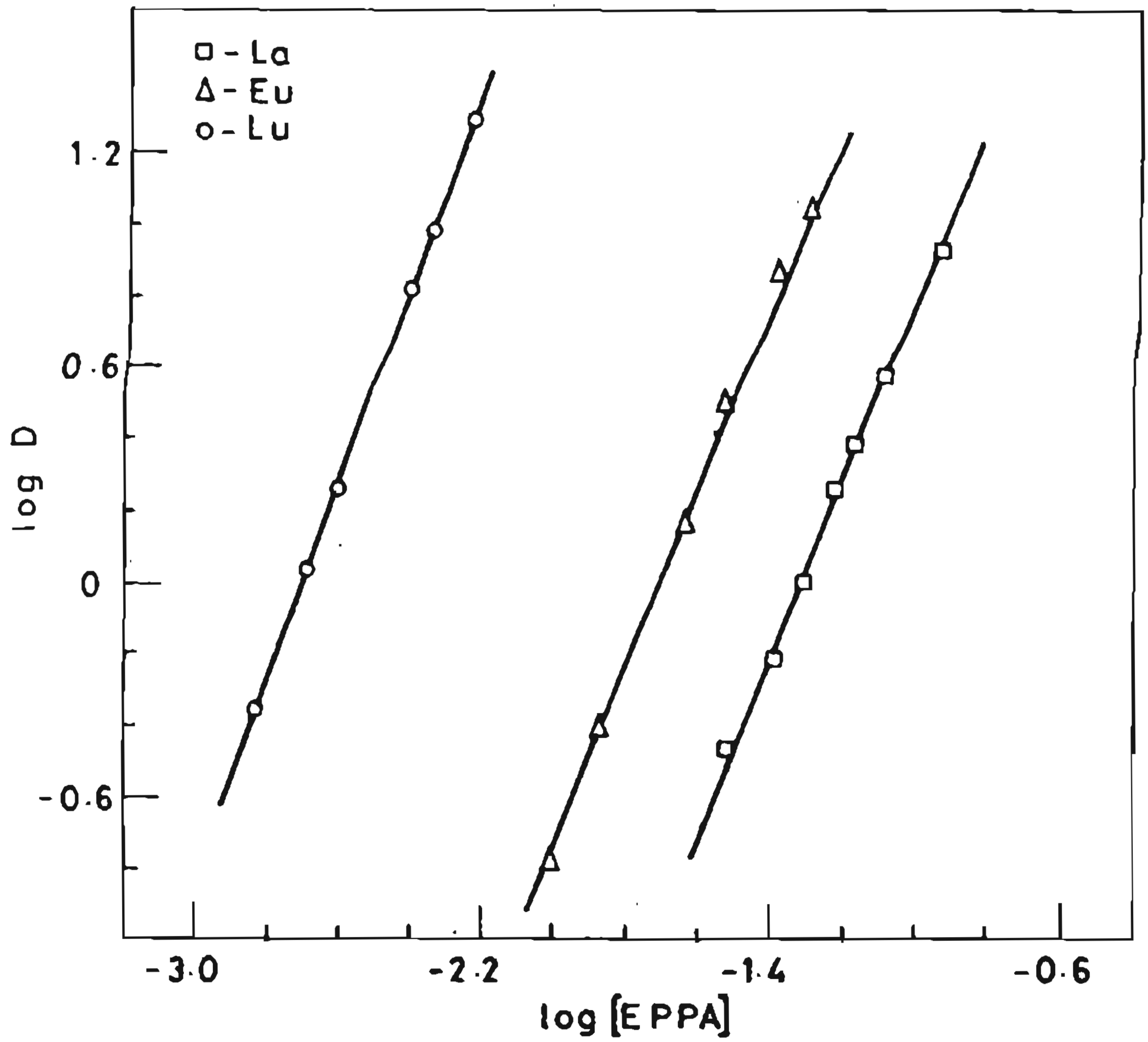


Fig. 5.1: Plot of log D vs log [EPPA] during the extraction of Lanthanum(III), Europium(III) and Lutotium(III) in presence of 0.1 M HCl into toluene

also investigated using MIBK as diluent. The concentration of EPPA used was 0.12-0.22 M for lanthanum(III), 0.076-0.14 M for europium(III) and 0.018 to 0.028 M for lutetium(III) in MIBK. The extraction increases with increase in concentration of EPPA for all the three elements. The percent extraction values range from 23.15 to 66.65 for lanthanum(III), from 24.60 to 72.41 for europium(III) and from 24.01 to 62.50 for lutetium(III). The plot of log D versus log [EPPA] using MIBK as diluent from hydrochloric acid solution is shown in Fig. 5.2. The plot is linear with a slope equal to three for all the three elements.

5.2.2 Effect of acid concentration

Toluene as diluent

The effect of H^+ concentration over the range 0.05 to 0.5 M at a constant concentration of chloride from a mixture of HCl and LiCl were studied for lanthanum(III), europium(III) and lutetium (III) using toluene as diluent. The concentrations of EPPA in toluene used in these studies were 0.08 M for lanthanum(III), 0.025 M for europium(III) and 0.01 M for lutetium(III). The extraction decreases with increase in H^+ concentration and was negligible at about 0.5 M hydrochloric acid. The percent extraction values obtained were found to range from 95.19 to 12.28 for lanthanum(III), from 88.33 to 0.06 for europium(III) and from 89.71 to 36.71 for lutetium(III). The plot of log D vs log $[H^+]$ from hydrochloric acid solution using toluene as diluent is shown

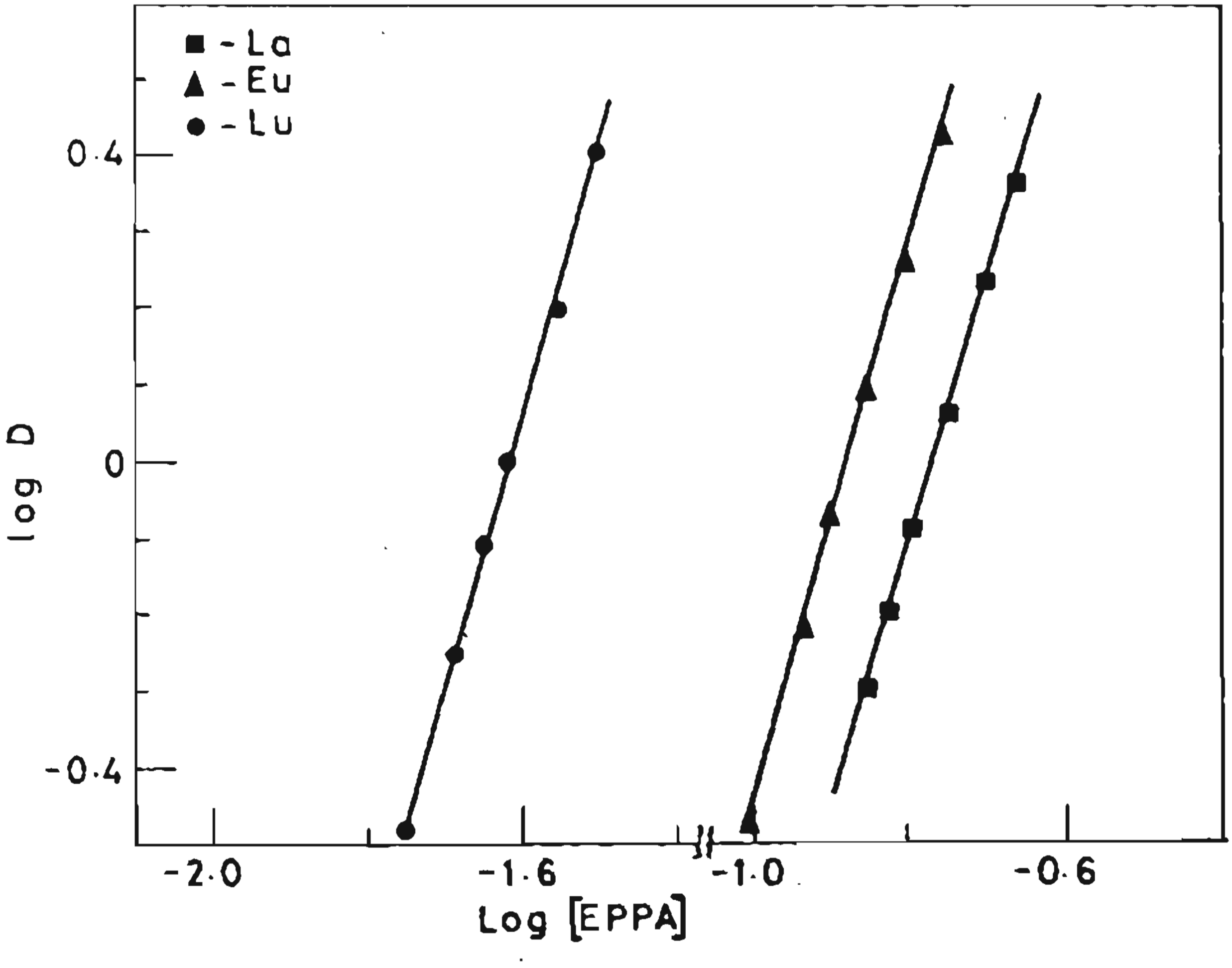


Fig. 5.2: Plot of log D vs log [EPPA] during the extraction of Lanthanum(III), Europium(III) and Lutetium(III) in presence of 0.1 M HCl into MIBK

in Fig. 5.3. The plot is linear with a slope equal to 3 for all the three elements.

MIBK as diluent

The effect of H^+ concentration over the range 0.05 to 0.5 M at a constant concentration of chloride using MIBK as diluent could not be done because the extraction decreases very drastically from 0.05 to 0.5 M. The percent extraction was too less to calculate the slope of log D vs log $[H^+]$ plots.

5.2.3 **Effect of metal ion concentration**

Toluene as diluent

The effect of varying the metal ion concentration on the extraction of lanthanum(III), europium(III) and lutetium(III) from 0.1 M hydrochloric acid solution using EPPA in toluene as diluent was studied. The molarities of EPPA used were 0.05 M for lanthanum(III), 0.02 M for europium and 0.002 M for lutetium(III). The extraction decreases slightly with increase in the initial metal ion concentration. A plot of the logarithm of equilibrium organic phase metal concentration against the log of equilibrium aqueous phase metal concentration is linear with a slope nearly equal to unity (Fig. 5.4).

MIBK as diluent

The effect of varying the metal ion concentration on the

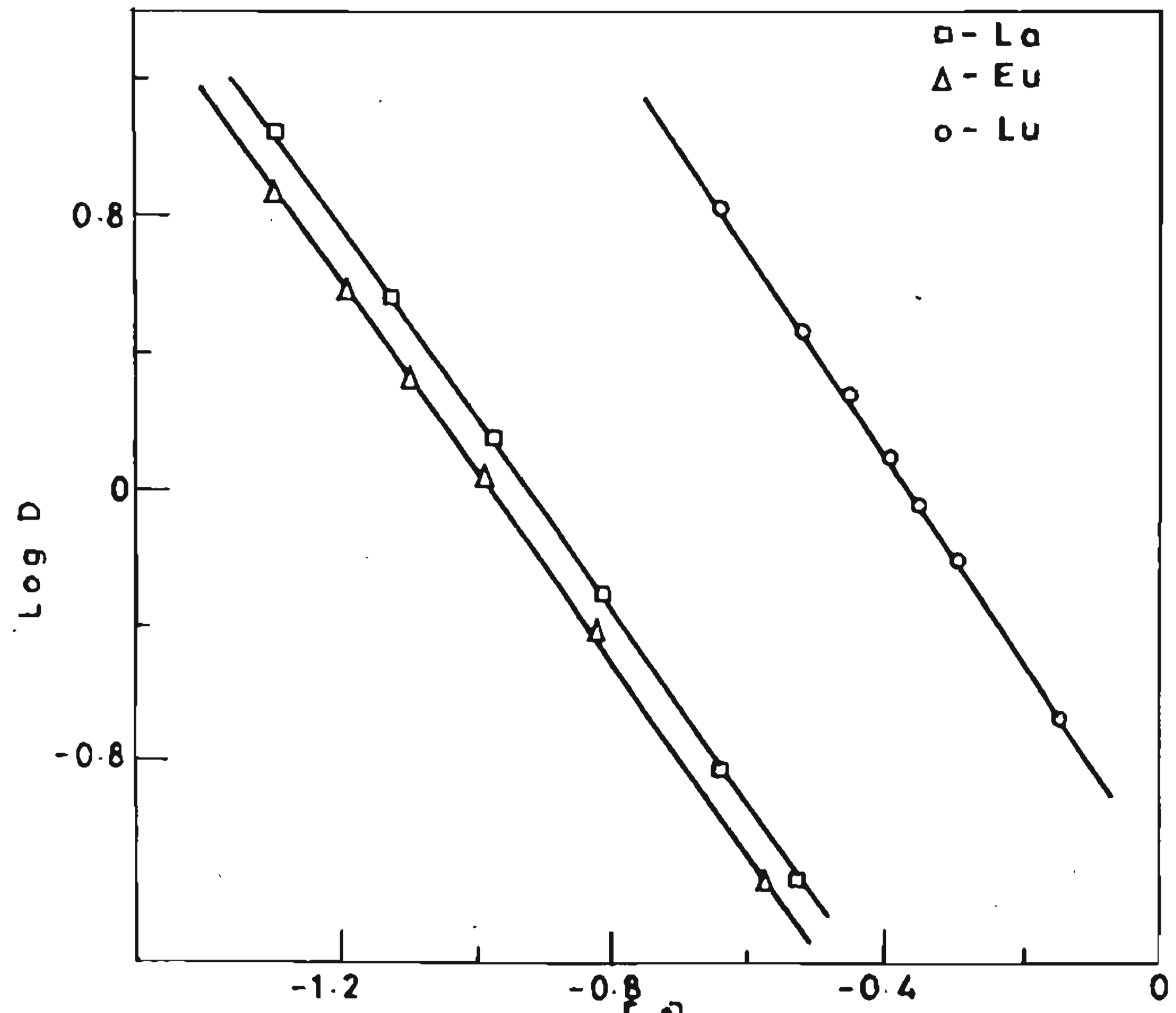


Fig. 5.3: Plot of log D vs log $[H^{+1}]$ during the extraction of Lanthanum(III), Europium(III) and Lutetium(III) with 0.08, 0.025 and 0.01 M EPPA respectively in toluene using HCl + LiCl mixtures

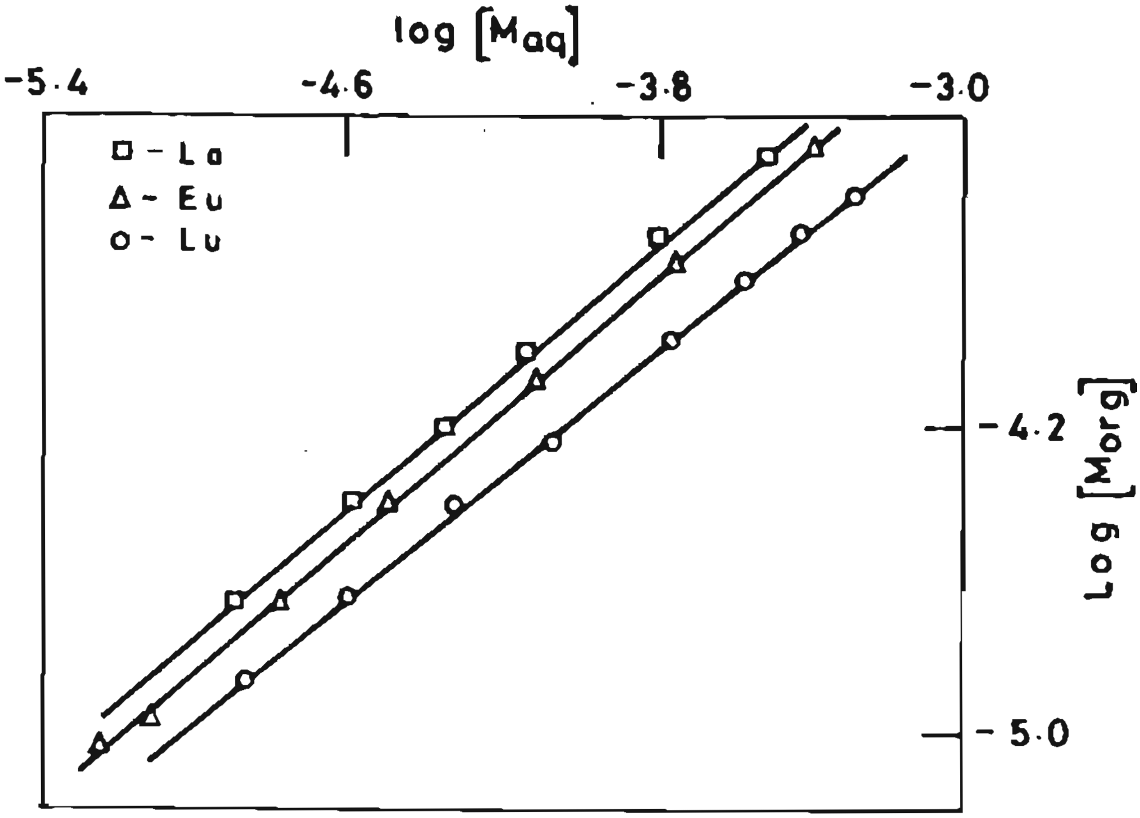


Fig. 5.4: Effect of metal ion concentration on the extraction of Lanthanum(III), Europium(III) and Lutetium(III) from 0.1 M HCl medium by EPPA (0.05 M for Lanthanum(III), 0.2 M for Europium(III) and 0.002 M for Lutetium(III)) in toluene

extraction of lanthanum(III), europium(III) and lutetium(III) from 0.1 M HCl by EPPA in MIBK as diluent was studied. The concentrations of EPPA in MIBK used were 0.18 M for lanthanum(III), 0.15 M for europium(III) and 0.025 M for lutetium(III). The slope of log-log plot (Fig. 5.5) of equilibrium organic phase metal concentration to equilibrium aqueous phase metal concentration was found to be nearly equal to one.

5.2.4 Dependence of extraction on the nature of solvents

The effect of various diluents on the extraction of lanthanum(III), europium(III) and lutetium(III) from 0.1 M hydrochloric acid using EPPA was studied. The concentrations of EPPA in these studies were 0.05 M for lanthanum(III), 0.02 M for europium(III) and 0.002 M for lutetium(III) in various solvents. The results obtained are summarized in Table 5.1. It was also observed that the rare earths are not extracted by pure solvents under the present experimental conditions.

5.2.5 Effect of time of equilibrium

Experiments were carried out to study the rate of the extraction of lanthanum(III), europium(III) and lutetium(III) from 0.1 M hydrochloric acid by EPPA in toluene and MIBK. The concentrations of EPPA in toluene as diluent were 0.05 M for La(III) , 0.02 M for europium(III) and 0.002 M for lutetium(III). In the case of MIBK as diluent the concentrations of EPPA used were 0.2 M for lanthanum(III), 0.14 M for europium(III) and 0.024 M for lutetium(III). The results obtained are shown in Table 5.2.

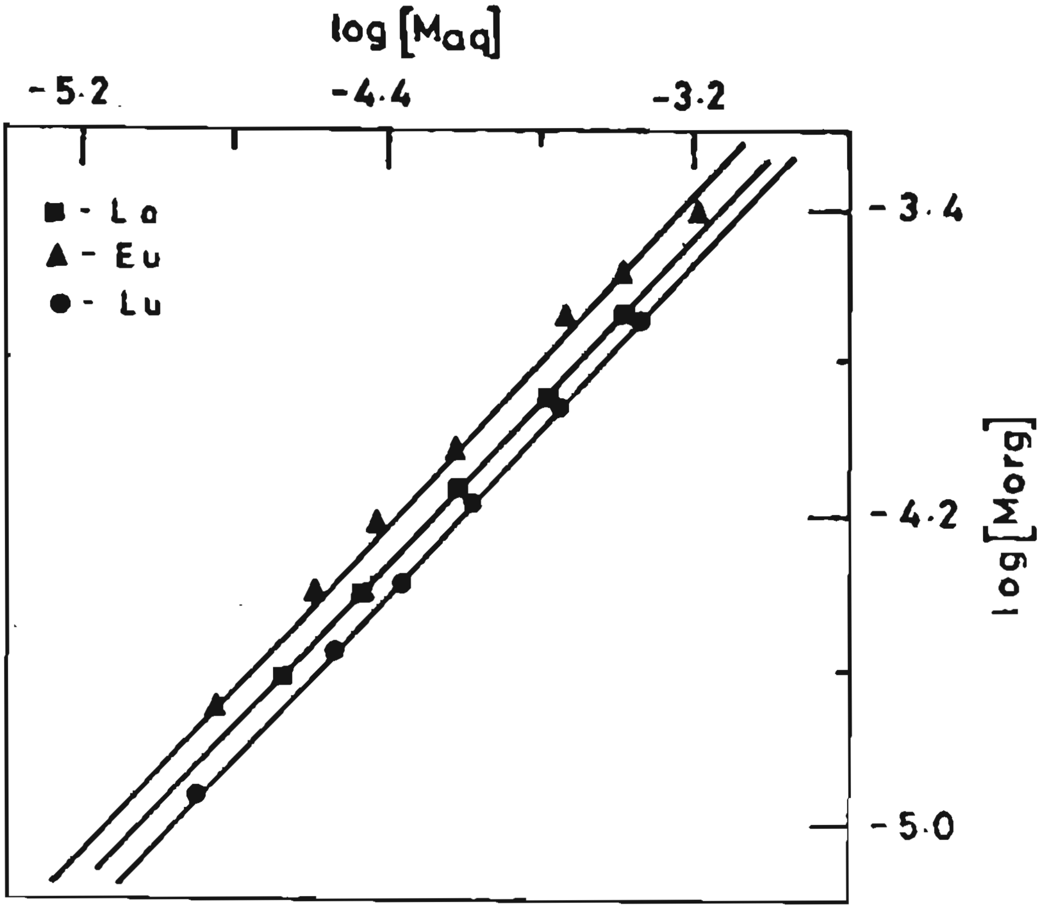


Fig. 5.5: Effect of metal ion concentration on the extraction of Lanthanum(III), Europium(III) and Lutetium(III) from 0.1 M HCl medium by EPPA (0.18 M for Lanthanum(III), 0.15 M for Europium(III) and 0.025 M for Lutetium(III) in MIBK

Table 5.1: Extraction of lanthanum(III), europium(III) and lutetium(III) with EPPA in different diluents from 0.1 M HCl solution

Diluent	Dielectric constant	Distribution coefficient		
		La	Eu	Lu
Nitrobenzene	34.8	0.82	0.69	0.91
MIBK	13.11	0.10	0.10	0.01
Chloroform	4.61	0.35	0.28	0.07
Toluene	2.36	1.00	1.6	1.30
Xylene	2.35	1.60	1.86	1.58
Benzene	2.26	0.82	0.97	0.92
Carbon tetrachloride	2.22	4.47	4.46	3.67

Table 5.2: Effect of time of equilibration on the extraction of lanthanum(III), europium(III) and lutetium(III) by EPPA in toluene and MIBK

Time of equilibration	Distribution coefficients					
	Toluene			MIBK		
	La	Eu	Lu	La	Eu	Lu
30 seconds	0.52	0.87	0.62	0.71	0.60	0.48
1 min	1.0	1.6	1.3	1.5	1.14	1.0
3 min	1.0	1.6	1.3	1.5	1.14	1.0
5 min	1.0	1.6	1.3	1.5	1.14	1.0

5.2.6 Extraction behaviour of other rare earths

Toluene as diluent

The extraction behaviour of lanthanum(III), praseodymium(III), neodymium(III), samarium(III), europium(III), gadolinium(III), holmium(III), ytterbium(III), lutetium(III) and yttrium(III) has been studied. The extraction abilities were determined at 0.002 M of EPPA using toluene as diluent from 0.1 M hydrochloric acid. The distribution coefficients calculated for Ln(III)-HCl-EPPA system using the two different concentrations of EPPA are shown in Table 5.3.

The separation factors between the rare earths using EPPA from 0.1 M hydrochloric acid are shown in Tables 5.4 and 5.5.

MIBK as diluent

The extraction behaviour of La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Ho(III), Yb(III), Lu(III) and Y(III) was investigated using MIBK as diluent. The extraction abilities were determined at two different concentrations i.e. 0.04 M and 0.1 M in MIBK from 0.1 M hydrochloric acid. The distribution coefficients obtained for the Ln(III)-HCl-EPPA system are shown in Table 5.6. .The separation factors between various rare earth elements from 0.1 M HCl are shown in Tables 5.7 and 5.8.

Table 5.3: Distribution coefficients of rare earths using Ln(III)-HCl-EPPA system with toluene as diluent

Reagent	Distribution coefficients									
	La	Pr	Nd	Sm	Eu	Gd	Ho	Yb	Lu	Y
0.1 M HCl + 0.002 M EPPA in toluene	<0.01	<0.01	<0.01	0.07	0.03	0.06	0.08	0.58	1.0	0.10
0.1 M HCl + 0.025 M EPPA in toluene	0.18	0.63	0.83	1.76	2.40	2.52	57.82	>99.99	>99.99	54.56

Table 5.4: Separation between the rare earths using
Ln(III)-HCl-EPPA system
(0.1 M HCl, 0.002 M EPPA in toluene)

	La	Pr	Nd	Sm	Eu	Gd	Ho	Yb	Lu	Y
La	-	∞	∞	∞	∞	∞	∞	∞	∞	∞
Pr	∞	-	∞	∞	∞	∞	∞	∞	∞	∞
Nd	∞	∞	-	∞	∞	∞	∞	∞	∞	∞
Sm	0	0	0	-	0.43	0.86	1.14	8.29	14.29	1.43
Eu	0	0	0	2.33	-	2.00	2.67	19.33	33.33	3.33
Gd	0	0	0	1.17	0.50	-	1.33	9.67	16.67	1.67
Ho	0	0	0	0.88	0.38	0.75	-	7.25	12.5	1.25
Yb	0	0	0	0.12	0.05	0.10	0.14	-	1.72	0.17
Lu	0	0	0	0.07	0.03	0.06	0.08	0.58	-	0.10
Y	0	0	0	0.7	0.3	0.6	0.8	5.8	10	-

Table 5.5: Separation factors between the rare earths using Ln(III)-HCl-EPPA (0.1 M HCl, 0.025 M EPPA in toluene)

	La	Pr	Nd	Sm	Eu	Gd	Ho	Yb	Lu	Y
La	-	3.50	4.61	9.78	13.33	14.00	321.22	∞	∞	303.11
Pr	0.29	-	1.32	2.79	3.81	4.00	91.78	∞	∞	86.60
Nd	0.22	0.76	-	2.12	2.89	3.04	69.96	∞	∞	65.74
Sm	0.10	0.36	0.47	-	1.36	1.43	32.85	∞	∞	31.00
Eu	0.08	0.26	0.35	0.73	-	1.05	24.09	∞	∞	22.73
Gd	0.07	0.25	0.33	0.70	0.95	-	22.94	∞	∞	21.65
Ho	0.003	0.01	0.01	0.03	0.04	0.04	-	∞	∞	0.94
Yb	∞	∞	∞	∞	∞	∞	∞	-	∞	∞
Lu	∞	∞	∞	∞	∞	∞	∞	∞	-	∞
Y	0.003	0.01	0.02	0.03	0.04	0.05	1.06	∞	∞	-

Table 5.6: Distribution coefficients of rare earths with Ln(III)-HCl-EPPA system with MIBK as diluent

Reagent	Distribution coefficients									
	La	Pr	Nd	Sm	Eu	Gd	Ho	Yb	Lu	Y
0.1 M HCl + 0.04 M EPPA in MIBK	<0.01	<0.01	<0.01	<0.01	0.05	0.06	0.12	4.67	7.16	0.23
0.1 M HCl + 0.1 M EPPA in MIBK	<0.01	0.14	0.25	0.29	0.33	0.51	5.94	52.99	43.50	21.00

Table 5.7: Separation factors between the rare earths using Ln(III)-HCl-EPPA (0.04 M EPPA in MIBK from 0.1 M HCl)

	La	Pr	Nd	Sm	Eu	Gd	Ho	Yb	Lu	Y
La	-	∞	∞	∞	∞	∞	∞	∞	∞	∞
Pr	∞	-	∞	∞	∞	∞	∞	∞	∞	∞
Nd	∞	∞	-	∞	∞	∞	∞	∞	∞	∞
Sm	∞	∞	∞	-	∞	∞	∞	∞	∞	∞
Eu	0	0	0	0	-	0.83	2.40	93.40	143.2	4.60
Gd	0	0	0	0	0.83	-	2.00	77.83	119.33	3.83
Ho	0	0	0	0	0.42	0.50	-	38.92	59.67	1.92
Yb	0	0	0	0	0.01	0.01	0.03	-	1.53	0.05
Lu	0	0	0	0	0.01	0.01	0.02	0.65	-	0.03
Y	0	0	0	0	0.22	0.26	0.52	20.30	31.13	-

Table 5.8: Separation factors between rare earths using Ln(III)-HCl-EPPA (0.1 M EPPA in MIBK from 0.1 M HCl)

	La	Pr	Nd	Sm	Eu	Gd	Ho	Yb	Lu	Y
La	-	∞	∞	∞	∞	∞	∞	∞	∞	∞
Pr	0	-	0.56	2.07	2.36	3.64	42.43	378.50	310.70	150.00
Nd	0	0.56	-	1.16	1.32	2.04	23.76	211.96	174.00	84.00
Sm	0	0.48	0.86	-	1.14	1.76	20.48	182.72	150.00	72.40
Eu	0	0.42	0.76	0.88	-	1.55	18.00	160.58	131.82	63.64
Gd	0	0.27	0.49	0.57	0.65	-	11.65	103.90	85.29	41.18
Ho	0	0.02	0.04	0.05	0.06	0.09	-	8.92	7.32	3.54
Yb	0	0.003	0.01	0.01	0.01	0.01	0.11	-	0.82	0.40
Lu	0	0.003	0.01	0.01	0.01	0.01	0.14	1.22	-	0.48
Y	0	0.01	0.01	0.01	0.02	0.02	0.28	2.52	2.07	-

5.2.7 Comparison with other organophosphorus acids

Toluene as diluent

The extraction efficiency of EPPA on the extraction of lanthanum(III), europium(III) and lutetium(III) from hydrochloric acid using toluene as diluent has been compared with other commercial acidic organophosphorus extractants like Di-2-ethylhexyl phosphoric cid (DEHPA) and 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester (DHEHPA). The concentrations of the reagents were maintained at two different molarities 0.002 M and 0.025M in toluene from 0.1 M HCl. The results are summarised in Table 5.9.

Table 5.9: Comparison of extraction capabilities of EPPA with DEHPA and EHEHPA in toluene

Reagent	Distribution coefficients					
	0.02 M Reagent			0.025 M Reagent		
	La	Eu	Lu	La	Eu	Lu
EPPA	<0.01	0.03	1.0	0.18	2.40	*
DEHPA	<0.01	<0.01	0.05	<0.01	0.03	39.82
EHEHPA	<0.01	<0.01	<0.01	<0.01	<0.01	0.24

* Quantitative extraction

MIBK as diluent

The extraction capabilities of EPPA on the extraction of lanthanum(III), europium(III) and lutetium(III) has been compared with commercial acidic organophosphorus extractants like DEHPA and EHEHPA from HCl solution using MIBK as diluent. The concentrations of EPPA used were 0.04 M and 0.1 M. The results are summarised in Table 5.10.

Table 5.10: Comparison of extraction efficiencies of EPPA with DEHPA and EHEHPA in MIBK from 0.1 M HCl

Reagent	Distribution ratios					
	0.04 M Reagent			0.1 M Reagent		
	La	Eu	Lu	La	Eu	Lu
EPPA	<0.01	0.05	7.16	<0.01	0.33	23.50
DEHPA	<0.01	<0.01	1.72	<0.01	<0.01	48.02
EHEHPA	<0.01	<0.01	0.34	<0.01	<0.01	8.8

5.3 DISCUSSIONS

5.3.1 Distribution of acid in the organic phase

The state of aggregation of EPPA was ascertained by Infrared absorption spectra. It was found that no band for the -OH in the vicinity of 2900-3500 cm^{-1} was observed. The absence of free -OH indicates hydrogen bonding which may be due to the association of EPPA molecules. From the ^{1}H NMR it was clear that the hydroxyl group of δ 12.1 exchanges for deuterium on D_2O exchange. This confirms the association of EPPA molecules in toluene or MIBK layer.

The association of EPPA molecules was further confirmed by vapour pressure osmometry. The observed molecular weight of EPPA was found to be 990 by vapour pressure osmometric measurements which is very close to twice the molecular weight of EPPA. Hence it is clear that EPPA is dimerised in toluene as $(HR)_2$ where HR is a EPPA molecule.

5.3.2 Extraction mechanism

The general mechanism of extraction of rare earths by an acidic organophosphorus extractant EPPA may be represented by the following general expression

$$Ln^{3+} + n\ (\overline{HR})_2 \rightleftharpoons \overline{Ln\ R_n(HR)_n} + nH^+$$

where Ln stands for the rare earth element and $(\overline{HR})_2$ refers to the dimer of the extractant in the organic phase. The extraction constant K_{ex} for the extraction process may be written as

$$K_{ex} = \frac{D . [H^+]^n}{[\overline{(HR)_2}]^n}$$

Taking logarithm and rearranging, the above equation takes the form

$$\log D = \log K_{ex} + n \log [\overline{(HR)_2}] - n \log [H^+]$$

By studying the distribution coefficient of a metal as function of $[\overline{(HR)_2}]$ and $[H^+]$, the composition of the extracted species may be determined.

5.3.3 Effect of EPPA concentration

The extraction of lanthanum(III), europium(III) and lutetium(III) from 0.1 M HCl increases with increase of EPPA concentration. The linear plot of log D against log (EPPA) has a slope of three indicating that three molecules of EPPA are involved in the extracted metal species using toluene.

Similarly the extraction of lanthanum(III), europium(III) and lutetium(III) from 0.1 M HCl solution using EPPA in MIBK increases with increase of EPPA concentration. Further the slope of three is obtained even in this case indicating the association of three molecules of the reagent with each of the extracted metal species.

5.3.4 Effect of H^+ concentration

The extraction of lanthanum(III), europium(III) and lutetium(III) decreases with increase of H^+ concentration. At a given total chloride ion concentration and reagent concentration under the experimental conditions the above equation simplifies to

$$\log D \propto n \log [H^+]$$

The plot of log D against log $[H^+]$ gives the number of H^+ ions released during the extraction of metal species. The corresponding slope is nearly -3 indicating that during the extraction of each metal species there is a release of three H^+ ions indicating that the extraction follows usual cation exchange mechanism.

5.3.5 Effect of metal concentration

The extraction of lanthanum(III), europium(III) and lutetium(III) decreases slightly with increase in the initial concentration of metal from 0.1 M HCl with EPPA in toluene and MIBK. The slope of log D against log of the initial metal concentration is zero for all the three elements. So there is a clear indication that the degree of polymerisation is the same in the two phases under the present experimental conditions. The plot of log of the equilibrium aqueous phase metal concentration against the log of the equilibrium organic phase metal concentration is linear with slope nearly equal to one indicating the existence of mononuclear species $\overline{LnR_3(HR)_3}$.

5.3.6 Dependence on the nature of solvent

The extraction behaviour of lanthanum(III), europium(III) and lutetium(III) from 0.1 M HCl with EPPA differs with various diluents. The extraction depends not only on the dielectric constant but on many other factors such as dipole moment[184-185] and electrostatic interactions between the complex and dipole of the solvent molecules[186] and work needed to form a hole in the organic medium as described in chapter 4.

5.3.7 Effect of time of equilibration

The extraction of lanthanum(III), europium(III) and lutetium(III) by EPPA in toluene and MIBK reaches equilibrium within 1 minute of shaking and remains same on further increase to 5 min. Hence it was decided to equilibrate the aqueous and organic phases for 5 min to ensure complete equilibrium.

5.3.8 Extraction behaviour of other rare earths

The extraction of rare earths by EPPA in toluene and MIBK is very selective for heavy rare earths especially ytterbium(III) and lutetium(III). The extraction of rare earths increases with increase in atomic number from lanthanum to lutetium. From the separation factors it is clear that yttrium behaves like a heavy rare earth and lies between holmium and ytterbium during the extraction with EPPA in toluene or MIBK from 0.1 M HCl media.

5.3.9 Comparison with other organophosphorus acids

The extraction of lanthanum(III), europium(III) and lutetium(III) by EPPA in toluene and MIBK are compared with DEHPA and EHEHPA. It is clear from the results that EPPA is a better extractant for heavy rare earths especially ytterbium(III) and lutetium(III) than DEHPA and EHEHPA.

5.4 EXPERIMENTAL

5.4.1 Apparatus

IR spectra were recorded on a Perkin Elmer Model 299 B IR spectrophotometer. IR of EPPA was taken in dilute solutions of toluene and MIBK in demountable KBr cell of 0.25 mm thickness.

The molecular weight was determined using Knauer vapour pressure osmometer Nr II.

A Hitachi 220 double beam microprocessor controlled molecular absorption spectrophotometer was used for measuring the absorbances. An ELICO LI - 120 digital pH meter was used for the pH measurements.

5.4.2 Reagents

Stock solutions of the lanthanides were prepared from their oxides (Rare Earth Products, Cheshire, U.K., 99.99%) by dissolving in 2 cm^3 of 1:1 hydrochloric acid and diluting to 100 ml.

Ammonium acetate buffer (pH 7.5) was prepared by dissolving 19.25 g in 250 cm^3 of water and adjusting the pH to 7.5 with HCl/NaOH.

Arzenazo-I (Fluka, Switzerland) was prepared by dissolving 25 mg of the reagent in 250 cm^3 of water.

All the other chemicals were of analytical reagent grade and were used without further purification.

5.4.3 The extraction conditions

Solvent extraction measurements were made employing aqueous solution of 0.05 to 1 M HCl. Except where stated otherwise, the initial concentration of lanthanum(III) was 7.20×10^{-5} M, that of europium(III) 6.58×10^{-5} M and that of lutetium(III) 5.82×10^{-5} M.

Solutions of EPPA used varied from 0.0015 M to 0.08 M with toluene as diluent and 0.018-0.220 M with MIBK as diluent. In all extraction systems the aqueous and organic phases were of equal volumes.

5.4.4 Extraction equilibrium procedure

Distribution coefficients were determined by shaking equal volumes of aqueous and organic phase (10 cm^3) for 5 minutes in a 60 cm^3 separating funnel at 303 ± 1 K (extraction equilibrium was attained in 2 minutes). The distribution coefficient D is given by

$$D = \frac{(\overline{Ln})}{(Ln)}$$

where $(\overline{Ln})$ and (Ln) are the concentration of the rare earth in the organic and aqueous phases respectively.

5.4.5 Method of estimation of rare earths

After extraction, the rare earth in the aqueous phase was estimated spectrophotometrically by complexing with Arzenazo I. After allowing the phases to settle, a 5 cm^3 aliquot of the aqueous phase was pipetted into a 25 cm^3 beaker and 1 cm^3 of ammonium acetate buffer and 5 cm^3 of Arzenazo I, were added for the determination of metal ion. After adjusting the pH to 7.5 ± 0.1 the solutions were transferred to 25 cm^3 volumetric flasks and made upto the mark.

The absorbances of the solutions were measured at 575 nm and the rare earth concentrations were computed from the respective calibration graphs. The rare earth concentration in the organic phase was obtained by difference. The concentration values were used to obtain the distribution coefficients, D. The percentage extraction was calculated from the distribution coefficient as follows:

$$\% E = \frac{100 D}{D + 1}$$

CHAPTER VI

LIQUID-LIQUID EXTRACTION STUDIES OF RARE EARTHS WITH BUTYL-3-PENTADECYLPHENYL PHOSPHORIC ACID

6.1 INTRODUCTION

Considerable interest has been shown recently in the development of better separation methods for the trivalent actinide and lanthanide elements. Liquid-liquid extraction methods hold much promise for solving some of the current problems in the actinide-lanthanide element field. Zheng et al[79] have compared the extractants like DEHPA, versatic acid and naphthenic acid for the separation of selected rare earths viz. lanthanum(III), dysprosium(III), yttrium(III) and yttrium(III). Ma et al[192] reported an average SF for the REE as high as 3.0 with EHEHPA as extractant. Their thermodynamic study of the extraction process showed no temperature effect for La, Ce, Pr and Nd. In addition EHEHPA has been shown to overcome such problems as high acidity required in extraction and stripping and emulsion formation which are dominant in the extraction with DEHPA. Cheng et al[193] have studied the extraction of rare earths from HCl with EHEHPA in molten paraffin wax as solvent.

Yuan et al[194] have evaluated mono-alkyl isopropyl phosphonic acids for the solvent extraction of the rare earth elements. A variety of straight or branched alkyl groups were introduced in these phosphonic acids. They obtained average separation factors ranging from 2.04-2.93, and observed that these extractants with a β substituted ester alkyl group showed high K_D values which were depressed by about two orders of magnitude with branching at the α position.

Jagodic et al [195] found that N-aryl substituted mono esters of α-aminophosphonic acid derivatives showed superior extractive properties over the N-alkyl substituted phosphonates. They synthesized and tested two extractants in the N-aryl group viz., α-monooctyl anilinobenzyl phosphonic acid (MO[ABP]) and mono octyl α-(2-carboxyanilino) benzyl phosphonic acid (MO[CABP]). MO[ABP] shows good extraction characteristics for tri-, tetra- and polyvalent metal ions while MO[CABP] exhibits particular extraction efficiency for divalent ions [196]. A comparison of both extractants in the extraction of La(III) and Eu(III) revealed that MO[CABP] is a better extractant than MO[ABP]. This was attributed to the availability of COOH to form hydrogen bonds between the extractant and extracted species in the organic phase as well as the greater solubility of MO[CABP] in water [197].

Bidentate phosphonates with composition $R'C(O)CH_2\ P(O)(OR)_2$ (β Keto phosphonates) have also been evaluated for liquid-liquid extraction of rare earths [198-200]. Alstad et al [201] have studied the extraction of rare earth elements with dibutylphenacyl phosphonate (HDB[PP]).

This chapter discusses the extraction studies of rare earths from weakly acidic solutions using a newly synthesised reagent butyl-3-pentadecylphenyl phosphoric acid (BPPA). The nature of extracting species was determined and the extraction behaviour of BPPA was compared with well known acidic organophosphorus acids under identical conditions. In addition, BPPA was compared with the other alkyl aryl phosphoric acids synthesised viz. IPPA and EPPA. The effect of steric hindrance on the extraction of the rare earths was considered.

6.2 RESULTS

6.2.1 Effect of butyl-3-pentadecylphenyl phosphoric acid (BPPA) concentration

The effect of varying the concentration of BPPA in MIBK on the *extraction behaviour of lanthanum(III)*, europium(III) and lutetium(III) (representative of light, middle and heavy rare earths) was investigated. The concentration of BPPA used were 0.07 M to 0.01 M for lanthanum(III), 0.08 to 0.02 M for europium(III) and 0.018-0.006 M for lutetium(III). The pH was maintained at 1.8 for lanthanum(III), 1.65 for europium(III) and 1.25 for lutetium(III) for these studies. The values of percent extraction range from 95.01 to 2.53 in case of lanthanum(III), from 91.67 to 13.04 in the case of europium(III) and from 95.92 8.17 for lutetium(III). The plot of log D against log (BPPA) for lanthanum(III), europium(III) and lutetium(III) is shown in Fig.6.1. The plot is linear with a slope nearly equal to three suggesting the involvement of three molecules of the reagent in the extracted species.

6.2.2 Effect of pH

The *effect of pH on the extraction of lanthanum(III)*, europium(III) and lutetium(III) using BPPA in MIBK was studied. *The pH ranges studied varied from 1.0 to 1.8.* The concentration of BPPA in MIBK used in these extraction studies were 0.05 M for lanthanum(III) and europium(III) and 0.01 M for lutetium(III).

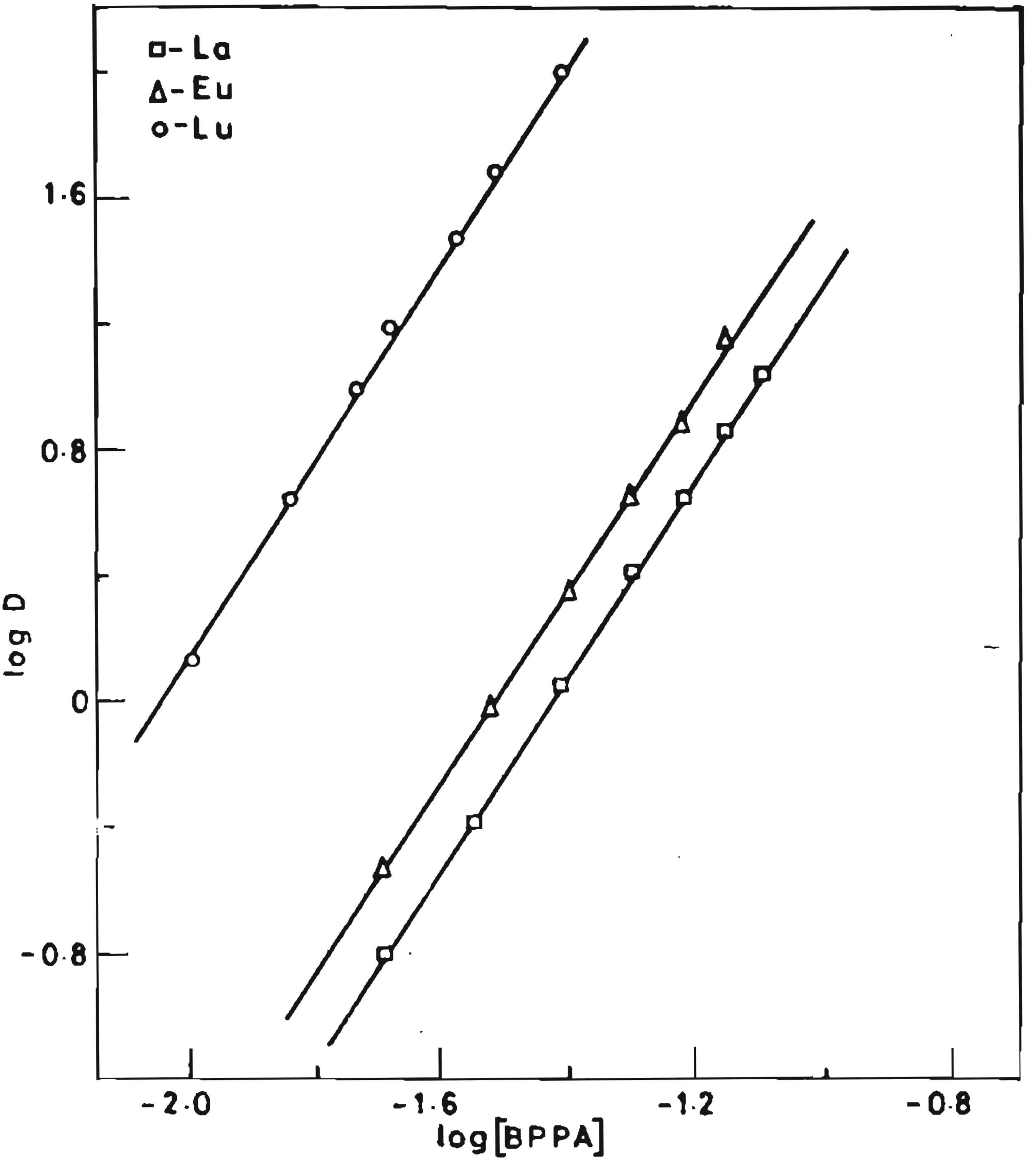


Fig. 6.1: Plot of log D vs log [BPPA] during the extraction of Lanthanum(III), Europium(III) and Lutetium(III) at various pHs (1.8 for Lanthanum(III), 1.6 for Europium(III) and 1.25 for Lutetium(III) into MIBK

The percent extraction ranges from 39.96 to 96.67 in case of lanthanum(III), from 18.70 to 58.33 in case of europium(III) and from 4.76 to 92.86 in the case of lutetium(III). The slope of the plot of log D against pH (Fig. 6.2) is linear with a slope equal to three suggesting the release of 3 H^+ ions.

6.2.3 Effect of metal ion concentration

The results of varying the metal ion concentration on the extraction of lanthanum(III), europium(III) and lutetium(III) using BPPA in MIBK as diluent were studied. The concentration of BPPA used were 0.03 M for lanthanum(III) and europium(III) and 0.01 M for lutetium(III). The equilibrium pH of the aqueous phases was 1.8 for lanthanum(III), 1.7 for europium(III) and 1.3 for lutetium(III). The extraction decreases slightly with increase in the initial concentrations of the metal. The slope of the log-log plot (Fig. 6.3) of the equilibrium organic phase metal concentration against equilibrium aqueous phase metal concentration is linear with a slope nearly equal to one.

6.2.4 Dependence of extraction on the nature of solvents

The effect of various diluents on the extraction of lanthanum(III), europium(III) and lutetium(III) at pH 1.3 was investigated. The solvents like CCl_4, $CHCl_3$, xylene , toluene, nitrobenzene, benzene etc. were tried. But due to emulsion formation the extractions could not be carried out.

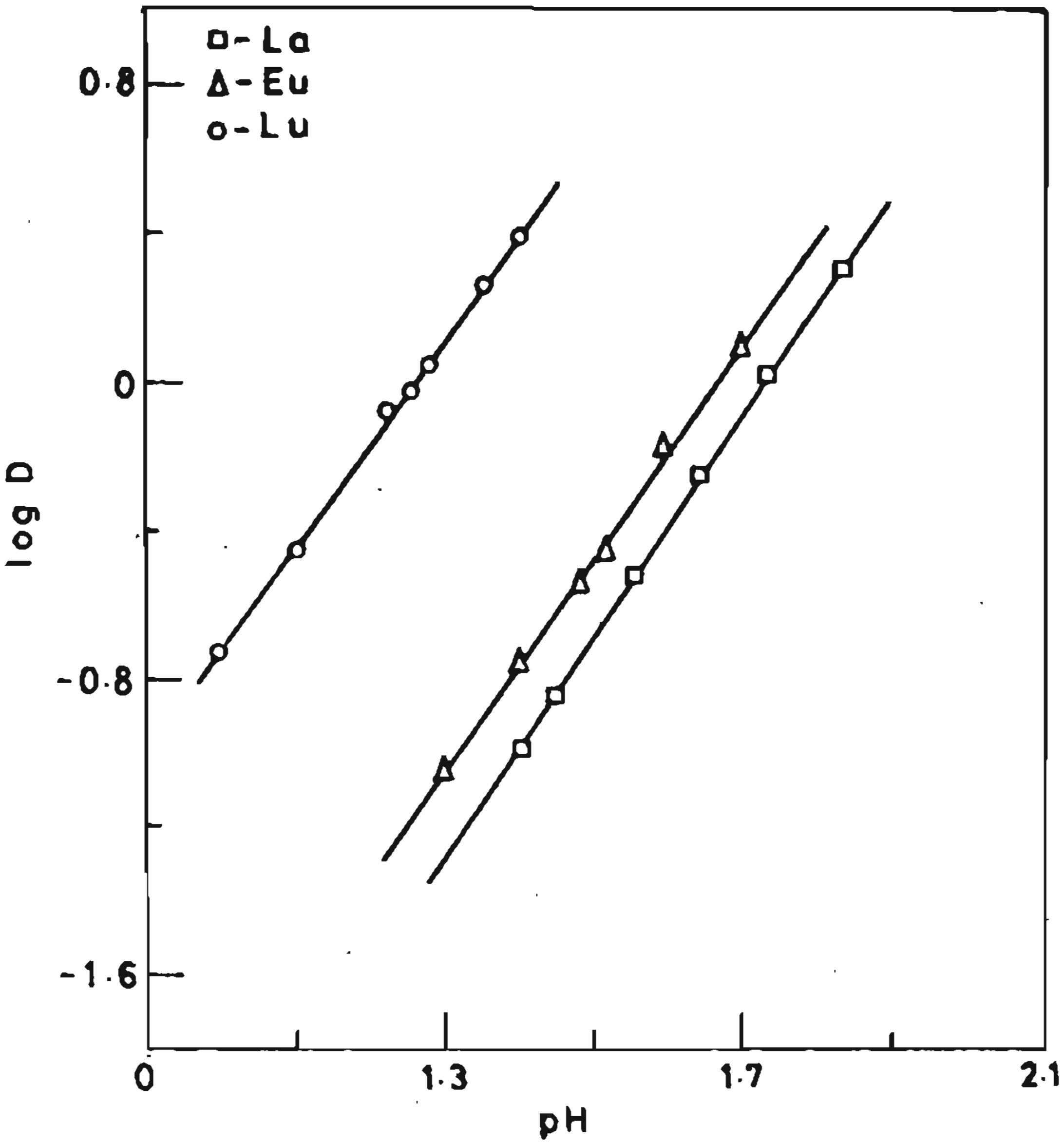


Fig. 6.2: Plot of log D vs pH during the extraction of Lanthanum(III), Europium(III) and Lutetium(III) by BPPA (0.05 M for Lanthanum(III) and Europium(III) and 0.01 M for Lutetium(III) respectively in MIBK

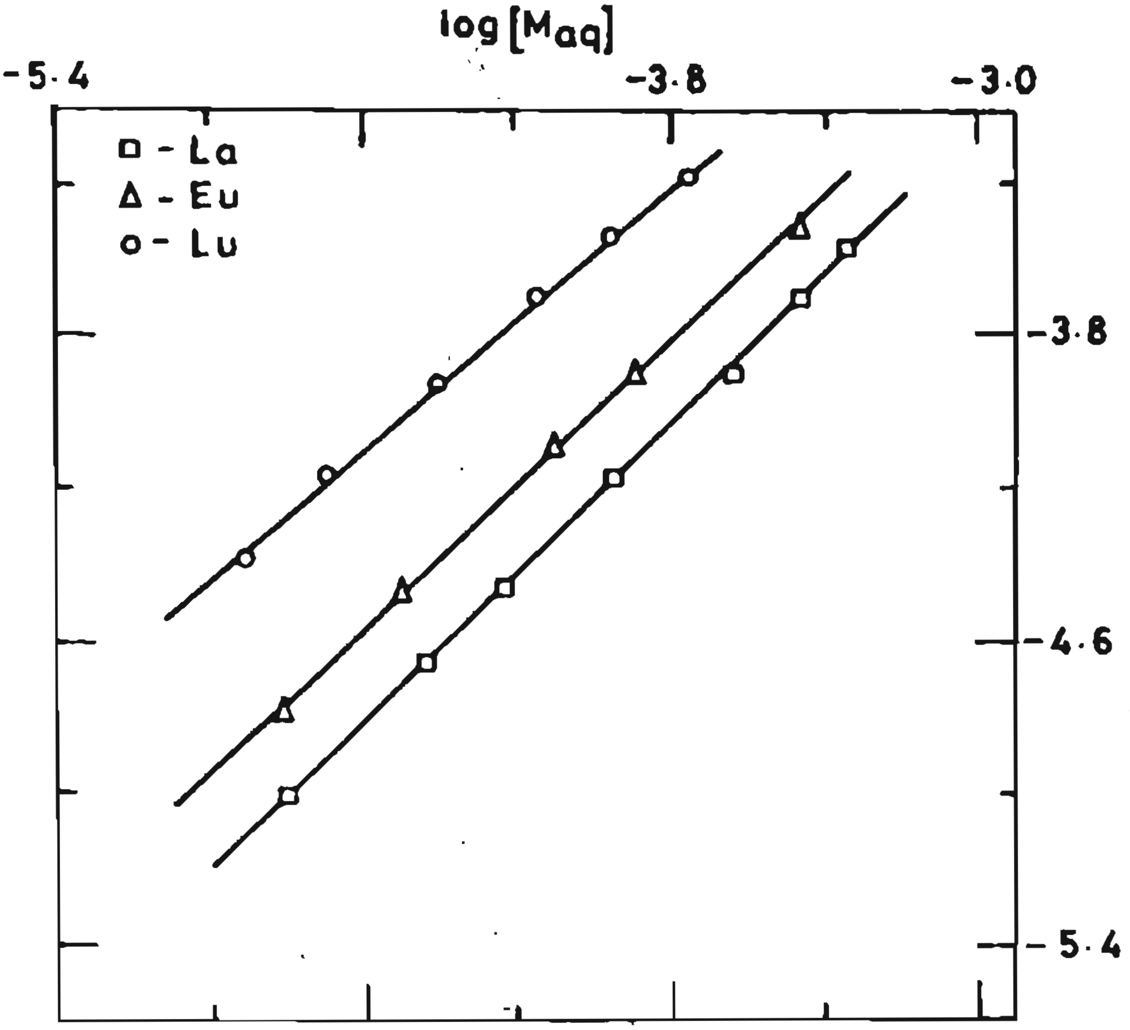


Fig. 6.3: Effect of metal ion concentration on the extraction of Lanthanum(III), Europium(III) and Lutetium(III) at a pH of 1.8 M for Lanthanum(III), 1.7 for Europium(III) and 1.3 for Lutetium(III) using BPPA (0.03 M for Lanthanum(III) and Europium(III) and 0.01 M for Lutetium(III) in MIBK

6.2.5 Effect of time of equilibration

Experiments were carried out to study the rate of extraction of lanthanum(III), europium(III) and lutetium(III) by BPPA in MIBK. The concentrations of BPPA used were 0.04 M for lanthanum(III), 0.04 M for europium(III) and 0.01 M for lutetium(III). The pH used were 1.8 for lanthanum(III), 1.65 for europium(III) and 1.25 for lutetium(III). The results obtained are shown in Table 6.1.

Table 6.1: Effect of time of equilibration on the extraction of lanthanum(III), europium(III) and lutetium(III) by BPPA in MIBK

Time of equilibration	Distribution coefficients		
	La	Eu	Lu
30 sec.	0.59	0.46	0.69
1 min.	1.23	0.91	1.33
3 min.	1.24	0.91	1.33
5 min.	1.24	0.91	1.33

6.2.6 Extraction abilities of other rare earths

The extraction behaviour of lanthanum(III), praseodymium(III), neodymium(III), samarium(III), europium(III), gadolinium(IIII), holmium(III), ytterbium(III), lutetium(III) and yttrium(III) has been studied. The extraction abilities were determined at two different pH conditions i.e. pH 1.3 and 1.8. The concentration of BPPA was maintained at 0.03 M in MIBK. The distribution coefficients calculated for the rare earths for Ln(III) - pH 1.3 and pH 1.8 - BPPA are shown in Table 6.2. The separation factors between the rare earths using BPPA in MIBK at pH 1.3 and pH 1.8 are shown in Table 6.3 and 6.4 respectively.

Table 6.2: Distribution coefficient of rare earths using BPPA in MIBK

Reagent	Distribution coefficients									
	La	Pr	Nd	Sm	Eu	Gd	Ho	Yb	Lu	Y
pH 1.3 0.03 M BPPA	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.08	2.78	11.25	0.12
pH 1.8 0.03M BPPA	0.97	3.00	3.90	4.80	12.33	13.50	22.60	26.20	>99.99	23.50

Table 6.3: Separation factors between the rare earths using 0.03 M BPPA in MIBK at pH 1.3

	La	Pr	Sm	Eu	Gd	Ho	Yb	Lu	Y
La	-	∞	∞	∞	∞	∞	∞	∞	∞
Pr	∞	-	∞	∞	∞	∞	∞	∞	∞
Sm	∞	∞	-	∞	∞	∞	∞	∞	∞
Eu	∞	∞	∞	-	∞	∞	∞	∞	∞
Gd	∞	∞	∞	∞	-	∞	∞	∞	∞
Ho	0	0	0	0	0	-	34.75	140.63	1.5
Yb	0	0	0	0	0	0.03	-	4.05	0.04
Lu	0	0	0	0	0	0.01	0.25	-	0.01
Y	0	0	0	0	0	0.67	23.17	93.75	-

Table 6.4: Separation factors between the rare earths using 0.03M BPPA in MIBK at pH 1.8

	La	Pr	Sm	Eu	Gd	Ho	Yb	Lu	Y
La	-	3.09	4.95	12.71	13.92	23.30	27.01	∞	24.23
Pr	0.32	-	1.60	4.11	4.5	7.53	8.73	∞	7.83
Sm	0.20	0.63	-	2.57	2.81	4.71	5.46	∞	4.90
Eu	0.08	0.24	0.39	-	1.09	1.83	2.12	∞	1.91
Gd	0.07	0.22	0.36	0.91	-	1.67	1.94	∞	1.74
Ho	0.04	0.13	0.21	0.55	0.60	-	1.16	∞	1.04
Yb	0.04	0.11	0.18	0.47	0.52	0.86	-	∞	0.90
Lu	∞	∞	∞	∞	∞	∞	∞	-	∞
Y	0.04	0.13	0.20	0.52	0.57	0.96	1.11	∞	-

6.2.7 Comparison with other organophosphorus acids

The extraction efficiency of BPPA on the extraction of lanthanum(III), europium(III) and lutetium(III) was compared with other commercial acidic organophosphorus extractants like DEHPA and EHEHPA. The comparisons were done at two pH conditions i.e. pH 1.3 and 1.8. The concentration of BPPA used was 0.03 M. The results obtained are presented in Table 6.5.

Table 6.5: Comparison of extraction efficiency of BPPA with DEHPA and EHEHPA

Reagent	Distributionn coefficients		
	La	Eu	Lu
PH 1.8			
BPPA	0.97	12.33	*
DEHPA	< 0.01	0.24	*
EHEHPA	< 0.01	0.28	*
pH 1.3			
BPPA	< 0.01	< 0.01	11.25
DEHPA	< 0.01	0.04	0.14
EHEHPA	< 0.01	0.11	0.15

* Quantitative extraction

6.2.8 Comparison with other alkyl aryl phosphoric acids

The reagent butyl-3-pentadecylphenyl phosphoric acid (BPPA) was compared with other alkyl aryl phosphoric acids synthesised earlier viz. isopropyl-3-pentadecylphenyl phosphoric acid (IPPA) and 2-ethylhexyl-3-pentadecylphenyl phosphoric acid (EPPA). The extraction efficiencies were compared at two different pH conditions 1.3 and 1.8. The concentration of the extractant was maintained at 0.02 M. The results obtained are summarised in Table 6.6. The extraction sequence lies in the order BPPA > EPPA > IPPA.

Table 6.6: Comparison of extraction efficiencies of BPPA, EPPA and IPPA at concentration of 0.02 M

Reagent	pH 1.3			pH 1.8		
	La	Eu	Lu	La	Eu	Lu
BPPA	<0.01	0.24	15.33	0.28	2.00	*
EPPA	<0.01	0.08	0.56	0.09	0.22	*
IPPA	<0.01	<0.01	0.03	0.05	0.17	*

* Quantitative extraction

The dissociation constant pK_a of BPPA, EPPA and IPPA were obtained by half neutralization method. 0.05 m mol of sample was dissolved in 95% alcohol and diluted with water and titrated against 0.1 N NaOH using a pH meter. The pK_a was estimated by the half neutralization method and the results obtained are shown in Table 6.7. The K_{ex} for lanthanum(III), europium(III) and lutetium(III) using BPPA, EPPA and IPPA were calculated using the equation

$$K_{ex} = \frac{D[H^+]^3}{[(HR)_2]^3}$$

The K_{ex} values obtained for BPPA, EPPA and IPPA are shown in Table 6.7.

Table 6.7: Structure reactivity relationship in extraction of rare earth by alkyl aryl phosphoric acid

Reagent	pK_a	K_{ex}		
		La	Eu	Lu
BPPA	1.83	1.40×10^{-1}	1.004	22.4×10^{2}
EPPA	2.40	4.52×10^{-2}	1.1×10^{-1}	8.75
IPPA	1.80	2.50×10^{-2}	8.5×10^{-2}	4.69×10^{-1}

6.3 DISCUSSION

6.3.1 Distribution of acid in the organic phase

The state of aggregation of the acid was ascertained by infrared absorption spectra. The absence of free-OH indicates hydrogen bonding which may be due to the association of two BPPA molecules. In the metal distribution studies MIBK was used as the solvent. From the ^{1}H NMR it is clear that the hydroxyl groups present at δ 12.05 exchanges for deuterium on D_2O exchange. Hence it is clear that BPPA molecules are dimerised in MIBK.

6.3.2 Extraction mechanism

The general mechanism of extraction of rare earths by an acidic organophosphorus extractant BPPA may be represented by the following general expression

$$Ln^{3+} + n\ \overline{(HR)_2} \rightleftharpoons \overline{LnR_n\ (HR)_n} + nH^{+}$$

where Ln stands for the rare earth element and $\overline{(HR)}_2$ refers to the dimer of the extractant in the organic phase. The extraction constant K_{ex} for the extraction process may be written as

$$K_{ex} = \frac{D[H^{+}]^{n}}{[\overline{(HR)_2}]^{n}}$$

Taking logarithm and rearranging, the above equation takes the form

$$\log D = \log K_{ex} + n \log [(\overline{HR})_2]^n - n \log [H^+]$$

By studying the distribution coefficient of metal as function of $(\overline{HR})_2$ and H^+, the composition of the extracted species may be determined.

6.3.3 Effect of BPPA concentration

The extraction of lanthanum(III), europium(III) and lutetium(III) from weakly acidic medium increases with increase of BPPA concentration. The linear plot of log D against log[BPPA] has a slope of three suggesting the association of three molecules of BPPA in the extracted metal species. The plot of percent extraction with molarity of BPPA shows a sigmoid graph.

6.3.4 Effect of pH

The effect of pH on the extraction of lanthanum(III), europium(III) and lutetium(III) shows a sharp increase with increase in pH. Under the experimental conditions it is clear that

$$\log D \propto -n \log H^+$$

$$\text{i.e.} \quad \log D \propto n\,\text{pH}$$

The plot of log D against pH gives the number of H^+ ions released during the extraction of metal species. The corresponding slope is nearly three, showing that during the extraction of each metal species, there is a release of 3 H^+ ions suggesting that the extraction of rare earths by BPPA follows the usual cation exchange mechanism.

6.3.5 Effect of metal concentration

The extraction of lanthanum(III), europium(III) and lutetium(III) decreases slightly with increase in initial concentration of the metal at pH ranges. The slope of log D against logarithms of initial metal concentration is zero for all the three elements. These results indicate that the degree of polymerisation in the two phases is the same under the present experimental conditions. The log-log plot of equilibrium organic phase metal concentration against the equilibrium aqueous phase metal concentration is linear with a slope equal to one indicating the existence of mononuclear species: $\overline{LnR_3(HR)_3}$.

6.3.6 Effect of time of equilibration

The extraction of lanthanum(III), europium(III) and lutetium(III) by BPPA in MIBK reaches equilibrium within one minute of shaking and remains same on further increase to 5 minutes. Hence, it was decided to equilibrate the aqueous and organic phases for 5 minutes to ensure complete equilibrium.

6.3.7 Extraction behaviour of other rare earths

The distribution coefficient of the rare earths shows that the BPPA is very selective for heavy rare earths especially ytterbium(III) and lutetium(III) at pH 1.3 and pH 1.8. From the separation factors it is clear that there is a very good separation between light and heavy rare earths using BPPA in MIBK.

6.3.8 Comparison with other organophosphorus acids

The extraction of lanthanum(III), europium(III) and lutetium(III) by BPPA in MIBK at pH 1.8 and 1.3 are compared with DEHPA and EHEHPA. It is clear from the Table 6.6 that BPPA is a better extractant for heavy rare earths especially ytterbium(III) and lutetium(III) than DEHPA and EHEHPA particularly at pH 1.3.

6.4 EXPERIMENTAL

6.4.1 Apparatus

IR spectra were recorded on a Perkin Elmer Model 299 B IR spectrophotometer. IR of BPPA was taken in dilute solutions of MIBK in demountable KBr cell of 0.25 mm thickness.

A Hitachi 220 double beam microprocessor controlled molecular absorption spectrophotometer was used for measuring the absorbances. An ELICO LI-120 digital pH meter was used for the pH measurements.

6.4.2 Reagents

Stock solutions of the lanthanides were prepared from their oxides (Rare Earth Products, Cheshire, UK, 99.99%) by dissolving in 2 cm^3 of 1:1 hydrochloric acid and diluting to 100 cm^3.

Ammonium acetate buffer (pH 7.5) was prepared by dissolving 19.25 g in 250 cm^3 of water and adjusting the pH 7.5 with HCl/NaOH.

Arzenazo I (Fluka, Switzerland) was p
ving 25 mg of the reagent in 250 cm^3 of v
chemicals were of analytical reagent grade
further purification.

6.4.3 The extraction conditions

Solvent extraction measurements were made employing aqueous solution adjusting pH from 1 to 2. Except where stated otherwise, the initial concentration of lanthanum(III) was 7.2×10^{-5} M, that of europium(III) 6.58×10^{-5} M and that of Lu(III) 5.82×10^{-5} M. Solutions of BPPA used varied from 0.006 M to 0.08 M in MIBK. In all systems the aqueous phase and organic phase were of equal volumes.

6.4.4 Extraction equilibrium procedure

Distribution coefficients were determined by shaking equal volumes of aqueous and organic phases (10 cm^3) for 5 minutes in a 60 cm^3 separating funnel at 303 ± 1 K (Extraction equilibrium was attained in one minute). The distribution coefficient D is given by

$$D = \frac{[\overline{Ln}]}{[Ln]}$$

where $[\overline{Ln}]$ and $[Ln]$ are the concentrations of the rare earth in the organic and aqueous phase respectively.

Method of estimation of rare earths

After extraction the rare earth in the aqueous phase was estimated spectrophotometrically by complexing with Arzenazo I. After allowing the phases to settle, a 5 cm^3 aliquot of the aqueous phase was pipetted into a 25 cm^3 beaker and 1 cm^3 of ammonium acetate buffer and 5 cm^3 of Arzenazo I were added for the determination of metal ion. After adjusting the pH to 7.5 ± 0.1, the solutions were transferred to a 25 cm^3 volumetric flask and made upto the mark.

The absorbances of the solutions were measured at 575 nm and the rare earth concentrations were computed from the respective calibration graphs. The rare earth concentration in the organic phase was obtained by difference. The concentration values were used to obtain the distribution coefficient, D. The percentage extraction was calculated from the distribution coefficient as follows:

$$\% E = \frac{100 D}{D + 1}$$

CHAPTER VII

THERMODYNAMIC MODELLING OF CHEMICAL EQUILIBRIA IN LIQUID-LIQUID EXTRACTION OF RARE EARTHS

7.1 INTRODUCTION

Liquid-liquid extraction methods for separation of lanthanides essentially deal with the extraction of metal inorganic complexes such as chloride, nitrate, sulphate and thiocyanate[202,203]. Moore[204] has for the first time advocated the use of carboxylic acids for the extraction of lanthanides, as they form strong anionic complexes which can be extracted with amine extractants and thus offering wide scope. Inspite of this, little work has been done on the liquid-liquid extraction studies of lanthanides from carboxylic acid media. Recently sodium succinate[205-207] and sodium malonate[208,209] solutions were used for inter and intra group separation of several P. block and transition metals with amine extractants. A possible separation of neodymium and samarium from sodium succinate solutions was reported by extracting with tri-n-octylamine[205]. These reports essentially deal with analytical separation. *The detailed study on equilibrium extraction behaviour of lanthanides from carboxylic acid media has not been reported.*

Models of equilibrium extraction data are being developed for use in computer simulations of metal extraction process. Present trends are towards an ever increasing reliance on the use of mathematical models for process design and control in hydrometallurgical operations. Empirical and semi-empirical models are[210,211] often described for computer simulation of metal extraction processes. When coupled with an optimization algorithm, process simulation models can be used to obtain an optimum flow sheet design or to determine the best operating condition[212].

An early attempt in this direction was the computer program developed by Robinson and Paynter[213]. Their program described a process simulator to which the design and operating parameters were systematically varied until arriving at a minimum in the projected capital costs while maintaining an optimum balance between production rate and operating costs. The output included details such as specification for the organic phase extractant concentration, the total number of stages required and the flow ratio of organic solvent to aqueous solution. Nowadays computer simulation models extend to the area of nuclear safeguards and materials control[214].

The computer simulation of metal extraction processes requires an ability to predict distribution equilibria. Empirical correlations used for this purpose often cannot be considered reliable under conditions that are outside the experimental data base that was used to validate the model.

Later many models were developed for the metal extraction processes. In order to study the theory of counter-current extraction Xu Guang Xian et al[215] developed a model based on Alder's liquid-liquid extraction theory[216,217] which is suitable for the separation of two component system having constant extraction factors. They have further developed the Alder's theory by removing the hypothosis and derived a set of new equations for calculating the minimum and optimized extraction and stripping stages as well as the extreme and optimized ratio of flow rates of the feed, the extractant and the stripping solution[218-220]. These models are widely used in process development of rare earths extraction industry in China[221].

Another model reported at almost the same time for countercurrent extraction of rare earth separation was by Li Han and Chen Zhichuan[222]. By the use of extraction mechanism, a modified model for two extraction systems namely EHEHPA-kerosene-HNO_3 (Sm-Nd) $(NO_3)_3$ system and DEHPA-kerosene-HCl (Tb-Dy) Cl_3 system was developed.

An optimization process for the separation of Tb and Dy was investigated by Shenyongu and Huang Wenmei[223]. The extraction equilibrium and modelling of the separation of Tb and Dy using EHEHPA were studied in detail. The factors affecting the optimization process were studied using Alder's formula, the relation between extraction factor and separation effect was correlated.

A recent trend has been the development of thermodynamic models for the process design work on liquid-liquid extraction of lanthanides[224], iron[225] and Americium[226].

This chapter describes the extraction equilibrium data of lutetium from sodium succinate solution with Aliquat 336 in benzene. The aqueous phase metal complexation and polymerisation in the organic phase were taken into account in obtaining extraction coefficients, stability constants, hydrolysis constant, solubility product and extraction constants. A thermodynamic model of the above equilibrium extraction data was developed for use in computer simulation of the extraction process. The correlations are based on chemical mass action principles in which the metal complexation in aqueous phase, polymerisation in the organic phase, precipitation in the aqueous phase and aqueous phase activity coefficients are considered. Further, extraction behaviour of other lanthanides from a succinate medium was also discussed.

7.2 RESULTS

7.2.1 Effect of sodium succinate

The extraction behaviour of lutetium with Aliquat 336 in benzene was studied as a function of sodium succinate concentration. An equilibrium pH of 7.2 was used during the extraction of lutetium (5.72×10^{-5} M) with 0.1 M Aliquat 336 in benzene. A plot of log D vs log succinate gave a slope of two at low succinate concentrations (curve A, Fig. 7.1) and three at high succinate concentrations (curve B, Fig. 7.1).

7.2.2 Effect of Aliquat 336 concentration

The extraction behaviour of lutetium (III) from sodium succinate (pH 7.2) was studied as a function of Aliquat 336 in benzene as the diluent. The concentration of Aliquat 336 in benzene was varied from 1% to 5%. The concentration of lutetium (III) was maintained at 5.72×10^{-5} M and that of sodium succinate solution at 0.025 M (pH 7.2). The extraction increases as the concentration of Aliquat 336 increases. The values of percent extraction range from 43.21 to 71.59 for lutetium (III). The plot of log D against log [Aliquat 336] for lutetium (III) from sodium succinate (pH 7.2) is linear with a slope nearly equal to one as shown in Fig. 7.2.

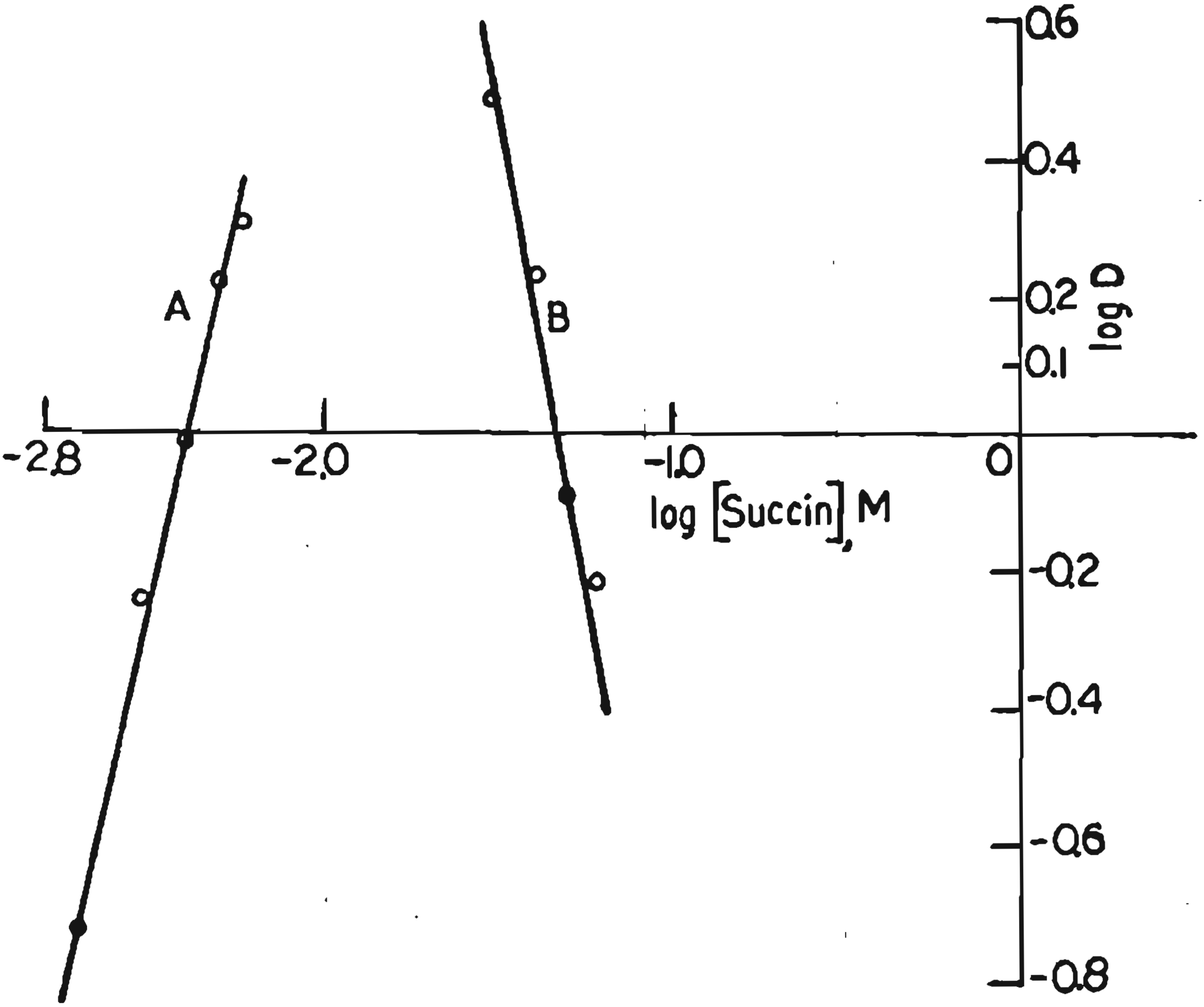


Fig. 7.1: Plot of log D vs log (L) during extraction of lutetium (5.72×10^{-5} M) with 0.1 M Aliquat 336 in benzene (pH 7.2)

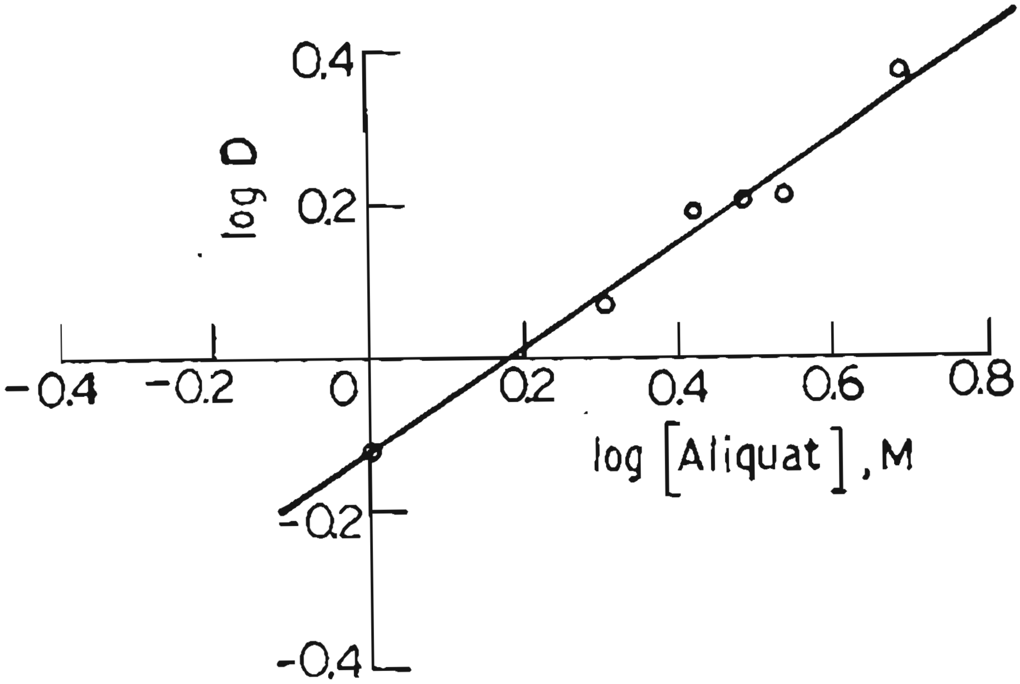


Fig. 7.2: Plot of log D vs log (R_4N) during extraction of lutetium (5.72×10^{-5} M) in the presence of 0.025 M sodium succinate (pH 7.2) in benzene

7.2.3 Effect of pH

The extraction behaviour of lanthanum(III), europium(III) and lutetium(III) as light, middle and heavy rare earths respectively was studied as a function of pH. In these studies equilibrium studies were carried out with 5.72×10^{-5} M individual rare earth ions from 0.025 M sodium succinate solution with Aliquat 336 in benzene. The pH was varied from 5 to 10. The extraction increases with increase in pH (see Fig. 7.3). The percent extraction values range from 6. 01 to 98.40 for lanthanum(III), from 12.12 to $\backsim$ 100 for europium(III) and 5.90 to 90.01 for lutetium(III).

7.2.4 Effect of metal ion concentration

The effect of varying the metal ion concentration on the extraction of lutetium(III) from sodium succinate by Aliquat 336 was investigated. The initial metal ion concentration was varied from 5.7×10^{-6} M to 1.5×10^{-4} M. The log-log plot of equilibrium organic phase lutetium(III) to that in the aqueous phase is shown in Fig. 7.4. The plot is linear with a slope equal to one.

7.2.5 Establishment of monomeric or polymeric nature of extractable metal ion associates

The possible polymerisation of extracted species in organic phase was next considered when initial lutetium(III) concentration was maintained at 5.72×10^{-5} M. The plots obtained from

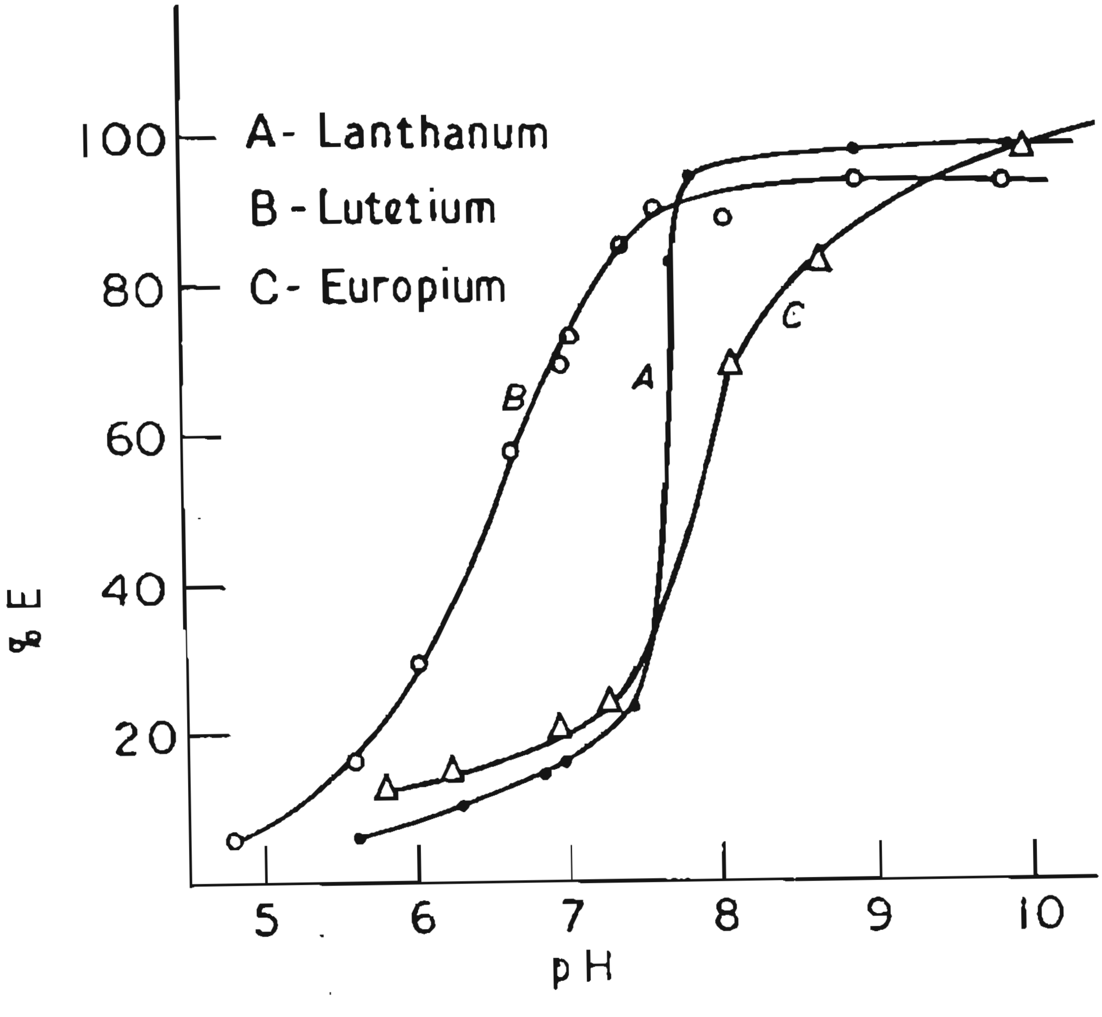


Fig. 7.3: Effect of pH on the extraction of lanthanum, europium and lutetium (∽5 x 10^{-5} M) from 0.025 M sodium succinate solution into 0.1 M Aliquat 336 in benzene

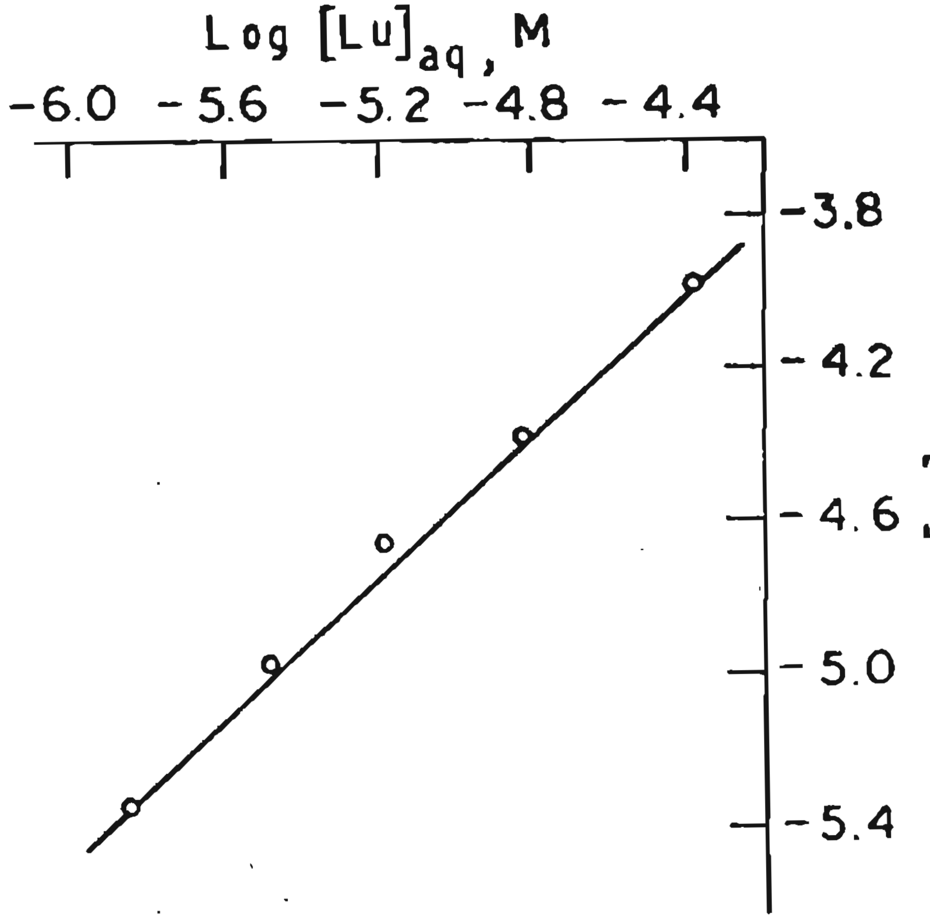


Fig. 7.4: *Effect of metal concentration on the extraction of lutetium from sodium succinate solution (pH 7.2) by 0.1 M Aliquat 336 in benzene*

equation (18), (19) and (20) (see in discussion) are shown in Fig. 2.8. The slope (m/n) values obtained from these plots are 1.109, 1.026 and 1.072 for m = 1, 2 and 3 respectively. Further, the extraction constants calculated from the intercept are 65.77, 4.58×10^{7} and 6.19×10^{13} for m = 1, 2 and 3 respectively.

7.2.6 Extraction behaviour of other lanthanides

The extraction behaviour of lanthanum(III), praseodymium(III), samarium(III), europium(III), gadolinium(III), holmium(III), ytterbium(III), lutetium(III) and yttrium(III) from succinate solutions with Aliquat 336 was studied. These studies were carried out at three different pH conditions, i.e. 6.25, 6.75 and 7.50. The distribution coefficients of the rare earths are listed in Table 7.1. The separation factors between the lanthanides using Aliquat 336 at pH ~ 7.00 are shown in Table 7.2.

Table 7.1: Distribution coefficients of rare earths using Aliquat 336 in benzene

pH	La	Pr	Sm	Eu	Gd	Ho	Yb	Lu	Y
6.25	0.111	0.083	0.158	0.168	0.168	0.250	0.519	0.613	0.159
6.75	0.168	0.062	0.200	0.219	0.179	0.277	1.308	1.553	0.250
7.50	5.000	0.449	0.610	0.389	0.282	2.529	4.455	6.060	1.018

Table 7.2: Separation factors values of rare earths obtained with rare earth - succinate - Aliquat 336 system

Separation factors of rare earths, pH 7.00, 0.025 M succinic acid

	La	Pr	Sm	Eu	Gd	Ho	Yb	Lu	Y
La	-	0.73	1.11	1.35	1.23	1.98	10.09	11.73	1.46
Pr	1.36	-	1.51	1.84	1.67	2.70	13.76	16.00	1.99
Sm	0.91	0.66	-	1.22	1.11	1.80	9.13	10.62	1.32
Eu	0.74	0.55	0.82	-	0.91	1.48	7.50	8.72	1.09
Gd	0.82	0.60	0..90	1.10	-	1.62	8.24	9.57	1.19
Ho	0.50	0.37	0.56	0.68	0.62	-	5.08	5.91	0.74
Yb	0.10	0.07	0.11	0.13	0.12	0.20	-	1.16	0.15
Lu	0.09	0.06	0.09	0.12	0.11	0.17	0.86	-	0.13
Y	0.68	0.50	0.76	0.92	0.84	1.36	6.91	8.03	-

7.3 DISCUSSION

7.3.1 Extraction mechanism

The extraction mechanism of lutetium(III) using Aliquat 336 in benzene from sodium succinate solution can be represented as

$$\mathrm{Lu} + 2\,\mathrm{L} + \mathrm{R_4N} \overset{K_o}{\rightleftharpoons} \overline{(\mathrm{LuL_2}).\mathrm{R_4N}} \qquad (1)$$

$$K_o = \frac{[\overline{\mathrm{LuL_2}\ .\ \mathrm{R_4N}}]}{[\mathrm{Lu}]\ [\mathrm{L}]^2\ [\mathrm{R_4N}]} \qquad (2)$$

$$\log K_o = \log D - 2 \log [\mathrm{L}] - \log [\mathrm{R_4N}] \qquad (3)$$

By studying the distribution coefficient of a metal as a function of [L] and $[R_4N]$, the composition of the extracted species may be determined.

7.3.2 Effect of sodium succinate

The extraction of lutetium(III) increases with increase of sodium succinate at low succinate concentration. A slope of two indicates that two sodium succinate molecules takes part in the extracted species. On the other hand at high succinate concentrations the extraction of lutetium decreases with increase in sodium succinate concentration as three molecules are involved in complex formation $(LuL_3)^{3-}$.

7.3.3 Effect of Aliquat 336 concentration

The concentration of lutetium(III) extracted from sodium succinate (pH 7.2) increases with increase in Aliquat 336 concentration. The linear plot has a slope of one indicating the association of a molecule of Aliquat 336 with each of the extracted species.

7.3.4 Effect of pH

The extraction of lanthanum(III), europium(III), lutetium(III) increases as pH increases. In the case of europium(III) and lutetium(III) the extraction increases steadily with increase in pH. But in the case of lanthanum(III) there is sharp increase in the extraction with increase of pH.

7.3.5 Effect of metal ion concentration

The extraction of lutetium(III) decreases drastically with increase in initial aqueous phase concentration of lutetium(III). The log-log plot of equilibrium organic phase lutetium(III) concentration against the equilibrium aqueous phase lutetium(III) concentration is linear with slope equal to one indicating the existence of mononuclear species. The percent extraction and distribution coefficients of lutetium(III) decrease drastically when the initial aqueous phase concentration of lutetium is greater than 1.5 x 10^{-4} M. It is possibly due to competition from (1) formation of nonextractable species such as LuL^+ and $Lu(OH)_n^{(3-n)+}$ or (2) formation of nonextractable polynuclear species in aqueous phase.

7.3.6 Establishment of monomeric or polymeric nature of extractable metal ion-associates

A method was evolved for distinguishing the monomeric or polymeric species of the extractable ion-association *complexes, for example* (A^+B^-) and $(A^+B^-)_2$. This is an extension of the method described by Holme et al[227] and subsequently modified by Sanchez et al[228] for distinguishing mononuclear and polynuclear coordination complexes in several aqueous spectrophotometric determinations, for e.g. boric acid-quinalizarin system, zinc(II)-1,2 cyclohexadione bisthiosemicarbazone system etc.

The extraction of lutetium as its succinate complex at pH 7 by Aliquat 336 in benzene can be described as

$$[\mathrm{Lu(Succinate)}_2^-]_m + \overline{(\mathrm{R_4N^+})_n} \xrightleftharpoons{K_o} \overline{(\mathrm{LuL}_2^-)_m\ (\mathrm{R_4N^+})_n} \tag{4}$$

$$K_o = \frac{[\overline{A_m B_n}]}{[A]^m [B]^n} \tag{5}$$

where

$A = [\mathrm{LuL}_2]^-$ and $B = [\mathrm{R_4N^+}]$

$$[A] = a - m\,[A_m\ B_n] \tag{6}$$

$$[B] = b - n\,[A_m\ B_n] \tag{7}$$

where a and b are initial concentrations of A and B respectively.

$$[A_m\ B_n] = \frac{\bar{C}}{M} \tag{8}$$

where C is concentration of $A_m\ B_n$ in g/L in the organic phase and M is atomic weight.

At a constant concentration of reactant A as the concentration of B is increased, C reaches a maximum value of $\bar{C}_o$, i.e.

$$\lim_{b \longrightarrow \infty} [A_m \; B_n] = a/m \tag{9}$$

then

$$\bar{C}_o/M = a/m \tag{10}$$

Combining equations (8) and (10)

$$[A_m \; B_n] = \bar{C}a/m \; \bar{C}_o \tag{11}$$

By combining (5), (6), (7) and (11)

$$K_o = \frac{(a/m) \; (\bar{C}/\bar{C}_o)}{\left(a - a \dfrac{\bar{C}}{\bar{C}_o} \right)^m \left(b - a \dfrac{n \; \bar{C}}{m \; \bar{C}_o} \right)^n} \tag{12}$$

Equation (12) may be written as

$$\frac{1}{[B]^n} = \frac{1}{\left(b - \frac{n}{m} \left(\frac{\bar{C}}{\bar{C}_o} \right)\right)^n} = \frac{K_o \; a^m \left(1 - \frac{\bar{C}}{\bar{C}_o}\right)^m}{\dfrac{a \; \bar{C}}{m \; \bar{C}_o}} \tag{13}$$

$$= K_o \; m \; a^{(m-1)} \left(1 - \frac{\bar{C}}{\bar{C}_o}\right)^m \frac{\bar{C}_o}{\bar{C}}$$

By taking m^{th} root of equation (13)

$$\frac{1}{[B]^{n/m}} = (K_o\ m\ a^{(m-1)})^{1/m} \ (1 - \frac{\bar{C}}{\bar{C}_o}) \ (\frac{\bar{C}_o}{\bar{C}})^{1/m} \qquad (14)$$

$$= (K_o\ m\ a^{(m-1)})^{1/m} \ (x^{1/m} - x^{(1/m)-1}) \qquad (15)$$

where $x = \bar{C}_o/\bar{C}$

By taking logarithms and multiplying by m/n

$$\log \frac{1}{[B]} = \frac{1}{n} \log (K_o\ m\ a^{(m-1)}) + \frac{m}{n} \log (x^{1/m} - x^{(1/m)-1}) \qquad (16)$$

The above equation has the general form

$$Y = C + Px \qquad (17)$$

i.e., a straight line with an ordinate $\log \frac{1}{[B]}$ and with an independent variable $\log (x^{1/m} - x^{(1/m)-1})$. The independent variable is different for every value of m. If the value of m tested on the independent variable is incorrect, the slope value i.e. (m/n) will deviate from correct value of m/n. The straight line obtained for complex AB is different from $(AB)_2$ and $(AB)_3$ because the independent variables and ordinates of the origin differ as shown below.

For complex AB,

$$\log \frac{1}{[B]} = \log K_o + \log (x-1) \qquad (18)$$

For complex $(AB)_2$

$$\log \frac{1}{[B]} = \frac{1}{2} \log 2\ a\ K_o + \log (x^{1/2} - x^{(1/2-1)} \qquad (19)$$

For complex $(AB)_3$

$$\log \frac{1}{[B]} = \frac{1}{3} \log 3\ a^2\ K_o + \log (x^{1/3} - x^{(1/3-1)}) \qquad (20)$$

The monomeric or correct polymer complex was identified by calculating the slope value obtained by equations (18) to (20) and choosing the one which is closer to an m/n value of one. The extraction constants were calculated from the intercept value by substituting in appropriate equation. The plot obtained from Equations (18), (19) & (20) are shown in Fig. 7.5. The slope m/n values obtained from these plots are 1.109, 1.026 and 1.072 for m = 1, 2 and 3 respectively, i.e. the more probable form of extracted species is $(AB)_2$. Further, the extraction constants calculated from the intercept are 65.77, 4.58×10^7 and 6.19×10^{13} for m = 1, 2 and 3 respectively. The extraction constant obtained with m = 2, i.e. dimerization of extracted species is of

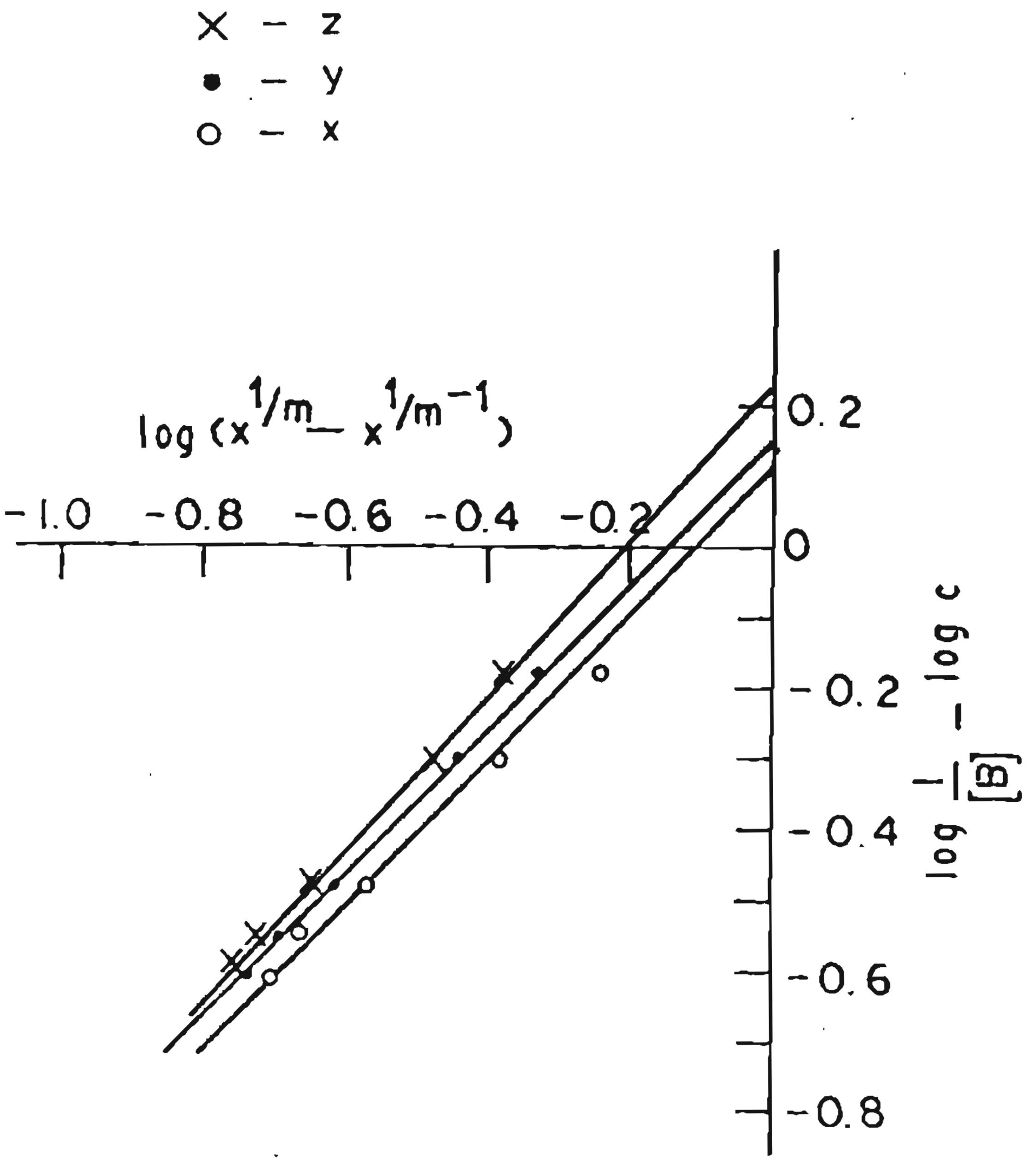


Fig. 7.5: Experimental lines obtained for the lutetium-succinate-Aliquat 336 system. Curves x, y, z were calculated from Equations 15, 16 and 17 respectively

the same order as was obtained from equation (3). Hence the extracted ternary ion-association complex $(\overline{LuL_2 \cdot R_4N})$ exists as dimer in benzene layer in the form $(\overline{LuL_2 \cdot R_4N})_2$.

7.3.7 Development of chemical equilibria based thermodynamic model of lutetium-succinate-Aliquat 336 system

The extraction of lutetium from sodium succinate solutions with Aliquat 336 in benzene at an equilibrium pH of 7.20 in simple form can be described as $D = \overline{\mathrm{Lu(Total)}} / \mathrm{Lu\ (Total)}$. However by taking the aqueous phase complexation viz., the presence of lutetium as $(LuL)^+$ alone or as the $(LuL_2)^-$ and $(LuL_3)^{3-}$ species and assuming the activity coefficients of all aqueous lutetium species ($< 10^{-4}$ M) to be constant Equation (2) can be rewritten as

$$D = \frac{K_0 \, [\overline{R_4N}] \, [L]^2}{1 + \beta_1 \, [L]} \tag{21}$$

where β_1 is equilibrium constant for the formation of (LuL^+)

$$D = \frac{K_0 \, [\overline{R_4N}] \, [L]^2}{1 + \beta_1 \, [L] + \beta_3 \, [L]^3} \tag{22}$$

β_3 is complexation or equilibrium constant for the formation of $(LuL_3)^{3-}$. Equation (21) and (22) can be rearranged in the form of a polynomial to give

$$\frac{[\overline{R_4N}]\ [L]^2}{D} = \frac{1}{K_o} + \frac{\beta_1}{K_o}\ [L] \qquad (23)$$

$$= \frac{1}{K_o} + \frac{\beta_1}{K_o}\ [L] + \frac{\beta_3}{K_o}\ [L]^3 \qquad (24)$$

The extraction and complexation constants obtained by a least squares fit of the extraction equilibrium data obtained at sodium succinate concentration of $\leq$ 0.01 M in Equations (23) and (24) are shown in Table 7.1.

Table 7.1: Extraction and complexation constants of lutetium-sodium succinate-Aliquat 336 system

Extraction/ complexation constant	Equations			
	23	24	26	31
K_0	1.38×10^6	3.62×10^5	5.03×10^5	2.24×10^7
K_1	-	-	-7.61×10^7	-9.0×10^{10}
β_1	4.04×10^2	1.31×10^2	71.9	30.86
β_2	-	-	2×10^4	4.98×10^9
β_3	-	1.87×10^6	1.59×10^6	1.93×10^6

The computer simulation of extraction coefficients as a function of sodium succinate concentrations based on Equations (23) and (24) are shown by curves A and B in Fig. 7.6, along with experimentally obtained points. The model based on Eq.(24) is more realistic and has the identical features of the experimental points. Even in this case, the fit is not good at sodium succinate concentrations > 0.01 M. The possibility of $(LuL_3)^{3-}$ being extracted with Aliquat 336 cannot be ruled out and Equation (24) has to be modified to incorporate this phenomenon. The extraction equilibria of $(LuL_3)^{3-}$ species with Aliquat 336 are written in similar fashion to that of Eq. (2), where K_1 is the extraction constant of elementary reaction expressed by Equation (25).

$$Lu^{3+} + 3L + 3(\overline{R_4N}) \xrightleftharpoons{K_1} \overline{LuL_3[R_4N]_3} \qquad (25)$$

By incorporation this equilibrium into Equation (19), the expression for D becomes

$$D = \frac{K_0[\overline{R_4N}]\,[L]^2}{1 + \beta_1[L] + \beta_3[L]^3} + \frac{K_1[\overline{R_4N}]^3\,[L]^3}{1 + \beta_1[L] + \beta_2[L]^2} \qquad (26)$$

where β_2 is complexation or equilibrium constant for the formation of (LuL_2^-).

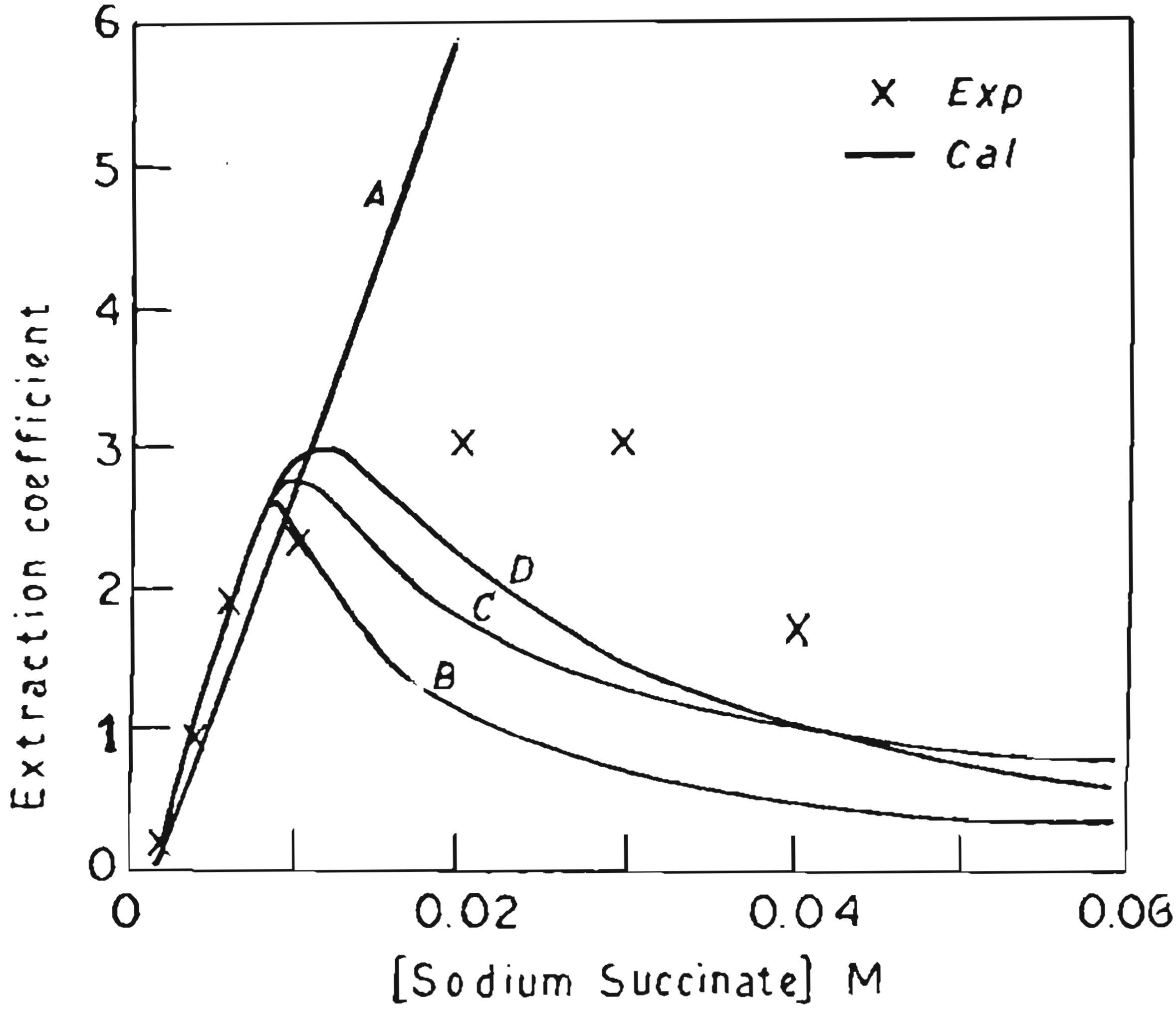


Fig. 7.6: Measured and calculated lutetium extraction by 0.1 M Aliquat 336 in benzene. Curves A, B, C and D were calculated from Equations 23, 24, 26 and 31 respectively

The extraction and complexation constants arrived at by solving Equation (26) by the Newton-Raphson method are presented in Table 7.1. As can be seen from curve C of Fig. 7.6, the addition of second term improves the prediction of extraction coefficient compared to earlier equations. In the model so far considered, the polymerisation of the extractant and that of the extracted complex in the benzene phase were not considered. The extracted ion-association complex was found to occur as a dimer (see earlier discussion). Further Gel permeation chromatographic experiments revealed that the succinate form of Aliquat 336 in benzene occurs as a trimer. Hence the extraction equilibria represented in Equation (2) is rewritten as

$$Lu^{3+} + \frac{1}{p}[\overline{R_4N}]_p + 2\,L \xrightleftharpoons{K_2} \frac{1}{x}[\overline{LuL_2 \,.\, R_4N}]_x \qquad (27)$$

$$K_2 = \frac{(\bar{C})^{1/x}}{[Lu]\,[(\overline{R_4N})_p]^{1/p}\,[L]^2} \qquad (28)$$

Since the total concentration of metal in the organic phase is x times the concentration of the complex C,

$$K_2 = \frac{x^{-1/x}\,[Lu]^{1/x}}{[Lu]\,[\overline{(R_4N)_p}]^{1/p}\,[L]^2} \qquad (29)$$

$$D' = \frac{[\overline{Lu}]^{1/x}}{[Lu]} = \frac{K_2\,[\overline{(R_4N)_p}]^{1/p}\,[L]^2}{x^{-1/x}\,(1 + \beta_1\,[L] + \beta_3\,[L]^3)} \qquad (30)$$

Again as earlier, by taking into consideration the extraction of $(LuL_3)^{3-}$ species.

$$D = \frac{[\overline{Lu}]^{1/x}}{[Lu]} = \frac{K_2\,[\overline{(R_4N)_p}]^{1/p}\,[L]^2}{x^{-1/x}\,(1 + \beta_1\,[L] + \beta_3\,[L]^3)} \qquad (31)$$

$$+ \frac{K_3\,[\overline{(R_4N)_p}]^{3/p}\,[L]^3}{x^{-1/x}\,[1 + \beta_1\,[L] + \beta_2\,[L]^2)}$$

The extraction constants and complexation constants obtained by solving Equation (31) are shown in Table 7.1. As can be seen from curve D in Fig. 7.6 the incorporation of polymerisation of extractant and the extracted complex in the benzene layer resulted in improvement of the model. The slight deviation at higher sodium succinate concentration is probably due to the fact that (1) the activities of succinate are not used in calculation of D and (2) the assumption that the presence of hydroxyl complexes of lutetium and the possible distribution of succinate in other forms are negligible at pH 7.2. All these phenomena will have a significant role in predicting the extraction coefficient as a function of pH and hence should be incorporated in the model. Thus, by taking into account the presence of various hydrolysed forms of metal, Equation (31) is modified as

$$D' = \frac{K_2 \, [\overline{(R_4N)_p}]^{1/p} \, [L_T]^2}{x^{-1/x} \, (1 + \beta_1 [L_T] + \beta_3 [L_T]^3 + \beta_4 [OH] + \beta_5 [OH]^2)} + \frac{K_3 \, [\overline{(R_4N)_p}]^{3/p} \, [L_T]^3}{x^{-1/x} \, (1 + \beta_1 [L_T] + \beta_2 [L_T]^2 + \beta_4 [OH] + \beta_5 [OH]^2)} \qquad (32)$$

where L_T is the total concentration of succinic acid. β_4 complexation or equilibrium constant for the formation of $[Lu(OH)^{2+}]$ and β_5 is complexation or equilibrium constant for the formation of $[Lu(OH)_2^+]$. Further, by considering the presence of different species of succinic acid i.e., L^{2-}, HL, and H_2L and representing the concentration of various species in activities:

$$[L^{2-}] = \frac{K_{a_1} K_{a_2} [L_T]}{p \left(\frac{K_{a_1} K_{a_2}}{\gamma_2} + \frac{K_{a_1} [H]}{\gamma_1} + [H]^2 \right) \left(1 + \frac{1}{p} \right)} \qquad (33)$$

K_{a_1} is the first acid dissociation constant of succinic acid and

K_{a_2} second acid dissociation constant of succinic acid.

7.3.8 Calculation of activity coefficients

In the modelling of hydrometallurgical processes a common difficulty has been the treatment of activity coefficients. While the extended Debye-Huckel equation can be used to an ionic strength of about 0.1 molal, the method developed by Bromley[229], Meissner et al[230], Pitzer et al[231] often work well for single and multicomponent electrolyte solutions. In this case the mean stoichiometric activity coefficients were calculated by using Bromley's method .

$$\log \gamma_{\pm} = \frac{-Az_{+} z_{-} I^{1/2}}{1 + PI^{1/2}} + \frac{(0.06 + 0.6\ B)\ z_{+}\ z_{-}\ I}{\left(1 + \frac{1.5}{z_{+}\ z_{-}}\ I\right)^{2}} + BI$$

where

$\gamma_{\pm}$ is the mean activity coefficient, molal concentration scale,

B is the constant per salt; B_{+} for cation, B_{-} - for anion

I is the ionic strength = 0.5 $\sum M_i z_i^2$, z is charge number on ion (only absolute values are used)

$$\{HL^{-}\} = \frac{[L_T]\ [H]}{K_{a_2}}$$

where HL is monoprotonated succinate ion.

$$\left\{H_2L\right\} = \frac{[L_T]\ [H]^2}{K_{a_1}\ K_{a_2}}$$

where H_2L is succinic acid.

Since Aliquat 336 in benzene is preequilibrated with succinate solutions to convert it into the succinate form Eq. (33) can be simplified by neglecting the partition coefficient term. Further, in the pH range under investigation aH_2L has a negligible influence on the distribution coefficient values.

The distribution coerficients calculated by using equation (32) match the experimental points in the pH range as seen in Fig. 7.7. The above model is then applied to predict the extraction isotherm of lutetium at different concentrations of sodium succinate and Aliquat 336.

The model fits well when the initial metal concentration is $\leq 1.5 \times 10^{-4}$ M. Above this value, the lutetium precipitates as $Lu(OH)_3$ and thus removal from the extraction equilibrium cannot be neglected.

$$\text{Lu as } Lu(OH)_3 \text{ (solid)} = K_s/[OH]^3$$

$$M_T' = M_T - M(OH)_3$$

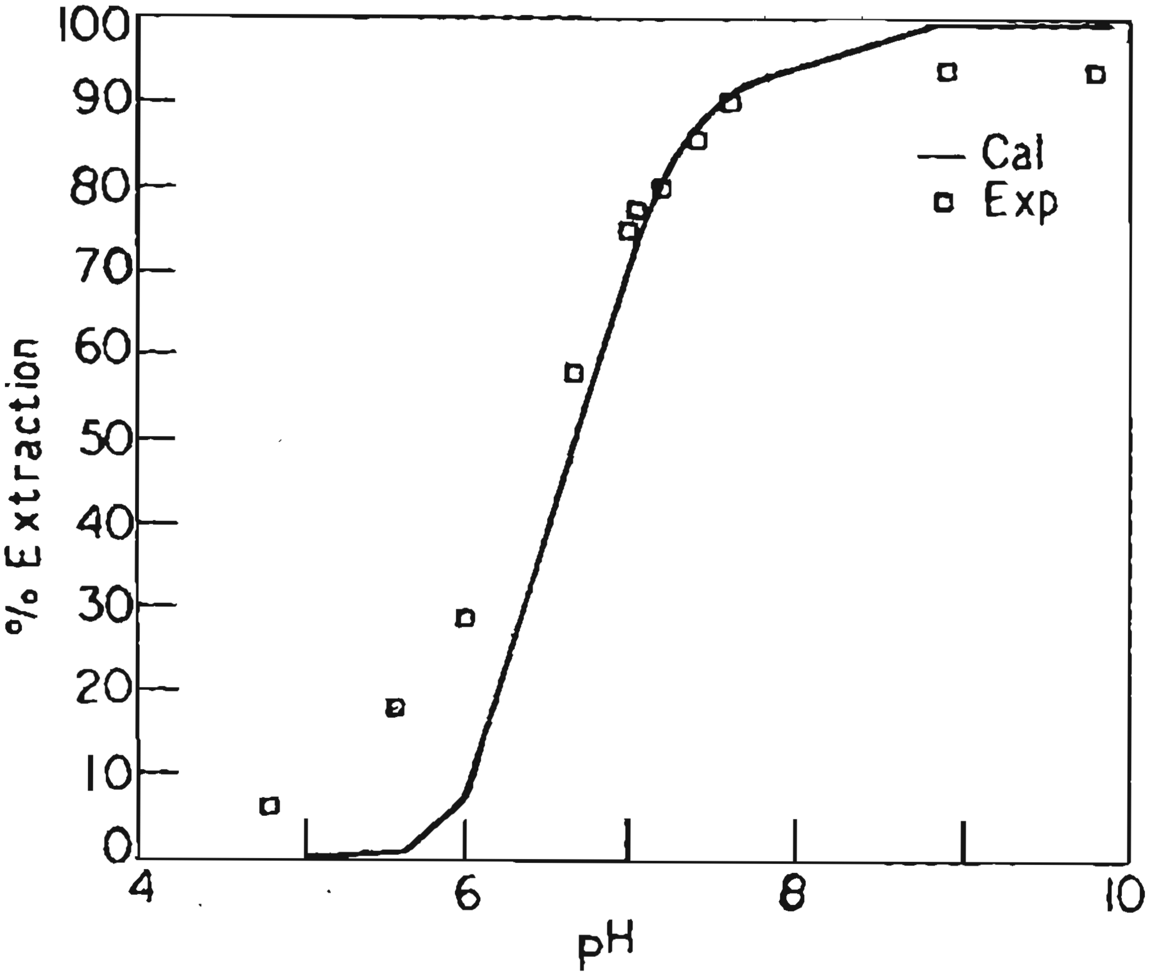


Fig. 7.7: Plot of calculated and measured extraction coefficients as a function of pH during the extraction of 5.72×10^{-5} M lutetium with 0.1 M Aliquat 336 in benzene from 0.025 M sodium succinate solutions

where

M_T = initial ion concentration

M'_T = initial metal ion concentration in equilibrium with Aliquat 336

$[\overline{Lu_T}]$ and $[Lu]$ were calculated with Equation (32) and $[Lu]_T$ was arrived at by incorporating the contribution due to $Lu(OH)_3$ which is removed from the extraction equilibrium. The K'_s value was calculated to be 7.59×10^{-25}. Modification of the above thermodynamic model after considering the separation of lutetium as $Lu(OH)_3$ from the extraction equilibrium when $[M^{3+}][OH^-]^3$ exceeds K'_s value was affected. The fit between calculated and experimental extraction isotherm is quite good as seen in Fig. 7.8. Fig. 7.9 shows the various chemical reaction equilibria involved in the lutetium-succinate-Aliquat 336 system.

7.3.9 Extraction behaviour of other rare earths

Table 7.2 gives the separation factors of rare earths obtained with Aliquat 336 from sodium succinate solution. It is seen that there is maximum separation of lutetium(III) from other rare earths at pH $\sim$ 7.00.

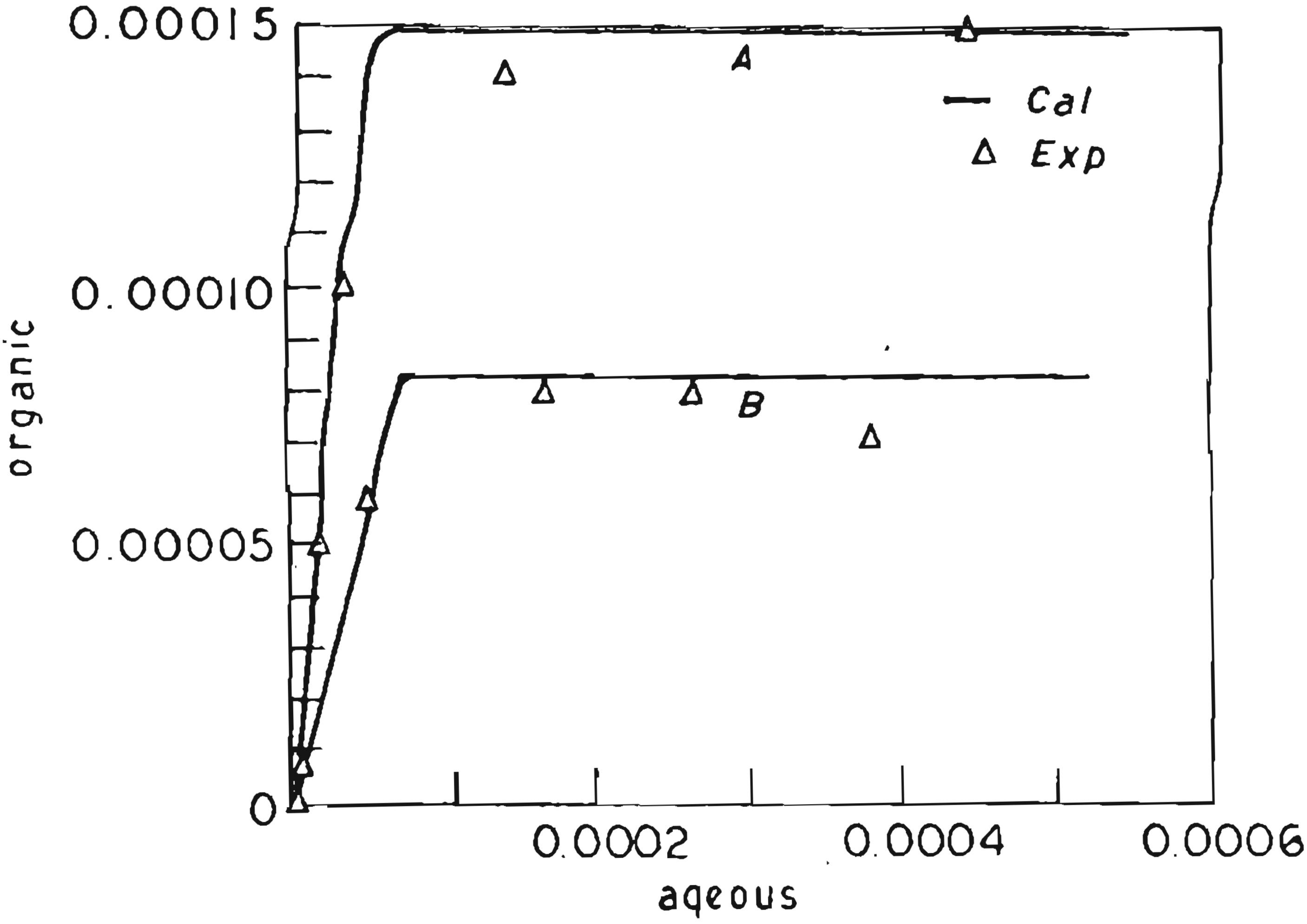


Fig. 7.8: Measured and calculated lutetium extraction isotherms for 0.01 M and 0.025 M sodium succinate solutions (Curves A and B)

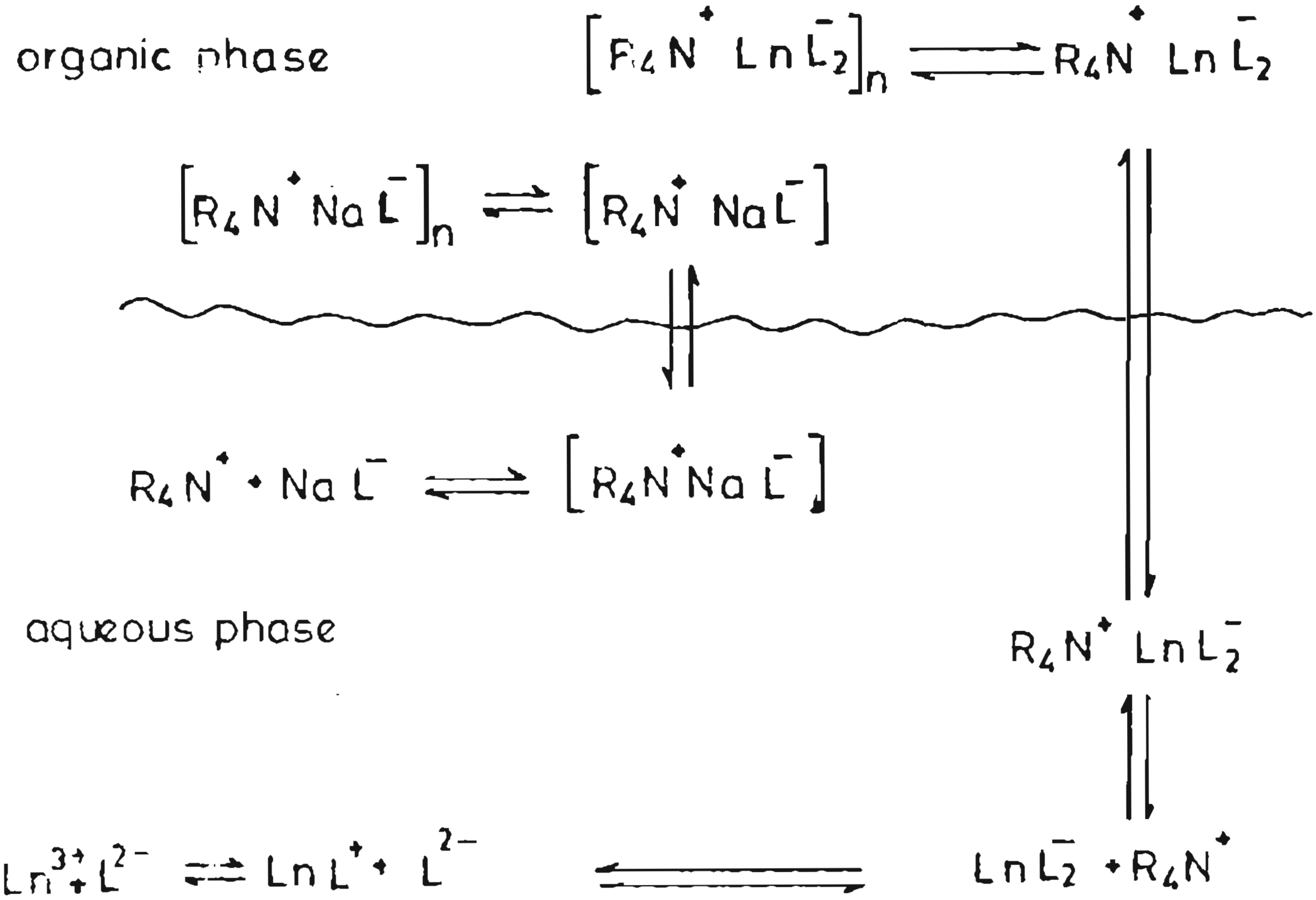


Fig. 7.9: Chemical reaction quilibria of lutetium-succinate-Aliquat 336 system

7.4 EXPERIMENTAL

7.4.1 Apparatus

A Hitachi 220 double beam microprocessor-controlled molecular absorption spectrophotometer was used for measuring absorbances. An ELICO digital pH meter was used for pH measurements. All the programmes were written in FORTRAN and executed on a 32 bit minicomputer (HCL, Horizon III).

7.4.2 Reagents

Aliquat 336 was procured from Fluka, Switzerland and was used without further purification. A 5% (v/v) solution in benzene was prepared by diluting 25 cm^3 of Aliquat 336 (chloride form) with benzene to 500 cm^3. This Aliquat 336 solution was converted into succinate form by equilibrating twice with 500 cm^3 of 0.1 M sodium succinate (pH 7.2). Stock solutions of the rare earths were prepared from their oxides (Rare Earth Products, Cheshire, UK, 99.99%) by dissolving in 2 cm^3 of 1:1 hydrochloric acid and diluting to 100 cm^3. Sodium succinate solution was prepared by dissolving succinic acid (BDH, GDR) in a minimum amount of sodium hydroxide and adjusting to the required pH by using dilute sodium hydroxide.

Arzenazo I (Fluka, Switzerland) was prepared by dissolving 25 mg of this reagent in 250 cm^3 conductivity water.

Ammonium acetate buffer (pH 7.5) was prepared by dissolving 19.25 g in 250 cm^3 water and adjusting the pH with HCl + NaOH.

All other chemicals were of analytical reagent grade and were used without further purification.

7.4.3 Extraction equilibrium procedure

Extraction coefficients were determined by shaking equal volumes of the aqueous and organic phases (10 cm^3) for 5 min. in a 60 cm^3 separating funnel at room temperature. The pH value of the aqueous phase measured after phase separation was taken as the equilibrium pH value. A 5 cm^3 aliquat of the aqueous phase was pipetted into a 25 cm^3 beaker and 1 cm^3 ammonium acetate buffer and 5 cm^3 Arzenazo I were added. After adjusting the pH to 7.5 ± 0.1, the solution was transferred to a 25 cm^3 volumetric flask and made upto the mark.

The absorbances of the solutions were measurd at 575 nm and the rare earth concentrations were computed from the respective calibration graphs. The rare earth concentration in the organic phase was periodically checked after stripping with 2 x 5 cm^3 perchloric acid. These concentration values were used to obtain the extraction coefficient, D defined as

$$D = [\overline{Ln}]/[Ln]'$$

[Ln] concentration of rare earth in aqueous phase

$[\overline{Ln}]$ concentration of rare earth in organic phase

CHAPTER VIII

CONCLUSIONS

Separation of rare earths has been one of the most difficult problems in inorganic chemistry. Liquid-liquid extraction is widely used for the separation of rare earths in view of its simplicity, versatility, rapidity and ready applicability to scaling up of the process. Hence the search for more selective and versatile extractants has resulted in the synthesis of esters of orthophosphoric, phosphonic and phosphinic acids and similar compounds containing polyfunctional groups.

Alkyl aryl phosphoric acids are reported to have greater extraction capacities than mono and dialkyl phosphoric acids. So a few alkyl aryl phosphoric acids were synthesised for their possible use in extraction and separation of rare earths. Cardanol was the starting material for the synthesis of these reagents and was obtained from technical CNSL. Cardanol was purified by vacuum distillation, then hydrogenated to 3-pentadecylphenol. 3-pentadecylphenol was phosphorylated using phosphorusoxychloride to obtain 3-pentadecylphenyl phosphorodichloridate. Using the dichloridate four compounds namely, (1) mono(3-pentadecylphenyl) phosphoric acid (MPPA), (2) Isopropyl-3-pentadecylphenyl phosphoric acid (IPPA); (3) 2-ethylhexyl-3-pentadecylphenyl phosphoric acid (EPPA)and (4) butyl-3-pentadecylphenyl phosphoric acid (BPPA) were synthesised. MPPA was obtained by the hydrolysis of 3-pentadecylphenyl phosphorodichloridate using NaOH in presence of $BaCl_2$. IPPA, EPPA and BPPA were obtained by the following procedure. 3-pentadecylphenyl phosphorichloridate was treated with stoichiometric amounts of the corresponding alcohol and triethylamine followed by a mixture of stoichiometric amounts of benzyl alcohol and triethylamine. The resulting benzyl ester was purified by column chromatography. The pure benzyl ester on hydrogenolysis using palladised charcoal gave the alkyl-3-pentadecylphenyl phosphoric acids. These acids were used to study the extraction behaviour of the rare earths.

The extraction of lanthanum(III), europium(III) and lutetium(III) representatives of the light, middle and heavy rare earths from hydrochloric acid and perchloric acid was investigated using IPPA in toluene. The effect of solvent viz. toluene and MIBK on the extraction of La(III), Eu(III) and Lu(III) using EPPA were studied. The extraction behaviour of the above rare earths were studied using BPPA and MPPA in MIBK. The extracted species were found to be $Ln(HR_2)_3$ in the case of IPPA, BPPA and EPPA and $Ln(H_2R)_3$ in the case of MPPA. In all the extraction systems extraction increases with increase of atomic number of rare earths. With all the extractants, the increase of H^+ concentration showed that extraction decreases drastically and becomes negligible at about 1 M HCl. In each case a plot of log D vs log H^+ was found to be -3 suggesting the release of three H^+ ions during extraction and hence confirms the cation exchange mechanism. The effect of varying the metal ion concentration on the extraction of La(III), Eu(III), and Lu(III) from acid solutions were studied. The log-log plot of equilibrium organic phase to equilibrium aqueous phase is linear with a slope nearly equal to one indicating the extraction of mononuclear complexes. The extraction behaviour of the other rare earths has been studied at different concentrations of MPPA, IPPA, EPPA and BPPA and it is clearly seen that these reagents are very selective for heavy rare earths particularly ytterbium and lutetium. These extractants were compared with the well known commercial acidic organophosphorus extractants like DEHPA and EHEHPA in extraction of La(III), Eu(III) and Lu(III). In all cases these extractants were found to be better extractants for heavier rare earths compared to DEHPA and EHEHPA.

The extraction abilities and selectivity of the reagents IPPA, EPPA and BPPA were compared. The extraction sequence obtained lies in the order BPPA > EPPA > IPPA. It is evidently shown that the extraction ability of acidic phosphates is governed chiefly by the reactivity of the coordinating group P(O)OH characterised as pK_a values. However, the extraction abilities of alkyl aryl phosphoric acids decreases in the order BPPA > EPPA > IPPA. From the PK_a values the extraction abilities should have been IPPA > BPPA > EPPA. But the pK_a values is not the only factor responsible for the extraction abilities. This anomaly can be explained by taking into account the steric hindrance of the extractant. The difference in K_{ex} values for BPPA and EPPA are according to the pK_a values. On the other hand, the difference in magnitudes of K_{ex} for BPPA and IPPA could not be explained by pK_a values alone. The K_{ex} for BPPA is very much high due to the fact that the alkyl group is a straight chain. But in the case of IPPA, the alkyl group is branched resulting in the steric hindrance in the extractant and thus lowering K_{ex} values. It is clear from the above that pK_a values do not entirely give a satisfactory explanation towards K_{ex} as steric effect plays an important role in the process of extraction of rare earths. The steric effect also has the obvious influence on the separation behaviour of alkyl aryl phosphoric acids in the extraction of rare earths. These alkyl aryl phosphoric acids with less steric hindrance like the straight chain group, BPPA demonstrate smaller separation factors with proper degree of isomerization in alkyl group (IPPA) possess excellent separations for rare earth, hence very high separation factor.

A thermodynamic model was developed for the extraction of lutetium from succinate solutions using Aliquat 336 in benzene as extractant. The factors affecting the extraction equilibrium of lutetium from succinate solutions into Aliquat 336 was investigated in detail. The aqueous phase metal complexation and polymerisation in the organic phase are taken into account in obtaining extraction coefficients, stability constants, hydrolysis constants, solubility product and extraction constants. A thermodynamic model of the above equilibrium extraction data was developed for use in computer simulation of the extraction process. The correlations are based on chemical mass action principles in which the metal complexation in aqueous, polymerisation in organic phase, precipitation in the aqueous phase and aqueous phase activity coefficients are considered. Further extraction behaviour of other lanthanides from a succinate medium was also studied.

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LIST OF PUBLICATIONS

1. Thermodynamic modelling of chemical equilibria in liquid-liquid extraction of lutetium
   S. Sreelatha, P.S.T. Sai, T. Prasada Rao, C.S. Narayanan and A.D. Damodaran
   Sep. Sci. and Technol., 26 (12), 1531, 1991.

2. Isopropyl-3-pentadecylphenyl phosphoric acid - A new reagent for liquid-liquid extraction and separation of rare earths
   S. Sreelatha, T. Prasada Rao, C.S. Narayanan and A.D. Damodaran
   Analytical Letters (in press).

3. Extraction equilibria of rare earths by a new reagent (2-ethylhexyl-3-pentadecylphenyl) phosphoric acid
   S. Sreelatha, T. Prasada Rao, C.S. Narayanan and A.D. Damodaran
   (Communicated to Talanta).

4. Mono(3-pentadecylphenyl) phosphoric acid - A new reagent for liquid-liquid extraction and separation of rare earths
   S. Sreelatha, T. Prassada Rao, C.S. Narayanan and A.D. Damodaran
   (To be communicated).

5. Extraction equilibria of rare earths by a new reagent - Butyl-3-pentadecylphenyl phosphoric acid
   S. Sreelatha, T. Prasada Rao, C.S. Narayanan and A.D. Damodaran
   (To be communicated).