Liquid-Liquid Extraction of Rare Earth Elements From Sulfuric Acid Solutions

Osman Abd El-Naby Desouky

Submitted in accordance with the requirements of the degree of ph.D.
Department of Chemistry
University of Leeds

June 2006

The candidate confirms that the work submitted in his own and that appropriate credit has been given where reference has been made to the work of others

Acknowledgements

Before all and above all, I thank and pray to my God "ALLAH" for explicit known and by grace of whom the progress and success of this work was possible.
I would like to express my deepest thanks to my supervisor Malcolm Halcrow for giving the opportunity to do this PhD, his enthusiasm, encouragement and trust during four years. His insight and patience on the professional and personal levels helped in the accomplishment of the present study and both Egyptian Government and Leeds University for funding. I received a lot of technical support and therefore I would like to thank Tanya Marinko-Covell for her help with mass spectroscopy and Martin Huscroft for the microanalysis, ICP (Geography Department) and atomic absorption spectroscopy.

My years in the school of chemistry would not have been the same without the Halcrow and McGowan groups past and present and more especially Jerome, Isabelle, Chokri, Claire Temple, Sade, Leigh, Stacey, Karen, James, Tony, Clare Tovee, Zahra, Habibat and Ahmed El-sokkary. A lot of thanks to Ruth and Gareth (you got the heart of all my daughters Aunty Ruth), Chris Pask you are the sweetest thing that I have come across, I would like to thank you for all your support, help and valuable discussion.

I would like to thank my big family dad, mum, all my brothers especially Mahmoud and all my sisters for their support and love. Finally, I would like to say a big thank you to my wife (Soria) and my daughters Essraa, Menatallah, Asmaa, who were extremely encouraging, patient and understanding during the many years of leisure time we consumed in this endeavour.

The University of Leeds

Liquid-liquid extraction of rare earth elements from sulfuric acid solutions

Submitted for the degree of Ph.D.

June 2006

Osman Abd El-Naby Desouky

Abstract

This thesis is concerned with the liquid-liquid extraction and separation of Y, Ce, La, binary mixtures, and ternary mixtures as well as synthesis of novel amide ligands for the extraction of rare earth elements.

Chapter 1 is the general introduction of the practical process and applications of solvent extraction and its theory. It describes systems involving compound formation, ion-association and solvation as well as solvent loading capacity, dispersion and coalescence. The aims of this thesis are also presented.

Chapter 2 presents an introduction to yttrium chemistry and recent developments in yttrium extraction chemistry. It describes the relevant factors affecting the liquid-liquid extraction process to determine the optimum conditions for yttrium extraction from sulfate liquor. These factors include TiOA concentration, contact time, pH value, temperature, aqueous phase composition, diluent and construct of McCabe-Thiele diagram. In addition, the synergistic effect of using TBP, TOPO and D2EHPA and the optimum conditions for the stripping process are determined.

Chapter 3 contains introduction to cerium chemistry and recent developments in cerium extraction chemistry. The optimum conditions for solvent extraction of cerium(III) from a sulfate medium, and synergistic effects using TOPO and D2EHPAon the extraction process are studied. Also, the relevant factors affecting cerium(III) stripping efficiency are determined.

Chapter 4 presents a brief introduction to lanthanum and recent developments in lanthanum extraction chemistry. The optimum conditions for solvent extraction of lanthanum from sulfate media, with synergistic effects using TOPO, D2EHPA and TBP are described. In addition, the suitable conditions for the lanthanum stripping process are determined.

Chapter 5 contains the principles of separation and liquid-liquid extraction of binary (Y/La) and ternary (Nd-La-Y) element systems. The optimum conditions for the separation of both systems were investigated.

Chapter 6 describes the synthesis and characterization of several novel piperazine and piperidine amide ligands. These ligands have good extraction ability for both light and heavy rare earth elements. The optimum conditions for solvent extraction of yttrium and cerium(III) using these ligands were studied. The chapter also, contains the experimental procedures and characterising data for ligand synthesis in this thesis.

Contents

List of Schemes

List of Figures

List of Tables

The nomenclature of solvent extraction.

A/O: Volume phase ratio of aqueous to organic phases; may also be expressed as O/A.

Aqueous Feed: The aqueous solution feed to the extraction stage, which contains the metal or metals to be extracted.

Crud: The materials resulting from agitation of an organic phase, an aqueous phase, and fine solid particles that form a stable mixture. Crud usually collects at interface between aqueous and organic phases.

Counter Current Extraction: Extraction in which the aqueous and organic phases flow in opposite directions.

Diluent: The organic liquid in which an extractant and modifier are dissolved to form a solvent.

Extract: Used as a verb to describe the transfer of a metal from one phase to another.

Extractant: The active organic component of the solvent primarily responsible for the extraction of a metal.

Extraction: The operation of transferring a metal from an aqueous to an organic phase.

Extraction Raffinate: The aqueous phase from which a metal (or metals) has been removed by contacting with an organic phase.

Loaded Solvent: The organic solvent containing the maximum concentration of a metal for the conditions under which extraction occurred.

Loading Capacity: Refers to the saturation limit of a solvent for a metal or metals.

Mixed Solvent: A solution of more than one extractant in an organic diluent.

Modifier: A substance added to a solvent to increase the solubility of the extractant, also added to suppress emulsion formation.

Scrubbing: The selective removal of a metal or impurities from a loaded solvent prior to stripping. Also removal of solvent degradation products and non-strippable complexes from the solvent usually after stripping.

Scrubbed Solvent: The organic phase after removal of contaminants by scrubbing.

Scrub Solution: The aqueous solution used to contact the loaded solvent for the removal of contaminants.

Scrub Raffinate: The aqueous phase after contacting the loaded solvent.

Stage: A single contact (dispersion and disengagement). Also refers to a theoretical stage, which is a contact that attains equilibrium conditions in a particular system.

Stripping: The removal of extracted metal from the loaded solvent. Selective stripping refers to separate removal of specific metals from a solvent containing more than one metal.

Strip Solution: The aqueous solution used to contact the loaded (or scrubbed) solvent to recover the extracted metal.

Strip Liquor: The aqueous solution containing the metal recovered from a loaded solvent by stripping.

Stripped Solvent: The solvent after removal of extracted metal by stripping.

Synergism: The cooperative and beneficial effect of two or more extractants or reagents that exceeds the sum of the individual effects.

Contactor: Advice for dispersing and disengaging immiscible solution mixtures; it may be single or multi-stage.

Distribution: The apportionment of a metal (solute) between two phases.

Equilibrium: The position when chemical potentials of both aqueous and organic phases are equal.

Solvent Equilibration: Treatment of the solvent prior to its entering the extraction stage.

Distribution (Extraction) Coefficient: The ratio of total concentrations of metal after contacting an aqueous and an organic phase under specified conditions.

D = Concentration of metal in organic phase/Concentration of metal in aqueous phase

Extraction Isotherm: The graphical presentation of isothermal equilibrium concentrations of a metal in the aqueous and organic phases over an ordered range of conditions in extraction.

Load: To transfer of a metal from an aqueous to an organic phase.

$pH_{1/2}$: That pH value at which the extraction coefficients unity.

Separation Factor: The ratio of the extraction coefficients of two metals being compared.

Settling: Separation of dispersed immiscible phases by coalescence or sedimentation.

Solvent Extraction (SX): Separation of one or more solutes from a mixture by mass transfer between immiscible phases in which at least one phase is an organic liquid.

Solvent: Mixtures of an extractant, diluent, and in some cases a modifier. The organic phase which preferentially dissolves the extractable metal species from aqueous solution.

List of abbreviations

D2EHPA	di-2-ethylhexyl phosphoric acid
PC88A or EHPNA	2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester
Cyanex 272	di-(2,4,4-trimethylpentyl) phosphinic acid
Cyanex 301	di-2,4,4,-trimethylpentyl dithiophosphinic acid
Cyanex 302	di-2,4,4,-trimethylpentyl monothiophosphinic acid
Cyanex 923	a mixture of four trialkyl phosphine oxides namely $R_3P(O)$, $R_2R'P(O)$, $R_2'RP(O)$, $R_3'P(O)$ where R is an n-octyl chain and R' is an n-hexyl chain
LIX63	2,8-diethyl-7-hydroxy dodecan-6-oxime
TTA	thenoyltrifluoroacetone
HTTA	2-thenoyltrifluoroacetone
TOA	tri-n-octyl amine
TiOA	tri-*iso*-octyl amine
MIBK	methyl *iso*butyl ketone
EDTA	ethylenediaminetetraaceticacid
DTPA	diethylenetriaminepentaaceticacid
HEDTA	hydroxyethylenediaminetriaceticacid
DOPEZ	*N,N'*-dioctanoylpiperazine
REE	rare-earth elements
SPANDS	2-(4-sulphophenylazo) chromotropic acid
COSY	correlation spectroscopy
ca.	circa
δ	chemical shift
dmso	dimethylsulphoxide
e.g.	*exempli gratia*; for example
et al	and others
etc.	*et cetera*; and so forth
g	grammes
$\{^1H\}$	^1H decoupled
Hz	Hertz
J	NMR coupling constant
K	Kelvin
MHz	megaHertz
MS	Mass Spectrometry
Mol	moles
NMR	nuclear magnetic resonance
ppm	parts per million

This work described herein took place in laboratory 1.29 of the Department of Chemistry, University of Leeds, under the supervision of Dr. Malcolm A. Halcrow between October 2002 and 2006. All the work is my own, unless otherwise stated, and has not been presented for any other degree at this or any other University

Chapter One

Introduction to liquid-liquid solvent extraction

1.1 General introduction.

Just over one hundred and thirty years have passed since Berthelot and Jungfleish (1) first enunciated a law governing the distribution of a metal species between two immiscible phases. Since that time the technique and theory of solvent extraction have advanced as the theories and knowledge of solution chemistry and metal complexes have progressed. Almost all of our present-day knowledge of this process has been derived from analytical chemistry.

In the 1940's the need for the separation and recovery of radioactive materials saw the introduction of solvent extraction to large-scale operations, and from this the technique has been applied to metallurgical processing. The large amount of continuing work on both reagents (different extractants) and systems (mixer-settler or column) has resulted in the adoption of solvent extraction as a unit process in hydrometallurgical operations for the recovery of a number of non-ferrous metals.

The process of solvent extraction, which also may be called liquid-liquid extraction, as applied in metallurgical processes, can be described quite simply by equation (1):

$$M + \overline{E} \rightleftharpoons \overline{ME} \qquad (1)$$

Where M is the metal, E is the extractant

In the first step (extraction stage) the metal, M, is transferred from an aqueous phase to an organic phase (the organic phase is represented by a superscript bar) to form complex ME, in which case the process requires that the equilibrium position in this equation be shifted to the right. The second step is the reverse of the first, that is, the metal is transferred from the organic phase to an aqueous phase (stripping stage). This process requires that the equilibrium position be shifted to the left. Essentially, the solvent extraction of metals is a simple operation requiring only a shift in the equilibrium between the extraction and stripping processes. In attempting to understanding the mechanism involved in metal extraction, however, the situation can become complex, depending on several factors, among which the type of extractant and the composition of the aqueous phase are the most important.

Thus the theory of metal extraction into and out of organic medium involves the chemistry of metal complexes in both aqueous and organic media.

1.1.1 The Practical Process of Solvent Extraction.

The general solvent extraction circuit is shown schematically in Fig. 1.1. The metal bearing-aqueous feed solution and solvent are fed, usually in a counter-current manner, into a contactor (mixer) in which the two phases are mixed. In this stage the metal of interest is transferred from the aqueous to the organic phase. After settling, the aqueous phase or raffinate is separated and treated for the recovery of other metals, or goes to waste. From the extraction stage, the loaded solvent may go to another contactor where it is scrubbed with a suitable aqueous solution to remove small amounts of metals or impurities co-extracted in the extraction stage. After scrubbing, the loaded solvent passes to a third stage in which the metal is stripped from the organic phase by some suitable aqueous solution producing a concentrated solution of metal salt, which then goes to further processing for metal production. The stripped solvent is recycled back to the extraction stage; if necessary it is treated (equilibrated) prior to entering the extraction stage. Each of the three stages described, namely extraction, scrubbing, stripping, may involve several contactors in each stage. Thus the extraction of uranium (for example) from sulfate liquors using a tertiary amine as the extractant may require three contactors for extraction, one for scrubbing, and two for stripping.

This chapter discusses the theory of solvent extraction processes. Additional information to practical aspects of solvent extraction is provided in Chapter 2.

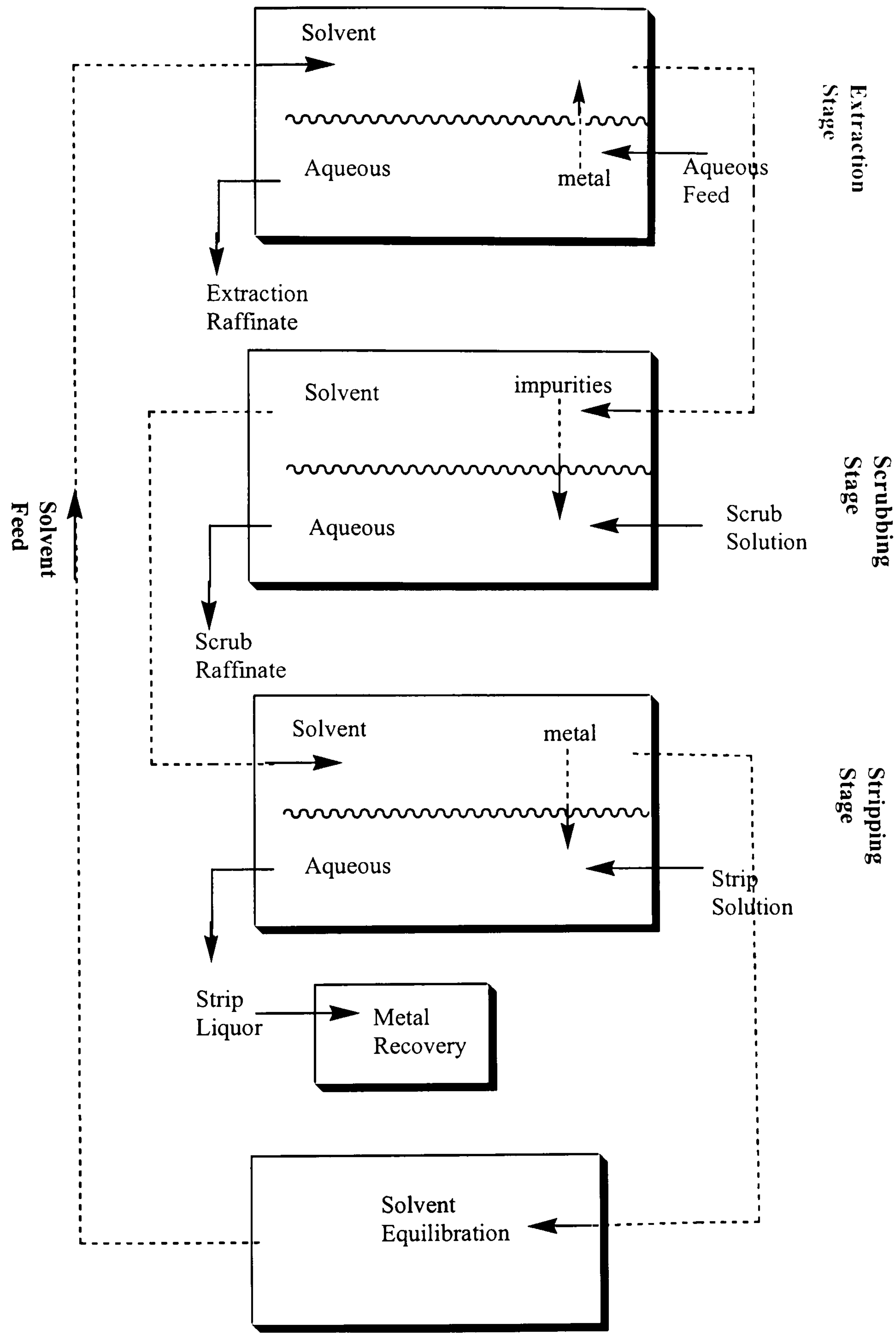


Figure 1.1: The General Process of Solvent Extraction

1.2 Liquid-liquid extraction applications and equipment (contactors).

The evolution and development of new liquid-liquid extraction processes has been strongly dependent upon the structural changes, which have occurred within the chemical industry as a whole. Liquid-liquid extraction currently plays a very important role in many area of chemical processing, which are now discussed in turn.

1.2.1 Nuclear fuel extraction

The traditional sources of energy used in the production of electricity, coal and oil have a finite availability. Consequently, research and development into alternative forms of energy will be needed. The renewable energy sources such as wind, solar, tide and geothermal power are unlikely to be able to meet more than a small fraction of the world's energy needs. In Britain, for example, hydroelectric power has been almost fully exploited, whilst the use of other renewable energy sources is limited. In contrast, nuclear power provides an energy source for the production of electricity, which is both available and reliable. Nuclear power is derived from uranium, which has no significant commercial use other than as a fuel for nuclear electricity generation. The fuel in a modern nuclear reactor comprises uranium oxide or mixture of plutonium and uranium oxides. The nuclear fission of the fissile heavy atoms releases huge amounts of heat, which can then be used to generate steam and drive a turbine to produce electricity as in any conventional power station. The nuclear fission process also produces gamma radiation, neutrons, and fission products. (2)

Most of the nuclear power stations in the world are thermal reactors. Thermal reactors use uranium-235 as their fuel, an isotope that makes up some 0.7 per cent of the naturally occurring uranium mined from earth's crust, the remainder being the isotope uranium-238 that does not undergo fission readily. In order to achieve the most efficient fission of uranium-235 a thermal reactor contains a moderator such as water or graphite, which slows down the fast neutrons produced in the fission process by repeated elastic collision.

A fast reactor differs from a thermal reactor in that it uses plutonium as a fuel, which needs fast neutrons to sustain the fission process, and has no moderator present which would slow down the neutrons. Fast reactors are fuelled with mixed plutonium and uranium-238 oxides and have a further blanket of uranium-238 around the reactor core. The plutonium is consumed in the reactor by the fission process to provide the heat to generate electricity whilst at the same time the uranium-238 captures some of the neutrons produced in the fission process and is transmuted into plutonium. Nuclear fuel reprocessing using solvent extraction is an essential component of the system required to maintain supplies to current and future electricity producing operating reactors (Fig. 1.3). Fig. 1.2 shows uranium refining and conversion from yellow cake by using liquid-liquid extraction technique.

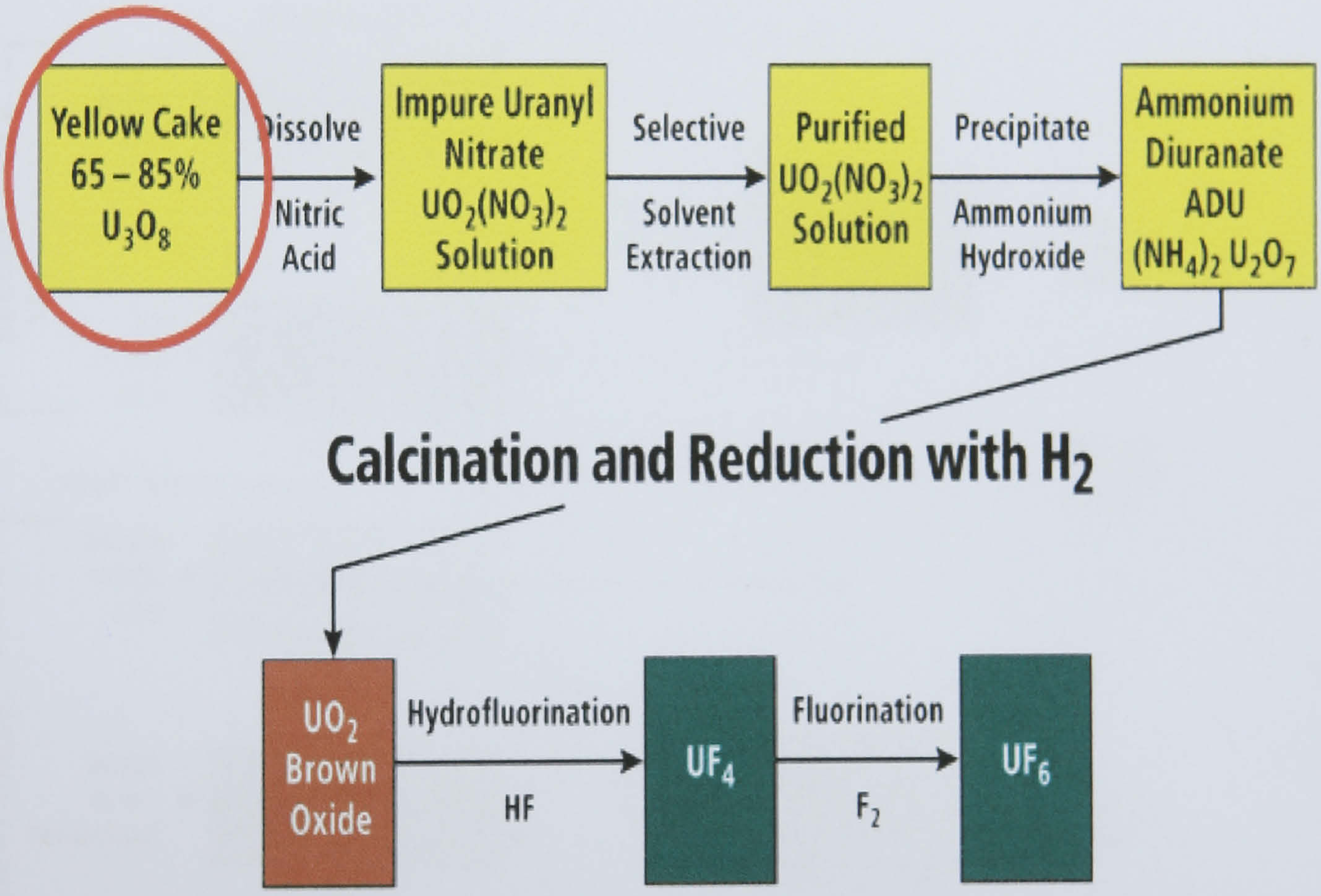


Figure 1.2: Yellow cake refining and conversion to UF_6. (3)

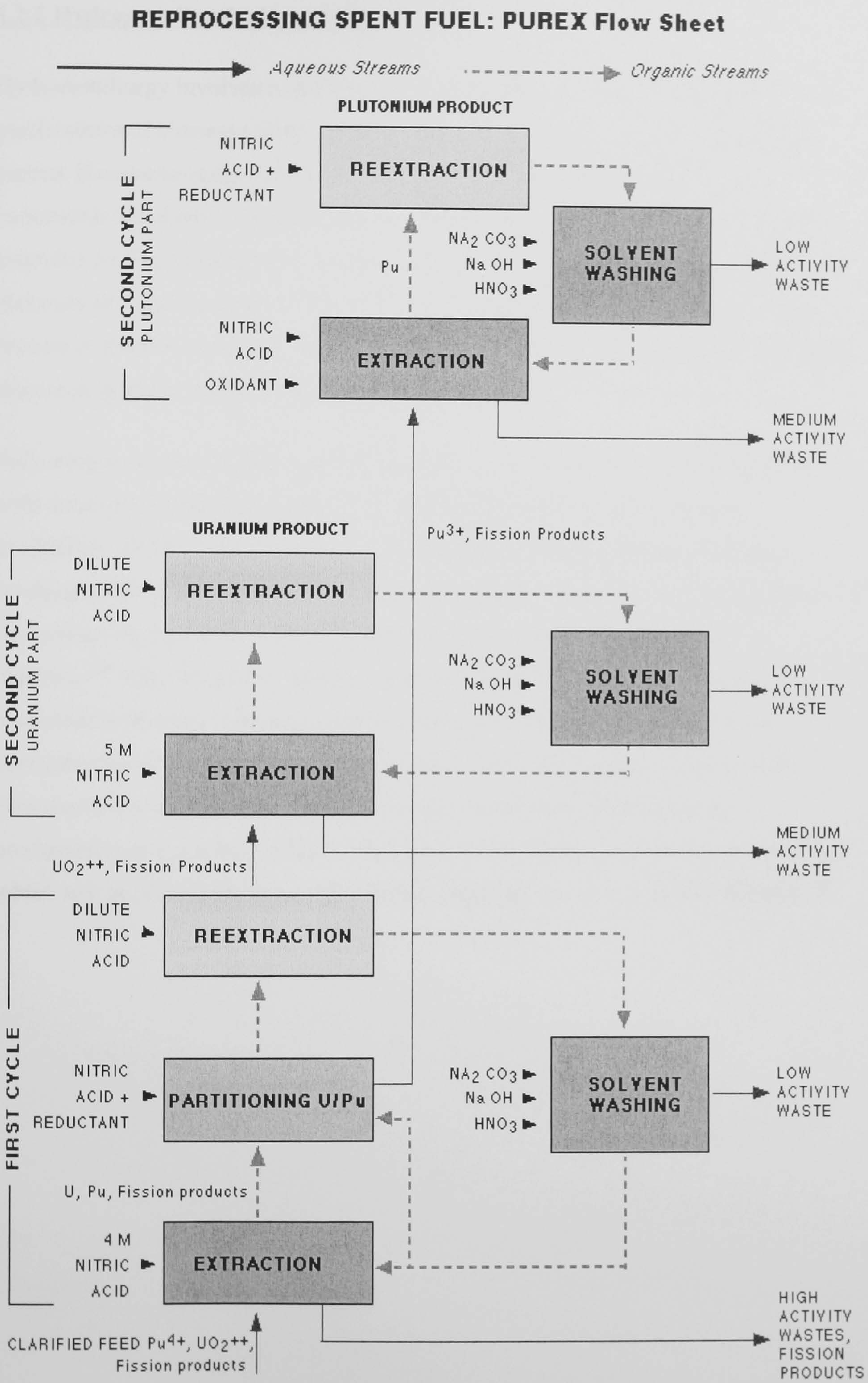


Figure 1.3: PUREX flow sheet, reprocessing spent fuel. (3)

1.2.2 Hydrometallurgical extraction.

Hydrometallurgy involves a series of interlinked unit processes for the recovery and purifications of elements using aqueous solutions. One of the essential features of present flowsheets is the inclusion of a solution treatment step to purify and concentrate the desired element before recovery (Fig. 1.4). Several techniques are available but liquid-liquid extraction has the greatest versatility for the separation of elements and also the range of solution concentrations, which can be treated. This process is therefore now seen as the preferred technique for the treatment of the leach liquors in gold and uranium operations for example. (4)

Following mining and preliminary ore treatment, the feed is subjected to leaching with an aqueous solution, chosen on the basis of the mineralogy of the ore, availability of chemicals, and overall flowsheet demands. Three major types of leaching solution are commonly used: acids, normally sulfuric; bases, for example ammonium carbonate or sulfate; and oxidizing solutions, such as iron(III) chloride. (2) This variation in solution species largely determines the nature of the extractant to be used. Also extractant selection is influenced by the nature and concentration of the elements present as impurities in the leachate. Thus in most flowsheets it is necessary to remove iron prior to solution purification, by precipitation as a complex sulfate, a hydrated oxide species, or to select an extractant which will preferentially extract the desired element leaving iron in the raffinate. (2)

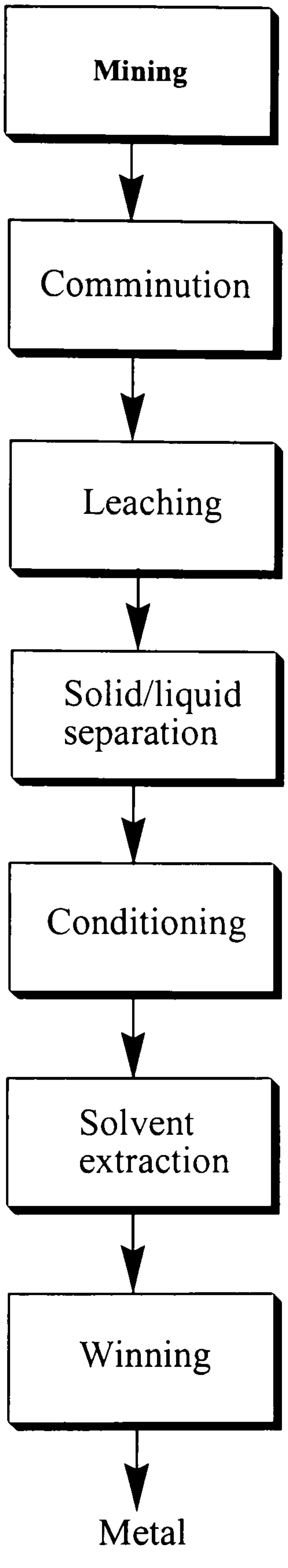


Figure 1.4: Hydrometallurgical route using solvent extraction for extraction of metals from ores. (2)

A list of common used hydrometallugical extractants is given in Table 1.1.
The general requirements that an extractant should satisfy for hydrometallurgical operation are as follows. (5) The strength of an extractant is a measure of its ability to transfer the metal both in extraction and stripping. This includes such properties as metal loading capacity; the ability of selectivity is to provide a pure product free from impurities; a high solubility in the chosen organic diluent of both the extractant and the metal complex. This determines the required volume of the organic phase and hence the size of the plant. Also, low aqueous solubility of the extractant is desirable to minimize its loss from the circuit to the environment. The speed, kinetics of extraction and stripping determine mixer size and stage efficiency in the solvent extraction process. Good separation of the aqueous and organic phases are required after contacting either in extraction or stripping, with little tendency to form stable emulsion; finally, the extractant should have good stability with regard to hydrolysis and oxidation, thereby allowing extensive recycling without degradation. In addition, any degradation products should preferably be inactive towards extraction.
An addition should be made to this list, that is, easy synthesis and low cost. Also, because it is unrealistic to assume that no organic phase will be released into the environment, (6) the extractant and diluent should be non-toxic and biodegradable.

Hydrometallurgical techniques have fewer environmental problems compared to older technologies for metal refining. As world supplies of high-grade ores are decreasing, techniques are required for the recovery of metals from low-grade ores, transition ore, dumpstocks, mixed metals and residues. (7) Hydrometallurgy is being developed as a more enviromentally sound and diverse technique to adress these challenges. (8) In addition, it has some economic benefits, as it avoids the high temperatures of pyrometallurgy. Transport costs can be reduced because plants can be situated near the ore bodies. Hydrometallurgical methods use reactions in aqueous solutions to extract selectively and/or concentrate targete metal ions. (9) The hydrometallurgical process often involves leaching of the ore as the initial step. Leaching is the selective dissolution of the metal and this is often carried out with sulfuric acid. Liquid-liquid extraction is the next stage in the process and involves the selective transport of metal ions into organic phase.

Table 1.1: Some extractants used in hydrometallurgical processes.

Extractants	**Chemical name**	**Trade name**	**Uses**
(A) Acidic extractants	**(1) di-2-ethylhexyl phosphoric acid**	**D2EHPA**	**Co/Ni separation, Zn, Be, Cu, Ga, Rare earths, and synergistic with TOPO for U from H_3PO_4**
	(2) di-p-octylphenyl phosphoric acid	**OPPA**	**U from H_3PO_4**
	(3) 2-ethylhexyl phosphoric acid mono-2-ethylhexyl ester	**PC-88A**	**Co/Ni separation, Zn, Th, U, and Rare earths**
	(4) di-2,4,4-trimethylphenyl phosphoric acid	**Cyanex272**	**Rare earths, Co/Ni, and V**
	(5) 5,8-dinonylnaphthyl sulfonic acid	**DNNS**	**Co, and Ni**
(B) Basic extractants			
(1) Primary amine	**1,1,3,3,5,5,7,7,9,9-decamethyl decylamine**	**Primene JMT**	**Th, U, and Rare earths**
(2) Secondary amine	**di-tridecyamine**	**Adogen283**	**Th, U, Cr, Cu, Cd, and Mo**
(3) Tertiary amine	**(1) tri-octylamine**	**TOA/Alamine**	**U, V, W, Mo, Cu, Co, and Rare earths**
	(2) tri-isooctylamine	**TiOA/Adogen381**	**U, V, W, Mo, Cu, Co, and Rare earths**
(4) Quaternary ammonium salt	**Tri-octylmethyl ammonium chloride**	**Aliquat336**	**U, Mo, V, and W**

Table 1.1 continued.

(C) Solvating extractants	**(1) tri-n-butylphosphate**	**TBP**	**U, Zr/Hf, Fe, and Rare earths**
	(2) tri-octylphosphine oxide	**TOPO**	**U from H_3PO_4**
	(3) tri isobutylphosphine sulfide	**Cyanex471**	**Ag/Cu, and Pd/Pt**
	(4) methyl isobutyl ketone	**MIBK**	**Ta/Nb, Hf/Zr, Au, and Li**
	(5) 2-hydroxy-5-dodecylbenzophenone oxime	**LIX64**	**Cu, and Ni**
	(6) 2-hydroxy-3chloro-5-nonylbenzophenone oxime	**LIX70**	**Cu**
	(7) 8-hydroxy-7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline	**Kelex**	**Cu, and Zn**

1.3 Types and selection of contactors

The technique of liquid-liquid solvent extraction for the separation of multicomponent mixtures involves the partitioning of two or more solutes between immiscible solvents and such processes in general require a greater number of theoretical stages than is necessary for the extraction of a single solute. The key piece of equipment for any solvent extraction process is the contactor in which the two immiscible phases are mixed together. The purpose of the contactor is to mix intimately the two phases to provide sufficient interfacial area across which the transfer of the required solute takes place. The types of contactor that have been used in reprocessing plants comprise box and pump mixer-settlers, pulsed columns, pulsed packed and plate columns, and centrifugal types. (10, 11)

There is no universal contacting equipment suitable for all solvent extraction operations. Even within a plant, it may be completely wrong to select the same type of contactor for all stages of the extraction process. Each plant, therefore, has to select the type of aqueous feed and composition, the solvent type govern the final selection on and composition, and how physical characteristics affect the mixing process, flow patterns and coalescence. (12) Naturally the mass transfer efficiency in the cycle must also be considered. With an adequate understanding of all physico-chemical variables present in the process that will thus have an effect on the extraction, as well as the minimizing of emulsion and crud, then the right equipment for that plant can be selected. (13, 14) The type of equipment and the method of agitation used to achieve mass transfer are of concern, if emulsion formation is to be minimized. (13) Degradation of the solvent may have to be considered in the equipment choice, depending on the chemical system. In one plant, centrifugal contactors were chosen over mixer-settlers because they resulted in lower solvent degradation. (15)

1.3.1 Basic principles of extractors. (16)

The basic requirements of an industrial contactor may be summarized as follows: Efficient extraction; maximum surface area of mass transfer; adjustable flow feeds for maximum solute recovery; and low capital, operating and maintenance costs.
In general, there are three main types of extractors, which are now briefly discussed in turn.

1.3.2 Mixer-settlers.

The mixer-settler is a multistage device, with each stage having two parts: the mixer where one phase is dispersed in the other by mechanical energy to permit solute extraction between two immiscible phases; and the settler where one phase disengaged from the other (Figs. 1.5, 1.6). Mixer-settlers may be stacked vertically or horizontally with flows generally counter current between devices. The aim of any design of mixer-settler is to make the total equipment volume as small as possible, and the mixer chamber should be of sufficient size to give an adequate residence time to bring the two phases close to equilibrium. In addition, the settler should be big enough to ensure complete phase disengagement. For such a system, the two liquid phases are added and mixed. Due to their density differences, one phase will settle out and the mixture will be separated. (17) There are many advantages of mixer-settlers: they are efficient, have a low head room, induce good contacting and can handle any number of counter-current stages. However, few disadvantages such as high operating costs and high set-up costs must be considered.

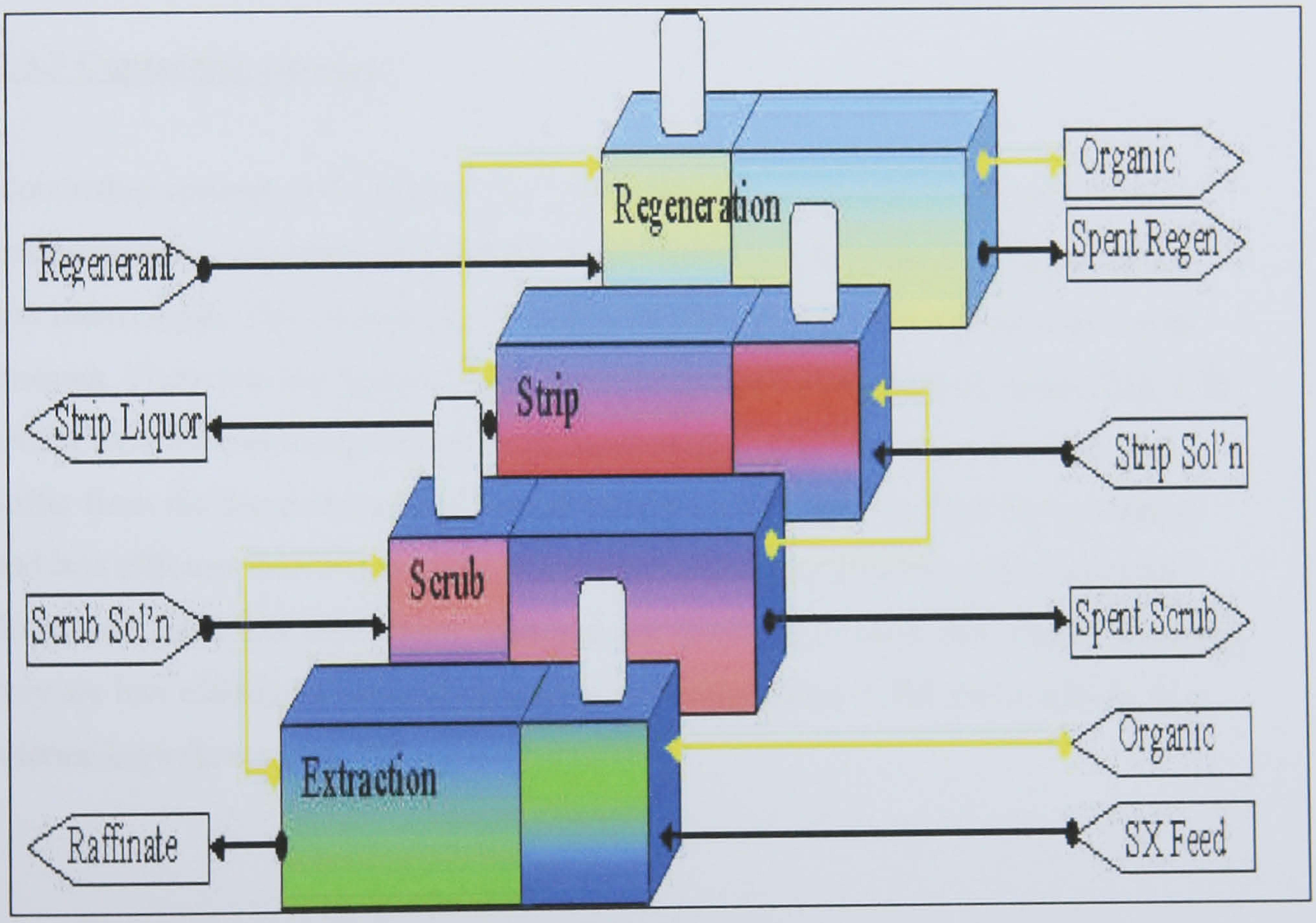


Figure 1.5: Use of mixer-settlers in a hydrometallurgical process. (18)

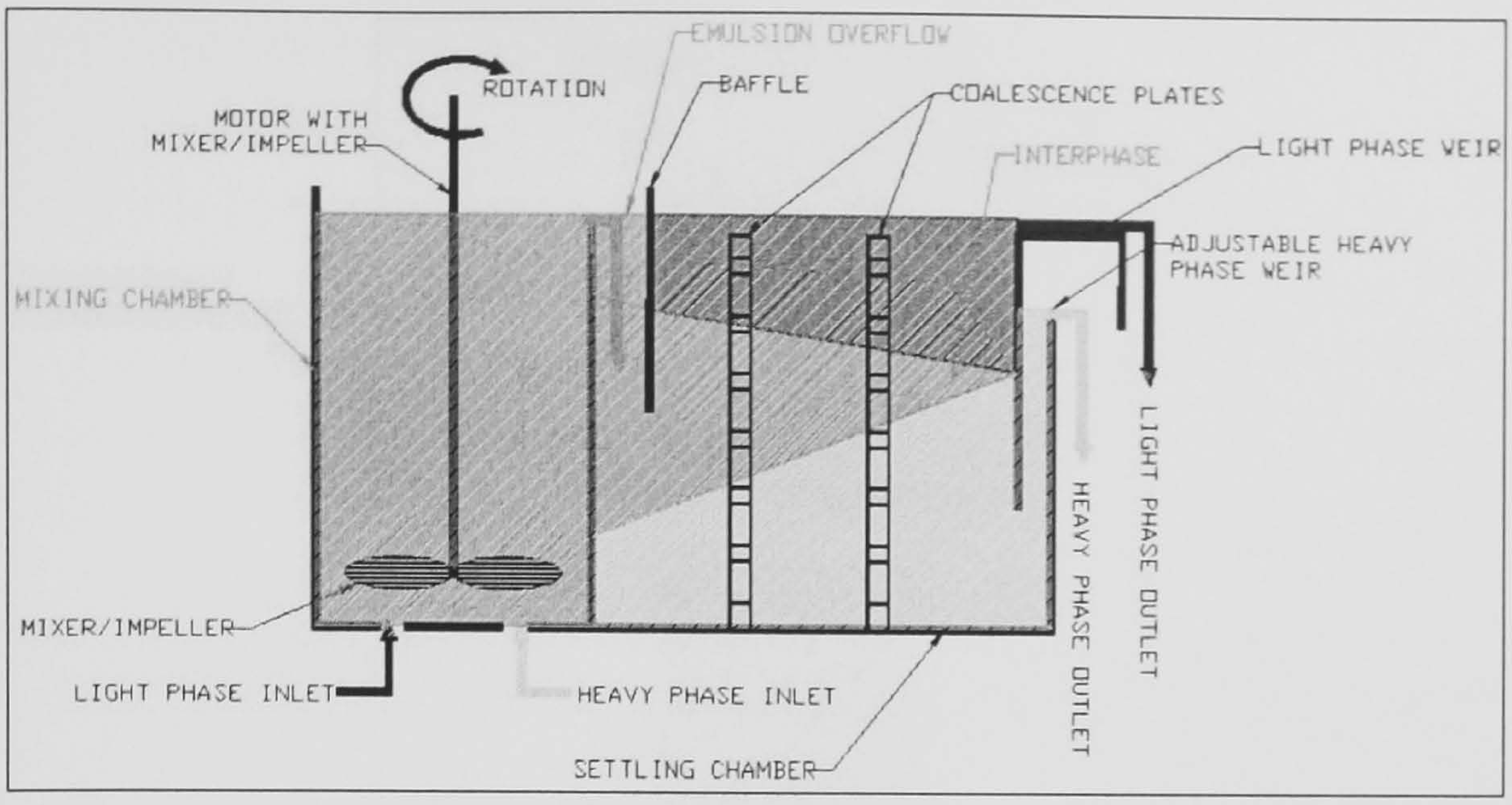


Figure 1.6: Unit operation in mixer-settlers. (18)

1.3.3 Contacting columns.

Contacting columns are practical for most liquid-liquid extraction systems. The packings, trays, or sprays increase the surface areas in which the two liquid phases can intermingle. This also allows for a longer flow path that the solution can travel through. There are two types of columns: Columns without agitation (static, Fig. 1.7) which have the advantages of small investment costs and low operating costs but suffer from the disadvantages of being both difficult to scale up from the laboratory and less efficient than mixer-settlers. Columns with agitation (Fig. 1.8) give good dispersion, have low investment costs and can handle any number of stages. However, they are less efficient at separating phases with small density difference and do not tolerate high flow ratios. (19)

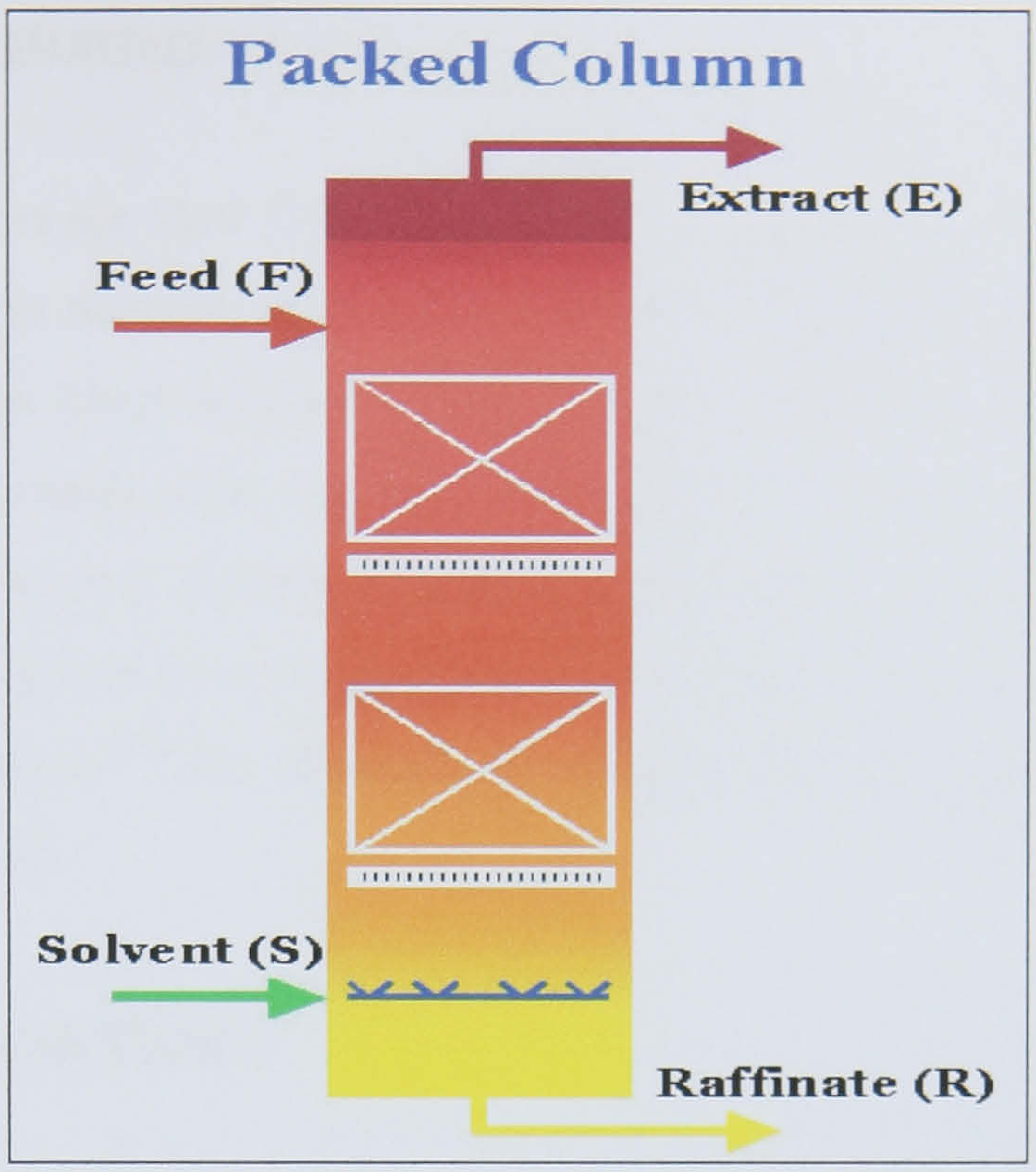


Figure 1.7: Static column (random packing). (20)

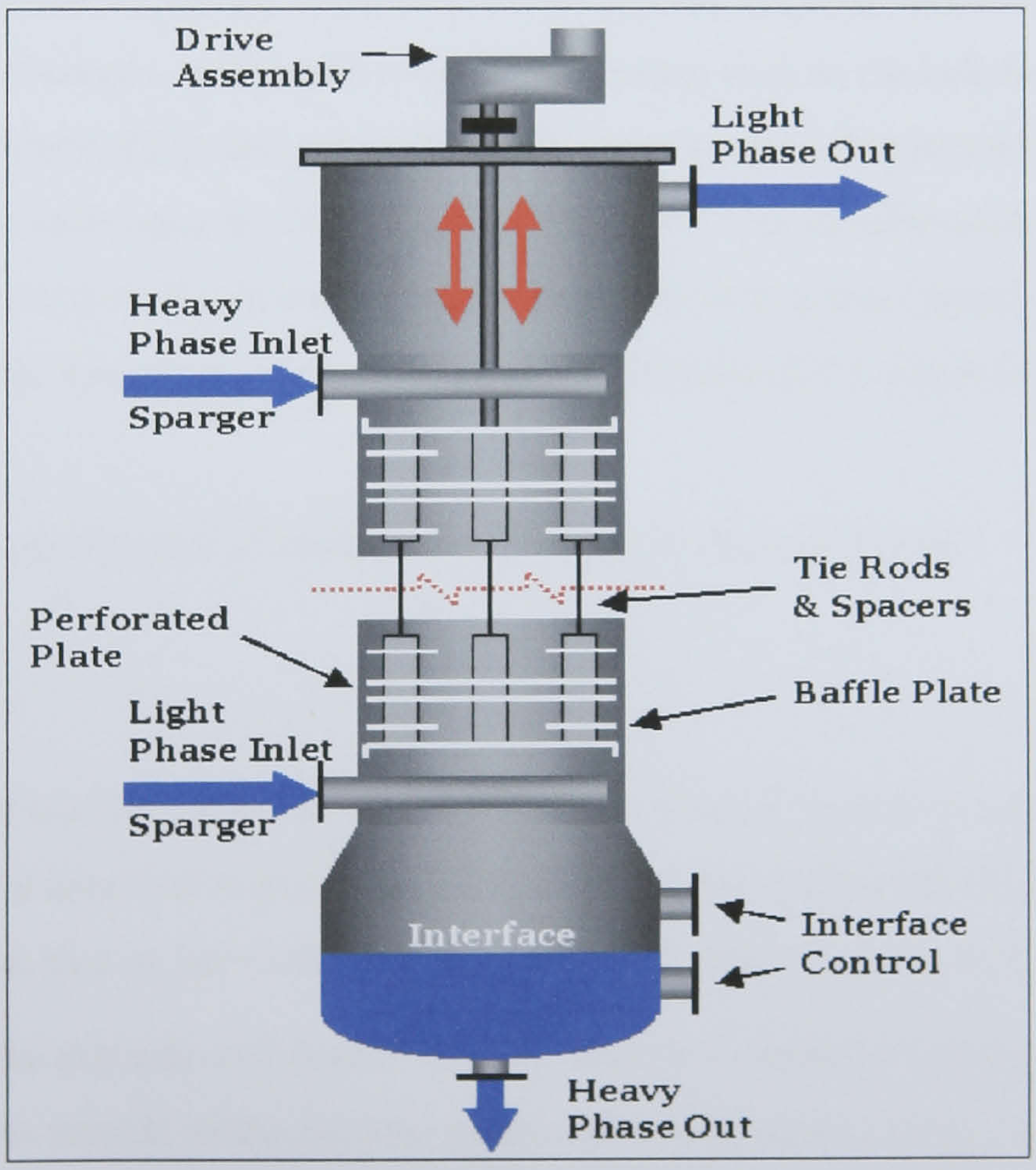


Figure 1.8: Agitated column (karr column). (21)

1.3.4 Centrifugal extractors.

Centrifugal contactors are ideal for systems in which the density difference between the phases is small. In addition, these systems have the following advantages over other contactor types: Short residence times, leading to less solvent damage; smaller space requirements; easier wash out; and greater flexibility with respect to physical properties of solutions (e.g. density, viscosity). Also, in these systems, mechanical devices are used to agitate the mixture to increase the interfacial area and decrease mass transfer resistance. (19) But they have both high set-up costs and high operating and maintenance costs.

1.4 Solvent Extraction Theory.

When a metal-containing aqueous phase is shaken with an organic phase the metal species will be distributed between the two phases. The distribution may be mainly chemical or physical in nature, depending on the system. Physical extraction involves the separation of simple, uncharged covalent molecules such as the halides of arsenic(III), antimony(III), and germanium(III), into organic solvents such as carbon tetrachloride. In such cases the Nernst distribution law (22) is usually valid, and the distribution coefficient, K_D, is independent of both the total solute (metal) concentration and the phase ratio (the ratio of the volumes of the aqueous and organic phases).

Then K_D is simply the ratio of metal concentrations in the two phases:

$$K_D = \frac{\overline{M}}{M} \tag{2}$$

Thus the Nernst law depends only on the solubility of metal species in the solvent phase. No strong chemical interactions between the metal species and the organic phase take place; that is, the metal is in an identical chemical form in both phases.

Alternatively, the extraction of metals can also involve a chemical reaction between the metal species present in the aqueous phase and one or more components of the organic (solvent phase). As a result, the Nernst distribution law does not hold in such systems, although it will be seen that the basic equation used in practical solvent extraction studies resembles closely the Nernst distribution equation (see below).

Normally a metal ion exists in aqueous solution as a hydrated ion with little or no tendency to transfer to an organic phase. Thus in order to achieve the required transfer the metal ion has to be modified. To convert a metal ion to an extractable species its charge requires neutralisation and some or all its water of hydration has to be replaced by some other molecule or ion. These requirements can be met by complexing the metal ion with an ion of opposite charge to form a neutral species, which at the same time replaces some or all of the water of hydration around the metal ion. The formation of ion-association complexes in this way also provides for the formation of a neutral complex with the extractant. We can consider the overall process as one of converting a hydrophilic species into a lipophilic species.

Complexation of a metal ion can be achieved as a process in which the hydrated water molecules are replaced by other more complex ligands. All complexation reactions are substitution reactions. The nature of the extractable metal species is therefore of fundamental importance in metal extraction systems. So, we can classify extraction systems on this basis, depending on whether they result in compound formation, ion-association, or simply solvate the metal ion.

This method of classification is not meant to imply that these systems are mutually exclusive, but to simplify discussions of the various systems. Indeed, some extractants can belong to more than one class. The theory of solvent extraction is based on that used in analytical chemistry, and because most metal extraction systems in this field involve metal chelate complexes, most of the theory also concerns such complexes. (23, 24) Our knowledge of the chemistry of metal-organic complexes and our understanding of solvent extraction processes involving metal chelates is much greater than for the other extraction systems.

1.5 Systems Involving Compound Formation.

The simplest equation that can be written to illustrate the extraction of a metal ion, M^{n+}, by an extractant, HA, is

$$M^{n+} + n\overline{HA} \rightleftharpoons \overline{MA_n} + nH^+ \qquad (3)$$

Since this resembles the process of solid-liquid ion exchange, in which HA is equivalent to an ion-exchange resin, it is not surprising that solvent extraction is also referred to as liquid ion exchange. Thus systems employing chelating and acidic extractants are cation-exchanger systems, while those basic extractants employing amines are anion-exchanger systems. One point, which should be made, is that we should consider the activities of the various species involved in metal extraction, rather than their concentrations. However, provided the concentrations of the metal are low, activity and concentration may be regarded as the same. In the following discussions we shall use concentrations, simply because this makes the equations much less cumbersome to deal with.

Equation (3) indicates that the extraction of a metal described by this equation is heavily dependent on the equilibrium pH of the aqueous phase. Thus, as the pH is decreased (and the hydrogen ion concentration increased), metal extraction will decrease since the equilibrium will be shifted towards the left. Conversely, as the pH is increased, metal extraction will increase. Of course, a limit is imposed here by the pH at which the metal chelate hydrolyses. The extraction is also dependent on the stability of the extractable metal complex formed, which is a function in part of the extractant.

For example, in the extraction of copper(II) by a monobasic reagent, HA, the extraction of one mole of copper will produce two moles of hydrogen ions.

$$CuSO_4 + \overline{2HA} \rightleftharpoons \overline{Cu(A)_2} + 2H^+ + SO_4^{2-} \qquad (4)$$

And in the extraction of ferric iron, three moles of hydrogen ions will be produced for every mole of Fe(III) extracted:

$$Fe_2(SO_4)_3 + \overline{6HA} \rightleftharpoons \overline{2Fe(A)_3} + 6H^+ + 3SO_4^{2-} \qquad (5)$$

In order to achieve high metal loading of the solvent, the hydrogen ion produced must be neutralised in order to drive equilibrium to the right.

The degree to which a metal is extracted by a solvent can be determined by an analysis of the aqueous phase. (25) Let us consider the extraction of copper as illustrated by the equation (4). If we shake together an aqueous solution of copper sulfate of known concentration with a volume of, 8-hydroxyquinoline (oxine) solution at suitable pH, at equilibrium we will have.

$$CuSO_4 + 2\overline{HOx} \rightleftharpoons \overline{Cu(Ox)_2} + 2H^+ + SO_4^{2-} \qquad (6)$$

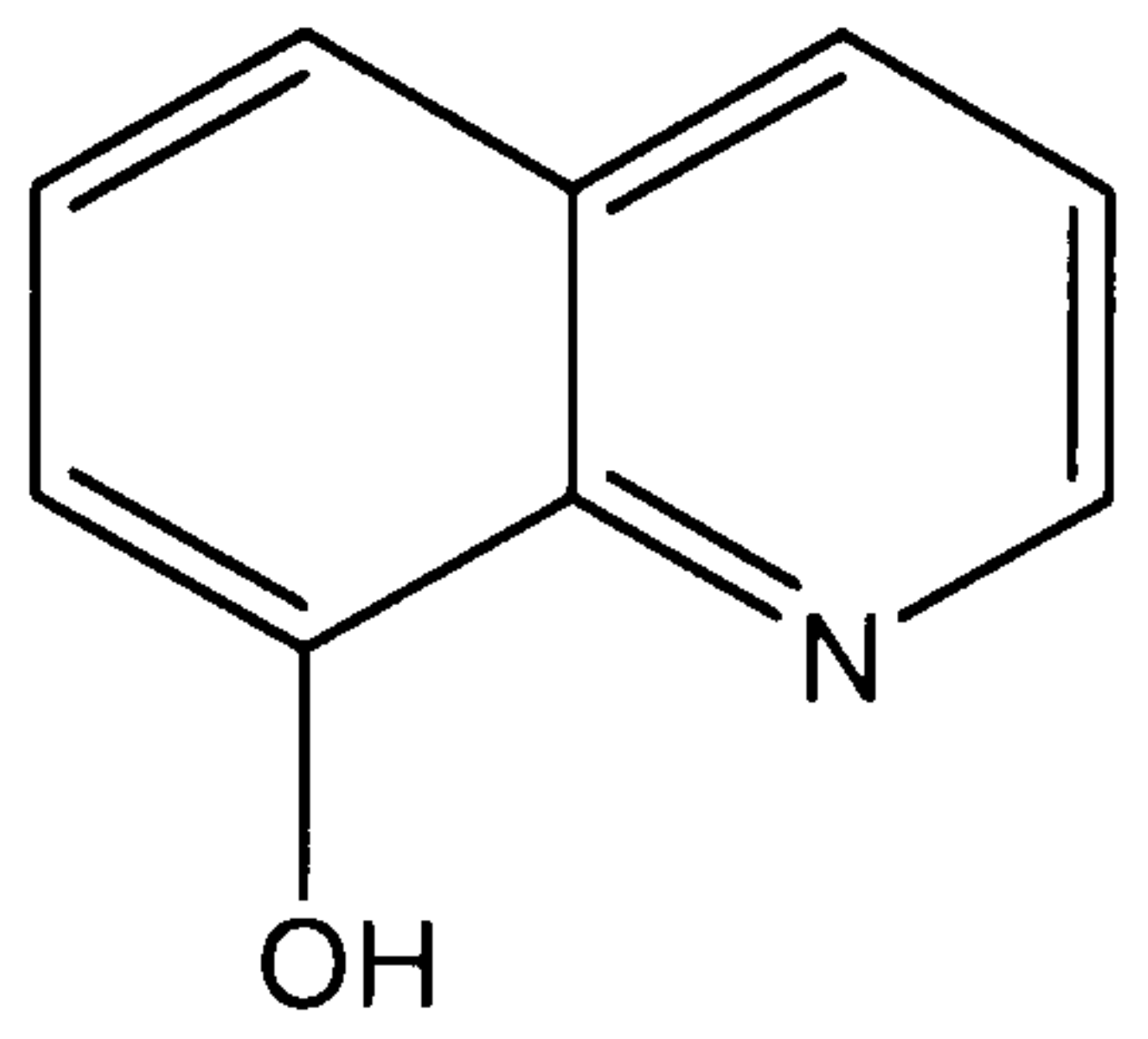


Figure 1.9: Chemical structure of 8-hydroxyquinoline (oxine).

The amount of copper extracted is determined by analysis of the aqueous phase (raffinate) after shaking. Since we know the initial concentration of copper we can calculate its concentration in the organic phase. This analytically determined distribution ratio of a metal between an aqueous phase and an organic phase is known as the extraction coefficient, or the distribution coefficient, D, and is defined as.

$$D = \frac{\text{concentration of metal in the organic phase}}{\text{concentration of metal in the aqueous phase}} \qquad (7)$$

This very simple relationship is basic to all solvent extraction studies, and provides much of the data on which solvent extraction processes are based. Calculation of D, based only on the initial metal concentration in the aqueous phase and its concentration in the raffinate, assumes that a mass balance of the metal ion is obtained. There are conditions that must be taken into consideration in the use of this approach to the determination of D.

These conditions are: No volume change occurs on shaking the two phases; no third phase is formed; and so-called crude (an emulsion between the aqueous and organic phase) should not be formed. The presence of crude, or a third phase, in any shake-out will mean that the system is unsuitable for a solvent extraction process.

As defined, D is independent of the phase ratio of the aqueous and organic phases. However, it would be evident that the phase ratio will influence the amount of metal extracted. For example, the amount of extractant available for extraction purposes is given by its concentration multiplied by the phase volume:

$$\text{Total amount of HA} = [\text{HA}] \times \text{V} \qquad (8)$$

where V is the volume of the organic phase.

Now the equilibrium constant (K_E) for the system described by equation (3) is given by:

$$K_E = \frac{\overline{(MA_n)}}{(M^{n+})} \cdot \frac{(H^+)^n}{\overline{(HA)}^n} \qquad (9)$$

which is a mathematical expression for the law of mass action. This law, due to Guldberg and Waage, (26) states that the velocity (rate) of a chemical reaction is proportional to the active masses of the reacting substances, where active mass will be taken as concentration.

If this law is applied to a simple reversible reaction at constant temperature, such as:

$$\text{A} + \text{B} \rightleftharpoons \text{C} + \text{D} \qquad (10)$$

then the rate, or velocity, at which A and B react is proportional to their concentrations:

$$V_f = K_f(\text{A})(\text{B}) \qquad (11)$$

where V_f is the velocity of the forward reaction which produces the reaction products C and D, and K_f is the proportionality constant. In the same way the reverse reaction can be written as:

$$V_r = K_r(\text{C})(\text{D}) \qquad (12)$$

Now at equilibrium, $V_f = V_r$ so:

$$K_f(\text{A})(\text{B}) = K_r(\text{C})(\text{D}) \qquad (13)$$

$$K_E = \frac{K_f}{K_r} = \frac{(C)(D)}{(A)(B)} \tag{14}$$

where K_E is defined as the equilibrium constant for the reaction at constant temperature. This equation tells us if one of the reactant or product concentrations is changed, the equilibrium will adjust itself so as to keep K_E constant. If the concentration of metal ion in the aqueous phase is increased, then the amount of metal extracted will increase to compensate and maintain K_E constant. This assumes that there is sufficient free extractant available in the solvent to extract more metal. This effect is prevalent in solvent extraction processes in which the solvent is loaded to near its maximum; an increase in metal concentration in the feed cannot be extracted and hence remains in the raffinate.

$$K_E = E\left[\frac{(H^+)}{(HA)}\right]^n \tag{15}$$

refer to eq. (3), (9) and so

$$E = K_E\left[\frac{(HA)}{(H^+)}\right]^n \tag{16}$$

The extraction coefficient E, is proportional to the equilibrium constant, to the n^th^ power of the extractant concentration in the solvent phase, and is inversely proportional to the n^th^ power of the hydrogen ion concentration in the aqueous phase. Also, E is independent of the total metal concentration.

If we sum the equilibria involved in solvent extraction (Fig. 1.10), assuming that ionisation of the extractant occurs in the aqueous phase, the equilibrium constant is then:

$$K_i = \frac{(H^+)(A^-)}{(HA)} \tag{17}$$

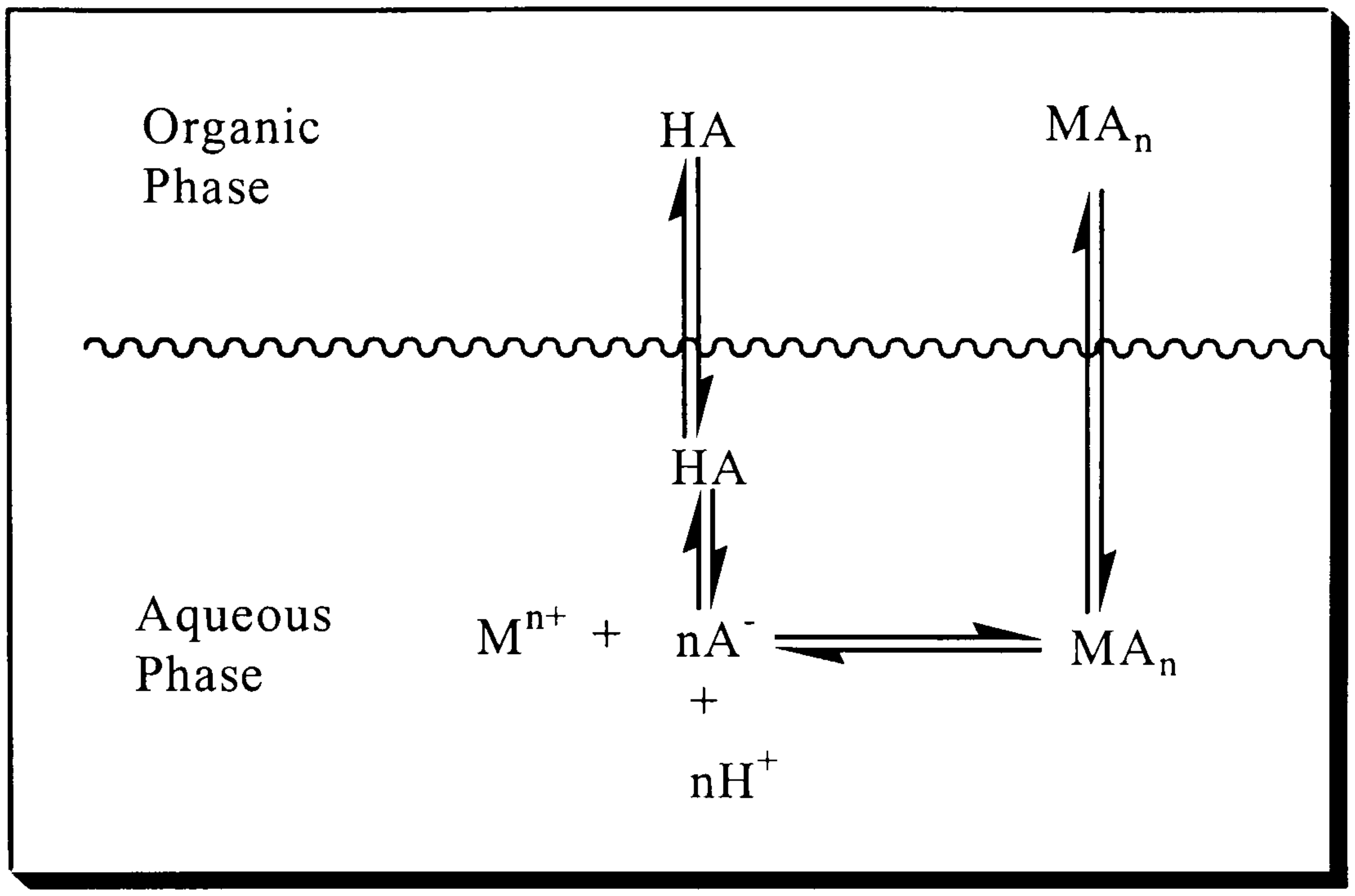


Figure 1.10: Some equilibria involved in the extraction of a metal.

This is followed by formation of the extractable metal complex, which is a stepwise series of reactions:

$$M^{n+} + A^- \overset{K_1}{\rightleftharpoons} MA^{(n-1)+}$$

$$K_1 = \frac{MA^{(n-1)+}}{(M^{n+})(A^-)} \tag{18}$$

$$MA^{(n-1)+} + A^- \overset{K_2}{\rightleftharpoons} MA_2^{(n-2)+}$$

$$K_2 = \frac{(MA_2^{(n-2)+})}{(MA^{(n-1)+})(A^-)} \tag{19}$$

$$MA_{(n-2)}^{2+} + A^- \overset{K_{n-1}}{\rightleftharpoons} MA_{(n-1)}^{+}$$

$$K_{(n-1)} = \frac{(MA_{(n-1)}^{+})}{(MA_{(n-2)}^{2+})(A^-)} \tag{20}$$

$$MA_{(n-1)}^{+} + A^{-} \overset{K_n}{\rightleftharpoons} MA_n$$

$$K_n = \frac{(MA_n)}{(MA_{(n-1)+})(A^-)} \tag{21}$$

The overall formation constant for the MA_n complex, K_f, is:

$$K_f = K_1 K_2 \ldots\ldots\ldots\ldots K_{n-1} K_n \tag{22}$$

For the distribution of the extractant between the two phases we have:

$$K_{ex} = \frac{\overline{(HA)}}{(HA)} \tag{23}$$

This value will depend on the solubility of the extractant in the aqueous phase. It should be noted that the value of K_{ex} could vary considerably depending on the salt concentration, temperature, and pH of the aqueous phase.

The other equilibrium conditions for the metal–extractant species between the queous and organic phases (K_{MAn}) are shown in Fig. 1.10.

$$K_{MAn} = \frac{\overline{(MAn)}}{(MAn)} \tag{24}$$

Other reactions which may be operative, but not shown in Fig. 1.10, are those involved in metal complexation in the aqueous phase hydrolysis:

$$M(H_2O)_m^{n+} \rightleftharpoons M(H_2O)_{m-1}(OH)^{(n-1)+} + H^+ \tag{25}$$

and complexation involving any anionic components in the aqueous phase:

$$M^{n+} + X^- \rightleftharpoons MX^{(n-1)+} \tag{26}$$

An example of the latter is ion-association or outer–sphere complexation such as:

$$Co(H_2O)_6^{2+} + SO_4^{2-} \rightleftharpoons Co(H_2O)_6^{2+}.SO_4^{2-} \tag{27}$$

1.6 Solvent loading capacity.

The major importance in commercial solvent extraction processing is the limiting portion of the extraction coefficient (E), expressed as E against percent of TBP in the organic phase plots as shown, for example, in Fig. 1.11. The extent of the limiting portion of the extractant depends on factors such as the pH at which hydrolysis or complexation of the metal ion occurs in the aqueous phase, the solubility of the extractable species in the solvent phase or the loading capacity of the solvent.

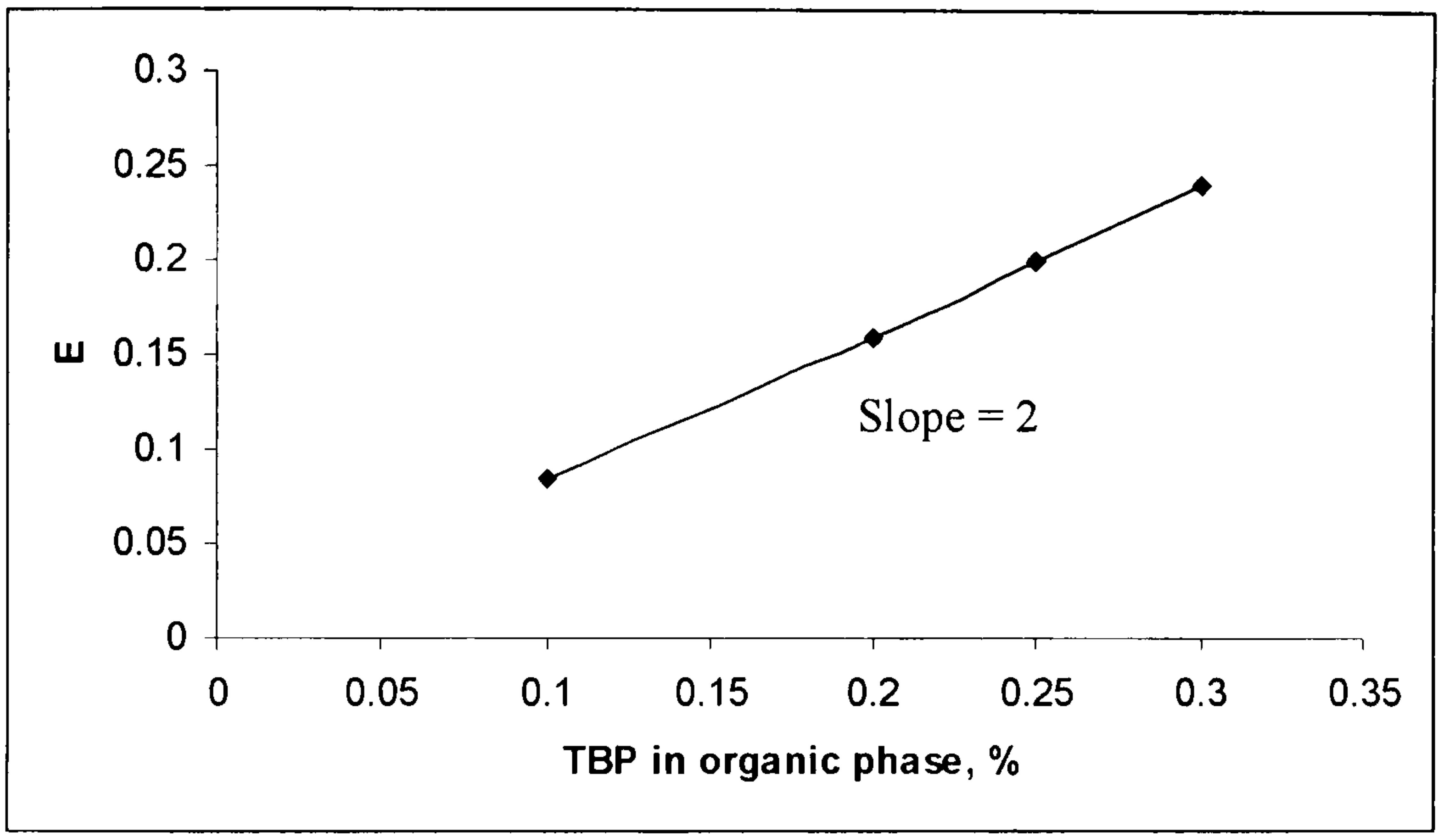


Figure 1.11: Variation of extraction coefficient of uranium with TBP concentrations. (26)

Many solvent extraction processes are operated in this region simply because this is where maximum utilisation of the solvent occurs under the particular set of conditions used. While it is not absolutely necessary, nor indeed always possible (for example, as a result of high viscosity of the solvent) to operate at the point of maximum solvent loading, doing so ensures that a minimum solvent flow rate is required, which is of considerable economic importance.

It should be pointed out that for a single-stage process (of which there are very few) the above comments apply directly. In a multi-stage process, and most commercial operations are of this type, we are talking about the last stage of the extraction circuit, and the stages prior to this will have lower solvent utilisation. For a system involving the separation of the two metals where the separation factor is small, it is usually best to operate under maximum solvent loading conditions consistent with low metal loss to the raffinate, in order to inhibit co-extraction of the metal having the lower extraction value.

The maximum loading obtainable by a solvent depends, among other things, on the total available or free extractant and on the solubility of the metal-extractant species, rather than any limitation in the extent of extraction. The solubility of an extractable species depends in large part on the diluent used in the solvent, and also on any modifier present. Poor solubility of an extracted species results, in many cases, in the formation of a third phase intermediate in density between the diluent and the aqueous phase. To inhibit third phase formation a modifier is usually added to the solvent to increase the solubility of the extracted species.

Extraction of a metal by a particular solvent does not necessarily increase linearly with increase in the extractant concentration in the solvent. An example is shown in Fig. 1.13, for the case of extraction of cobalt with D2EHPA (di-2-ethylhexyl phosphoric acid).

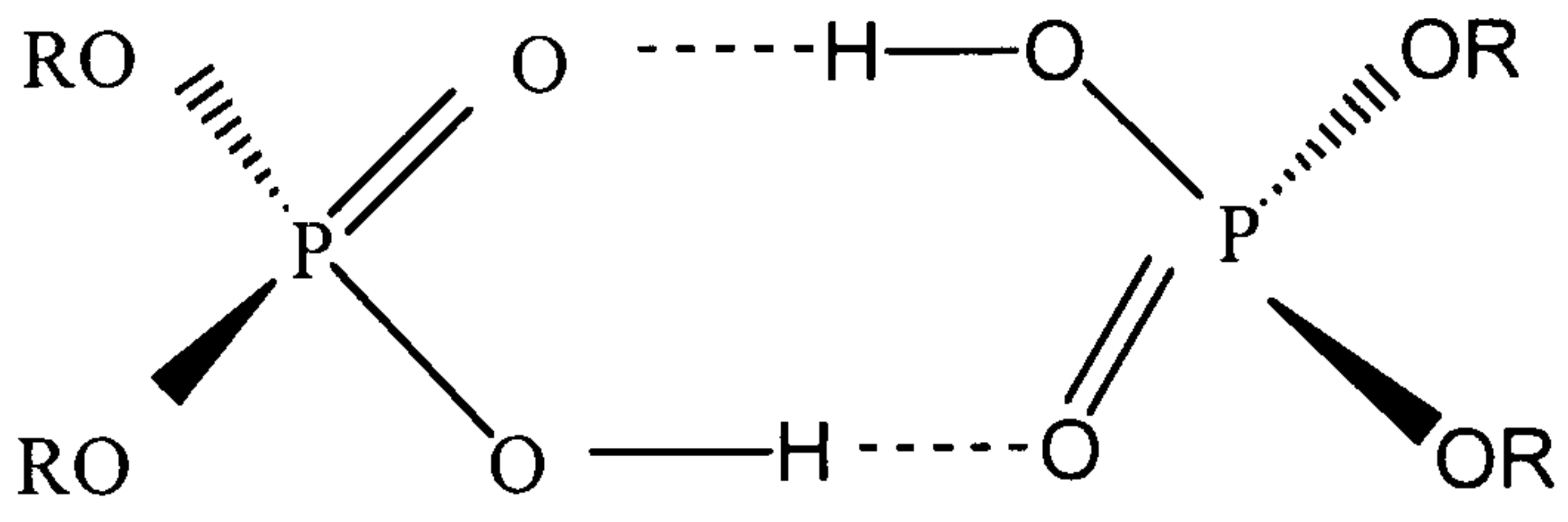


Figure 1.12: Dimer form of D2EHPA.

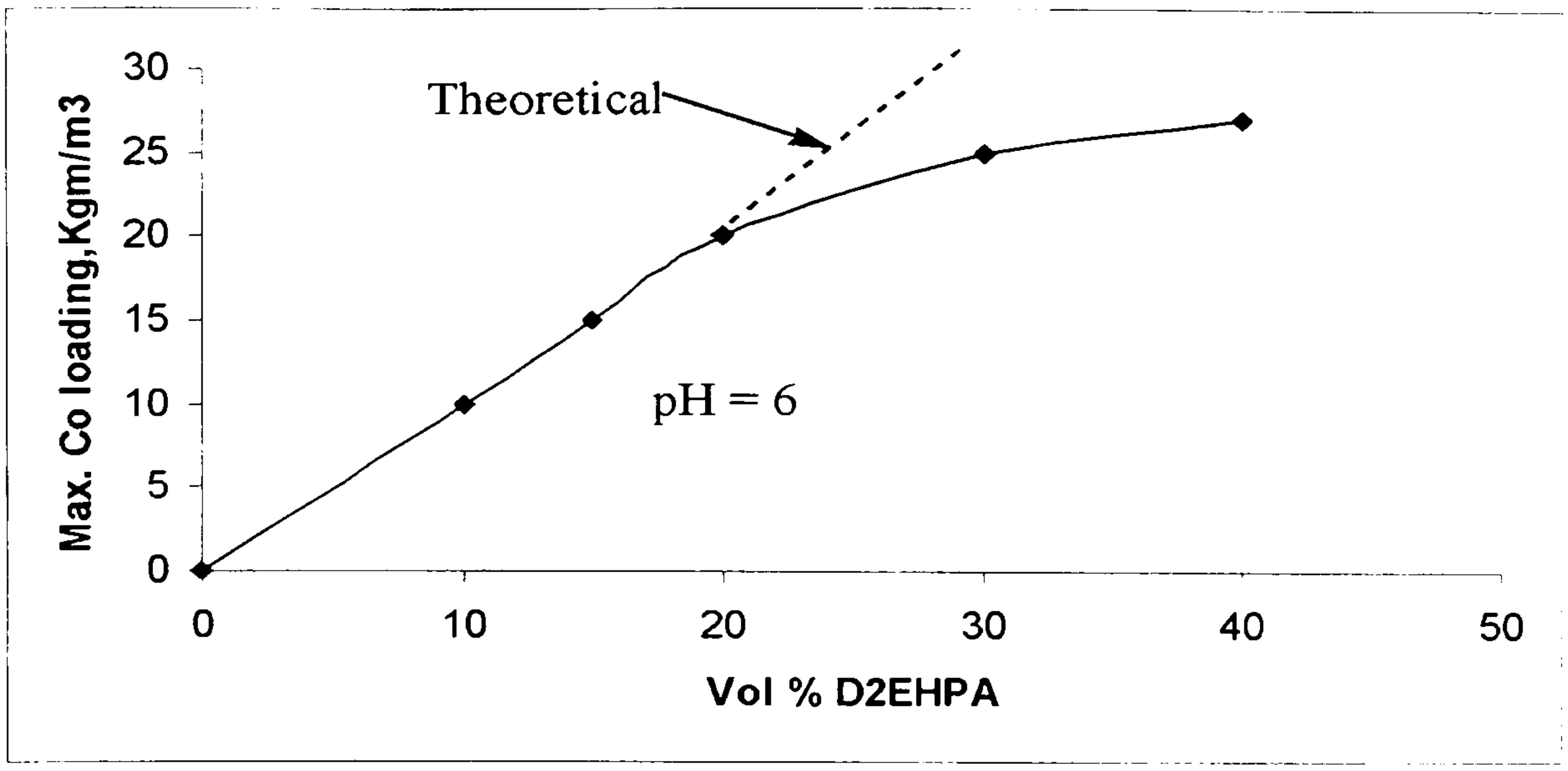


Figure 1.13: Extraction of cobalt by D2EHPA as a function of D2EHPA concentration. ⁽²⁷⁾

The deviation from linearity may be due to dimerisation or polymerisation of the extractant, or a decrease in solubility of the extractable cobalt complex without the formation of a third phase. An approximate idea of the loading capacity of a particular solvent can be calculated knowing the composition or structure of the extracted species, and the concentration of the extractant in the solvent. For example kelex100, a substituted 8-hydroxyquinoline, forms a 1:2 metal: extractant complex with copper ion (Cu^{2+}). Thus a 0.5 M solution of kelex100 (Fig. 1.14) in an inert diluent should have a maximum loading capacity of 0.25 M copper, that is, 0.25 × 63.5 =15.9 g Cu dm^{-3}. This agrees well with the experimentally determined loading of such a solvent, namely 15.0 g Cu dm^{-3}. (25) Similarly, kelex100 forms a 3:1 complex with Fe^{3+}, thus the same solvent should load 0.5/3 × 55.8 = 9.3 g Fe dm^{-3}. (25)

Generally, the greater the ratio of extractant to metal in the extractable species, the lower will be the loading capacity of a given solvent unless, the atomic weight of the metal is sufficiently high to reverse this. The theoretical loading capacity of solvents is usually attained in practice only for those, which contain a low extractant concentration. The higher the extractant concentration, the greater is the deviation from theory.

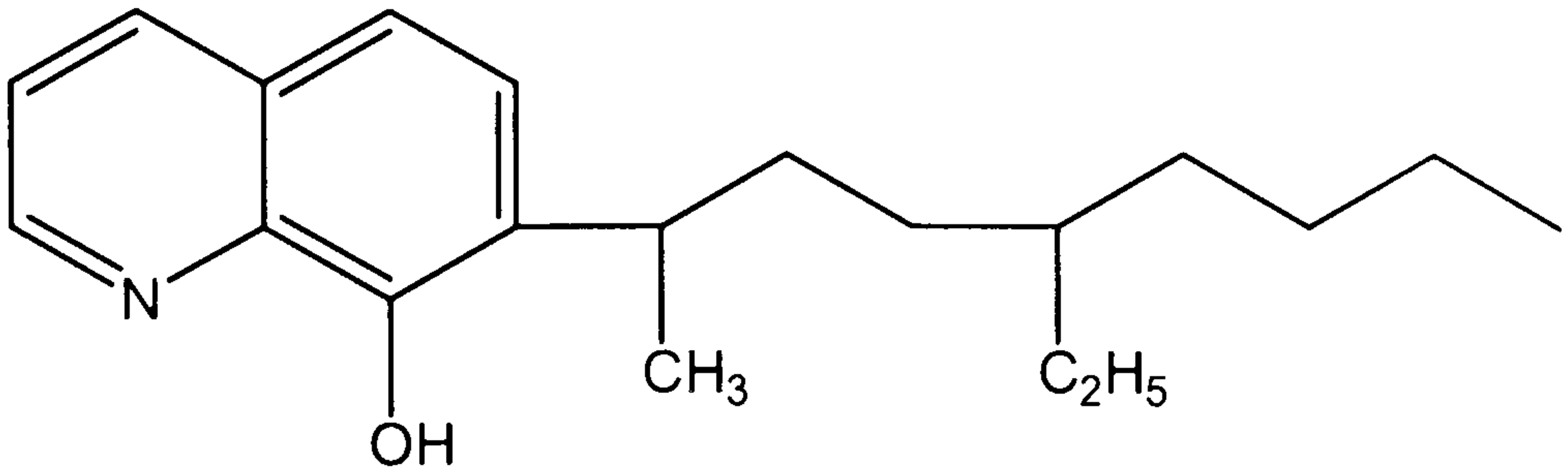


Figure 1.14: Chemical structure of (kelex100) 7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline.

1.7 Systems involving ion-association.

Systems employing ion-association are much more difficult to analyse than the other types. This difficulty arises from our lack of understanding of species in concentrated solutions. Ion-association or outer-sphere complexation results from physical attractive forces between oppositely charged species. For example, the association of ions A^+ and B^- to form an ion-association complex $A^+.B^-$.

$$A^+ + B^- \rightleftharpoons (A^+.B^-) \tag{28}$$

for which the association constant, K_{ass}, is given by:

$$K_{ass} = \frac{[(A^+.B^-)]}{[A^+][B^-]} \tag{29}$$

Ion-association is largely dependent on dielectric constant, ϵ, and will increase with a decrease in the ϵ of the solvent. The high ϵ of water (78.5 at 25 °C) would tend to inhibit ion-association, but as the ionic concentration is increased then ϵ decreases. In solvents of low ϵ, ion-association would tend to be the rule.

Ion-association also increases with temperature in solvents of high ϵ since ϵ decreases significantly with increasing temperature. For solvent extraction systems employing high ionic concentrations in the aqueous phase, considerable ion-association between metal complexes and other ions will occur, whose compositions will vary depending on many factors. Let us consider the organic phase and the problems associated in trying to understand reactions occurring between it and the aqueous phase components. Commercial processes involving ion-association systems employ long chain aliphatic primary (RNH_2), secondary (R_1R_2NH) or tertiary ($R_1R_2R_3N$) amines, or quaternary ammonium salts ($R_1R_2R_3R_4N^+.X^-$) as the extractant.

All these reagents, when dissolved in a diluent, aggregate to a greater or lesser extent. Because of this aggregation the number of equilibria involved is a largely unknown factor, and especially so when we include the equilibria involved in the aqueous phase. Thus the number of equilibria to describe the ion-association extraction of metals is many times that involved in a chelate extraction system. The major complication in amine extraction systems is the molecular association of amine salts into dimers, trimers, etc.:

$$R_3NH^+.X^- \rightleftharpoons (R_3NH^+.X^-)_2 \rightleftharpoons .. \rightleftharpoons (R_3NH^+.X^-)_n \quad (30)$$

One of the more important factors affecting aggregation is the nature of the diluent used. Extraction of M^{n+}, which forms anionic complexes with an anion A^- in the aqueous phase, by an amine salt $R_3N.HA$ can be represented as an anion exchange process such as:

$$MA_m^{(m-n)-} + \overline{(m-n)(R_3N.HA)} \Leftrightarrow \overline{(R_3N^+H)_{m-n}MA_m^-)} + (m-n)A^- \quad (31)$$

In order to achieve this exchange the amine must first be converted to an appropriate salt to provide an anion to exchange with the metal species.

$$\overline{R_3N} + HX \Leftrightarrow \overline{R_3NH^+.X^-} \quad (32)$$

When the amine in the solvent phase mixed with an aqueous acid (HX) solution extracts the acid, it forms an amine salt or polar ion-pair, $R_3NH^+.X^-$ in the solvent phase. Thus on contacting this solvent with an aqueous solution containing an anionic metal species MY^-, exchange can occur according to:

$$R_3NH^+.X^- + MY^- \rightleftharpoons R_3NH^+.MY^- + X^- \quad (33)$$

It is not necessary to have anionic exchange occur in order to extract an anionic metal species. Thus in the extraction of uranium, which is usually represented as the extraction of a uranyl sulfate anion ($UO_2(SO_4)_3^{4-}$), the neutral uranyl sulfate species can also be extracted. (28)

$$\overline{(R_3NH)_2SO_4} + UO_2SO_4 \Leftrightarrow \overline{(R_3NH)_2UO_2(SO_4)_2} \tag{34}$$

The degree to which the extraction of an anionic or neutral uranium species is involved depends on the species present in the aqueous phase, which is a particular problem in the sulfate systems. The importance of pH becomes more pronounced than for nitrate or chloride systems as a result of the dibasic nature of sulfuric acid, which gives rise to the sulfate-bisulfate equilibria:

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^- \tag{35}$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \tag{36}$$

Thus at high acid concentrations (low pH), bisulfate is the major anionic species present, and as the acid concentration is decreased, the sulfate ion will be the predominant species. The use of high bisulfate concentrations results in a decrease in uranium extraction because uranyl bisulfate is not extracted under these conditions. Conversely, at pH values, which produce high sulfate concentrations, the amine does not easily form its sulfate salt and is present as free amine. This does not extract the anionic uranyl sulfate complex.

Another factor which influences metal extractions by amines is the nature of the carbon chain, and the number of carbon atoms, in the amine molecule. Normally, aliphatic amines are the best extractants since aromatic groups, especially when attached to the amine nitrogen weaken the extractive properties, probably as a result of the electron-withdrowing nature of the aromatic ring. In many ways the problems encountered with the use of amines as metal extractants are similar to those involving acidic extractants, namely salt effects, aggregation of the extractant in the solvent phase, third phase formation, solubility and so on. Salt effects generally decrease metal extraction by amines in the order: $ClO_4^- > NO_3^- > Cl^- > SO_4^{--} > F^-$, which is the reverse order of the complexing ability of these anions.

1.8 Systems involving solvation

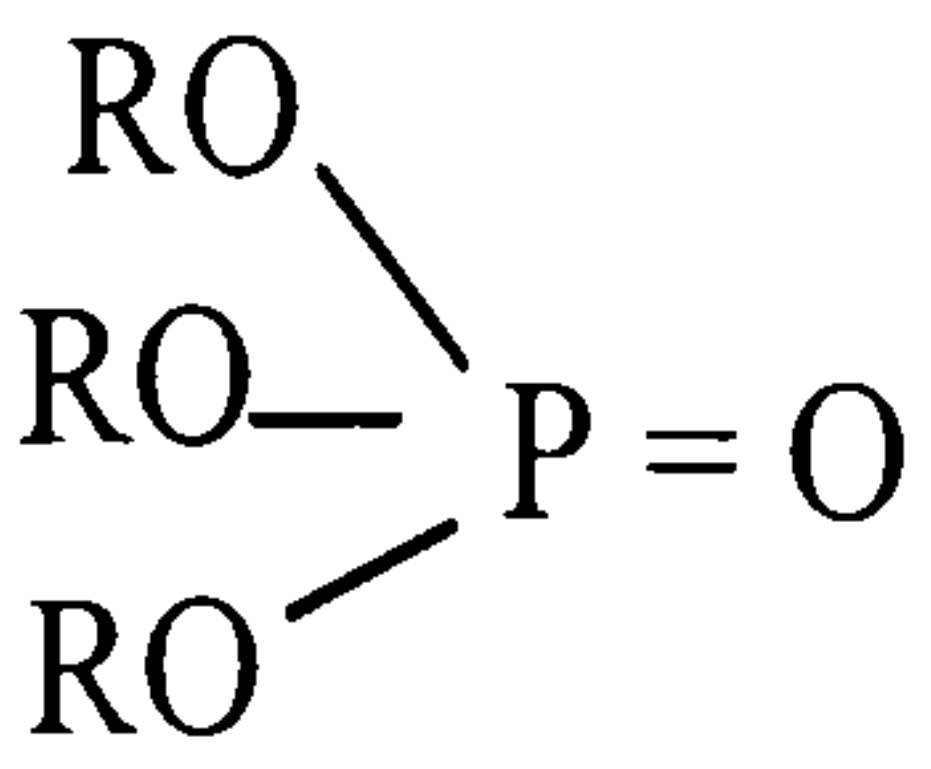
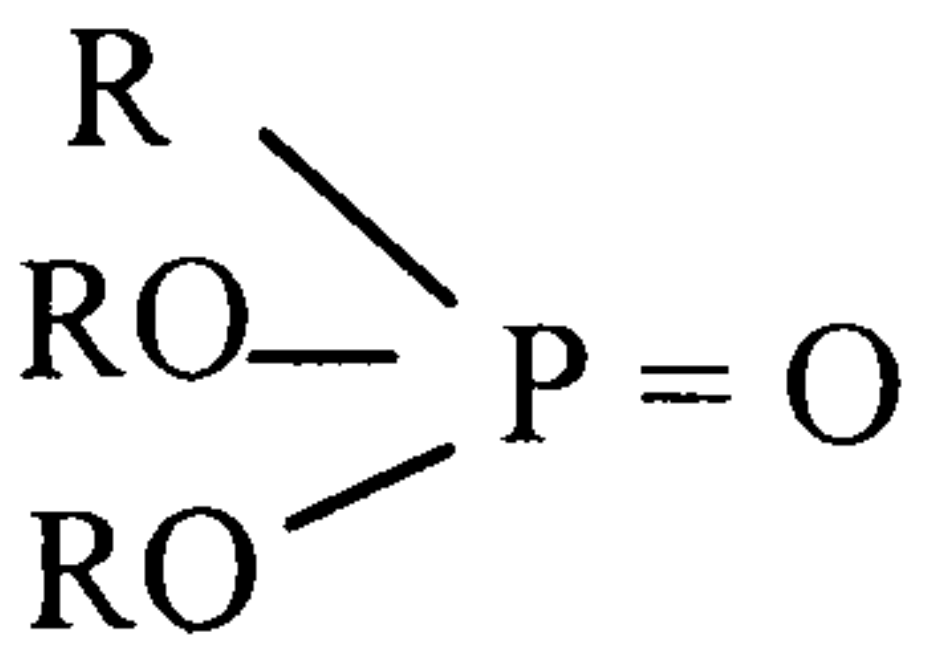
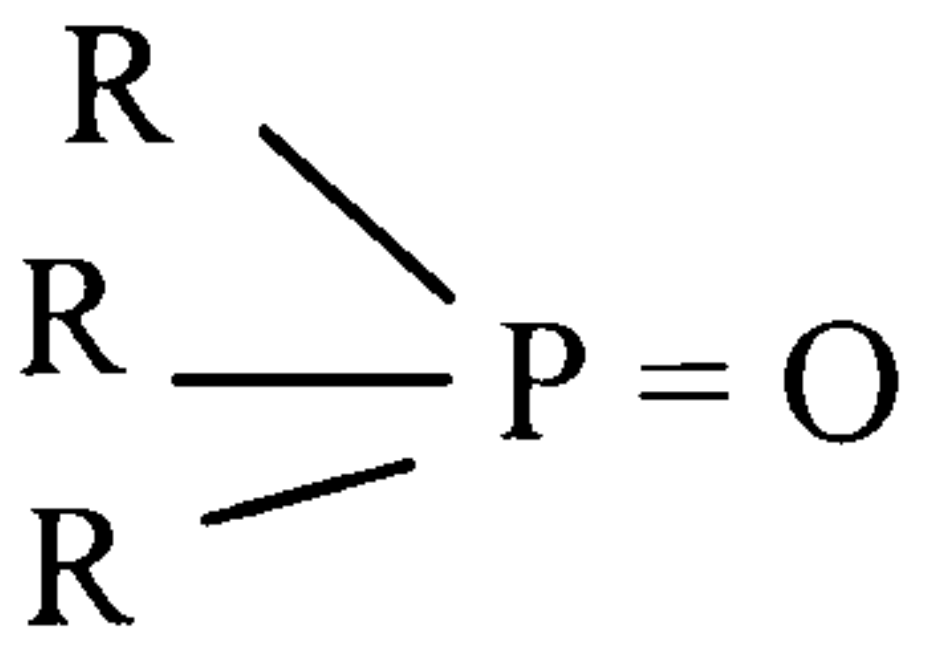
Another important group of extraction systems is that based on the power of oxygen-containing organic extractants to solvate inorganic molecules or complexes. By such solvation the solubility of the inorganic species in the organic phase is greatly increased. There are two main groups of extractants; those containing oxygen bonded to carbon, such as ethers (C-O-C), esters (COOR), alcohols (C-OH), and ketones (C=O); and those containing oxygen bonded to phosphorus such as alkyl-phosphate esters (P=O). One distinguishing feature between these extractant types involves the role played by water. The strongly polar organophosphorus compounds compete with water and replace water molecules in the first hydration sphere of a metal atom. With ethers and ketones water is a necessary part of the complex, probably forming bridges between the organic and metal components of the complex through hydrogen bonding.

One marked feature of extractants containing C-O bonds is the high degree of metal hydration that occurs in the solvent phase. For example, in the extraction of ferric chloride into ether, five molecules of water were associated with the extracted metal complex in the solvent phase. (25) These systems are non-ideal in the organic phase, even at low concentrations, making a general theoretical treatment impossible.
The most well known and most used of the organphosphorus esters is undoubtedly tri-n-butyl phosphate (TBP), because of its wide use in the processing of nuclear materials. These neutral extractants can be classified into two different types.

1.8.1 Extractants containing phosphorus-oxygen bonds.

Extractants in this group could be considered as the derivatives of phosphoric acid as indicated in Table 1.2.

Table 1.2: General structures of esters of organophosphorus acids.

Structure	Ester	Example
	Trialkyl phosphate	tri-n-butyl phosphate (TBP)
	Dialkyl alkyl phosphonate	dibutyl butylphosphonate (TBBP)
	Trialkyl phosphine oxide	tri-n-octylphosphine oxide (TOPO)

While the first two members of this group are esters of the previously mentioned phosphoric and phosphonic acids, the last member is a derivative of phosphine. The extraction mechanism is primarily the same for all of them and it is the oxygen of the phosphoryl group responsible for the coordination bond formed with the metal.

There is the possibility of more than one coordination bond formation in the esters, through their other oxygen atoms. In such cases inter-or intra-molecular bifunctional complexes are formed influencing the extraction rates for different metals as well as their stripping. From the above Table 1.2, the last group is the phosphine oxides, where TOPO is the main representative. This change influences the extractive properties of the extractants, since for every replacement of an OR group which is electron withdrawing, an electron releasing R group enhances the stability of the phosphoryl oxygen for coordination.

Neutral organophosphorus extractants have the ability to extract acids. Considerable work has been done in attempts to understand the mechanism of extraction, but with little success. The fact that most metal extraction processes are carried out from acid solution implies the possibility of co-extraction of the acids to be considered. This ability of extractants to extract acids has been used in the production of pure phosphoric acid, by extraction of this acid from solutions produced by the dissolution of phosphate rock in sulfuric acid. (29-31) One of the properties of these reagents, which have been of particular interest, is the ability to form complexes with mineral acids in ratios of acid to extractant of greater than unity. e.g. TBP.xHNO$_3$, where x = 1, 2, 3, or 4. (25)

In the extraction of metals by TBP, the general extractable complex appears to be one in which two molecules of TBP are associated with the metal complex. The effect of acid concentration on the extraction of metals by TBP is similar to that with amines. As the acid concentration is increased, the extraction of metal increases until a certain point, where the extraction begins to decrease.

1.8.2 Extractants containing carbon-oxygen bonds.

Extractants in this class are ethers, ketones, esters and alcohols. They are all electron donating reagents but alcohols are amphoteric, exhibiting both donor and acceptor properties. Alcohols are used mainly for the extraction of phosphoric acid solutions resulting from the dissolution of phosphate rock. Only one ketone appears to have been used commercially for the extraction of metals, namely methyl isobutyl ketone (MIBK Fig. 1.15), and processes involving this reagent are limited to the separation of zirconium and hafnium, also, niobium and tantalum. (32, 33)

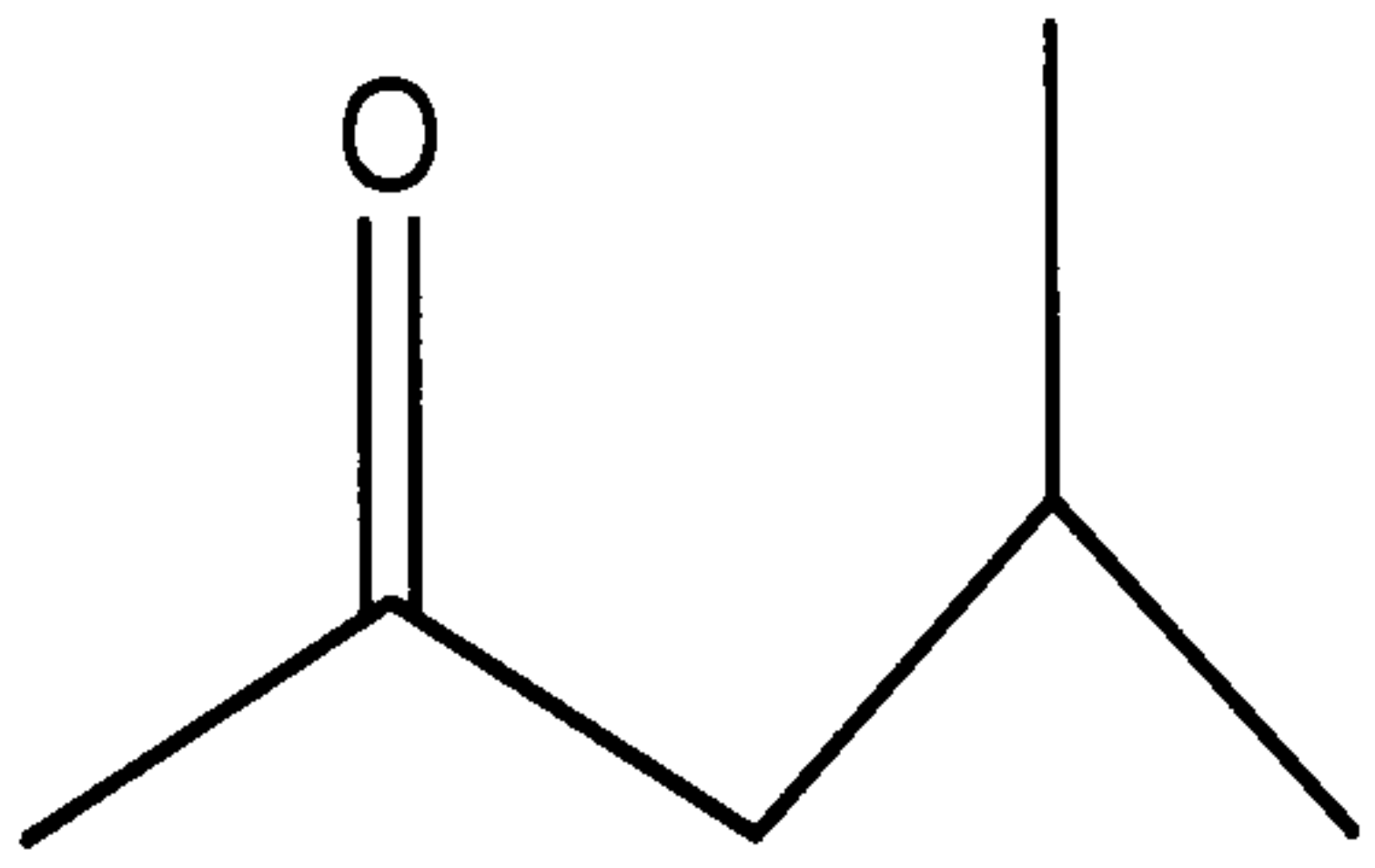


Figure 1.15: Chemical structure of (MIBK) methyl isobutyl ketone.

1.9 Solvent pre-treatment

Most solvents require some pre-treatment, or pre-equilibrium, prior to entering the extraction stage of the solvent extraction process. The reasons for this are:
To remove soluble impurities, acids or bases from the solvent phase; to produce the required form of the extractant for the extraction of a metal; and to form the required

salt of the extractant in order to maintain the necessary equilibrium pH in the extraction stage.

Commercial extractants generally contain small amounts of starting materials or by-products of the manufacturing process. Many of these are removed on recycling the solvent, especially if they are water-soluble. In bench-scale tests, where recycling is not possible, freshly prepared solvents are usually treated with an aqueous solution similar to that of the feed solution to be used, or with acidic or basic solutions. Such pre-treatment may accomplish one, two, or all three of the points given above.

Acidic and chelating extractants, which are stripped with acids, can be recycled directly to the extraction stage. Examples are the LIX extractants (Fig. 1.16), organophosphoric and carboxylic acids. Thus for a monobasic extractant:

$$CuSO_4 + \overline{2HA} \Leftrightarrow \overline{CuA_2} + H_2SO_4 \quad \text{Extraction} \tag{37}$$

$$\overline{CuA_2} + 2HX \Leftrightarrow CuX_2 + 2HA \quad \text{Stripping} \tag{38}$$

and for a tertiary amine:

Extraction

$$UO_2(SO_4)_3{}^{4-} + \overline{2(R_3NH)_2SO_4} \Leftrightarrow \overline{(R_3NH)_4UO_2(SO_4)_3} + 2SO_4^{2-} \tag{39}$$

Stripping

$$\overline{(R_3NH)_4UO_2(SO_4)_3} + 2H_2SO_4 \Leftrightarrow UO_2(SO_4)_3^{4-} + \overline{2(R_3NH)_2SO_4} + 4H^+ \tag{40}$$

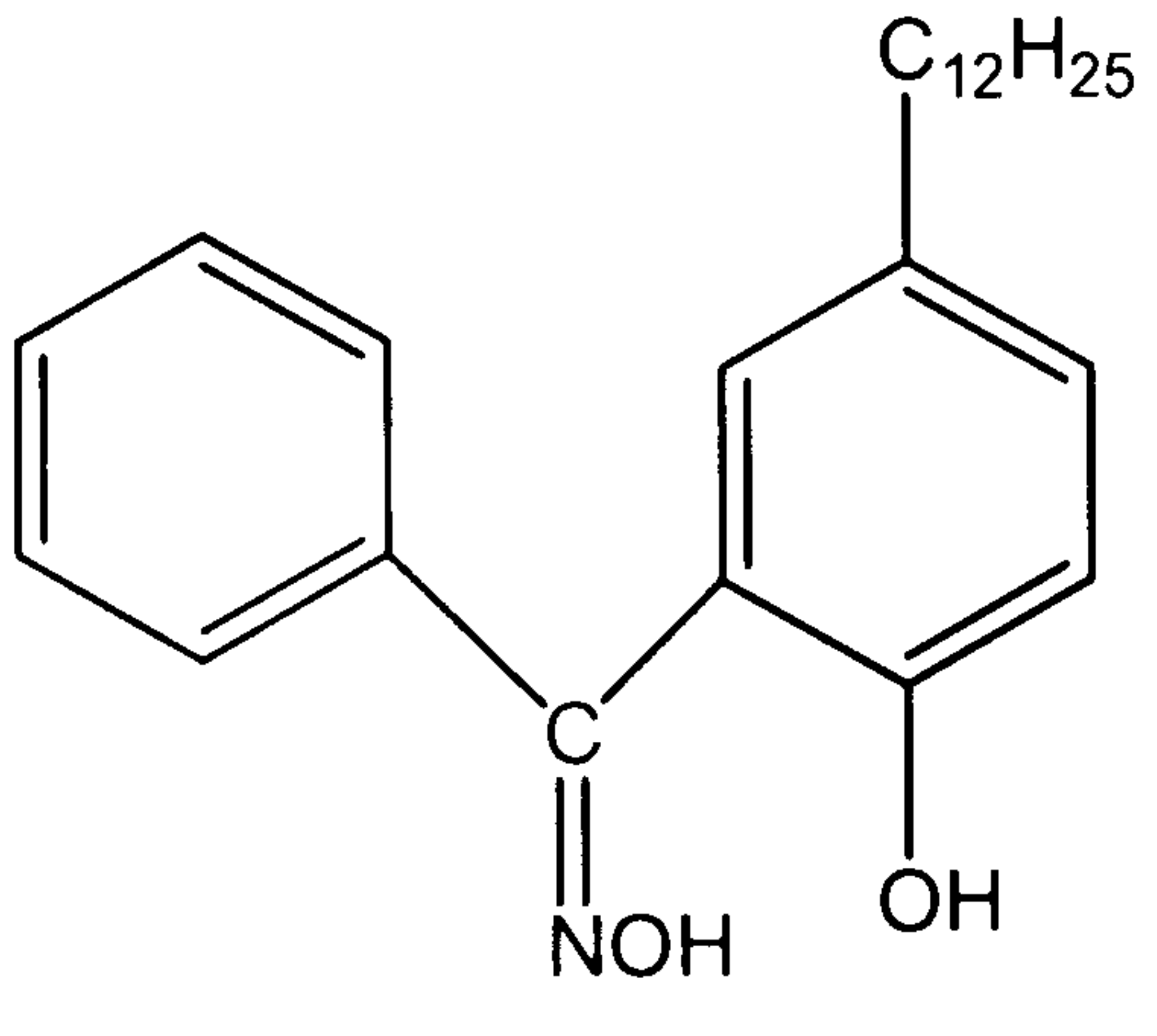


Figure 1.16: Chemical structure of LIX64 (2-hydroxy-5-dodecylbenzophenone oxime).

If an alkali carbonate solution is used for stripping uranium, the stripped solvent requires equilibration with sulfuric acid solution prior to recycling to the extraction stage. Other systems in which the solvent requires additional treatment after stripping are those, for example, in which a metal-metal or similar exchange is involved in the extraction stage. Thus for the system where the sodium salt of D2EHPA is used as the extractant for the extraction of cobalt (Fig. 1.17) (34) we have:

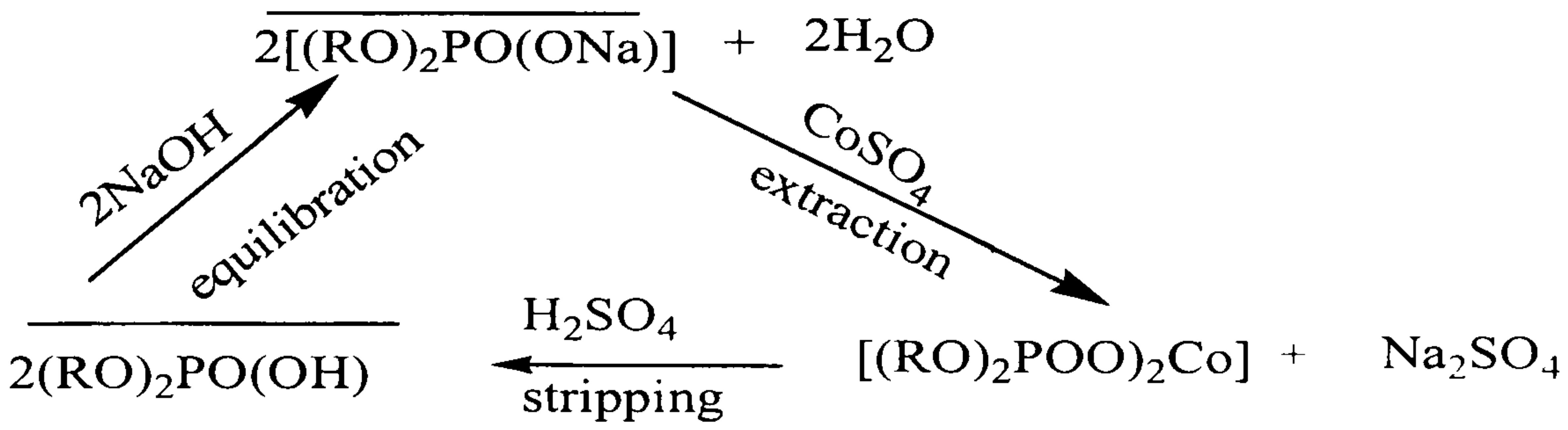


Figure 1.17: System for the D2EHPA extraction of cobalt.

which involves an additional equilibration stage to regenerate the solution salt. Systems such as this are particularly useful for maintaining an essentially constant pH in the extraction stage since sodium ions, rather than hydrogen ions are liberated, yielding a neutral sodium salt in the aqueous phase rather than an acid. Equilibration of a solvent can also be accomplished in the extraction stage, although this is not usually very efficient.

1.10 Dispersion and coalescence

In the preceding discussion we have been concerned primarily with the more chemical aspects of the solvent extraction process. In this section some of the physical phenomena involved will be discussed. The physical aspects of solvent extraction are primarily concerned with the dispersion of the two phases on mixing, the type of droplet formation, and the rate and completeness of phase disengagement or coalescence. Both of these processes, dispersion and coalescence, are integral steps in the solvent extraction process, and in any type of extraction equipment used.

Thermodynamically, the coalescence of the two dispersed phases in a binary system is expected to occur in order to reduce the surface free energy associated with the large interfacial area produced on dispersion. (25) The rate of coalescence, on which the design of mixing and separating equipment is based, is of prime importance in solvent extraction operations. Thus in order to achieve practically useful coalescence of the two dispersed phases, the dispersion must be of a temporary nature.

The dispersion of one liquid in another in a binary system can result in two extreme types of dispersion, one is temporary, which requires a minimum time for coalescence of the dispersed phase, and other is the formation of a stable emulsion or dispersion. The former may or may not result in a rate of high mass transfer of the metal from the aqueous to organic phase; the latter would make a solvent extraction system inoperative. The rate of mass transfer across a phase boundary is a function of the drop size distribution or interfacial area between the phases. The drop size is governed by the speed and type of agitator, and the surface tension and densities of the two phases. Thus it might be assumed that the smaller the drop size (greater dispersion) the greater the rate of mass transfer. Thus agitation of the two phases affects both the mass transfer rates of a metal and the coalescence of the dispersed phase. High mass transfer rates, which are usually indicated by a high extraction coefficient, may warrant only relatively gentle agitation in the contactor, while the converse may be true of systems having low mass transfer rates. (35, 36)

Gentle agitation is generally what is obtained in a pulsed sieve plate column, thus such a contactor will generally require high mass transfer rates. On the other hand, a mixer-settler is better for systems having low mass transfer rates because of the much higher agitation and large settling areas it provides.

1.10.1 Coalescence in a binary dispersed system

The prime importance in the operation of a solvent extraction system is the rate at which the dispersed phases disengage, since this governs the size of the settling area and throughput of a plant. The main factors involved in the coalescence of the two phases in the solvent extraction process are as follows:

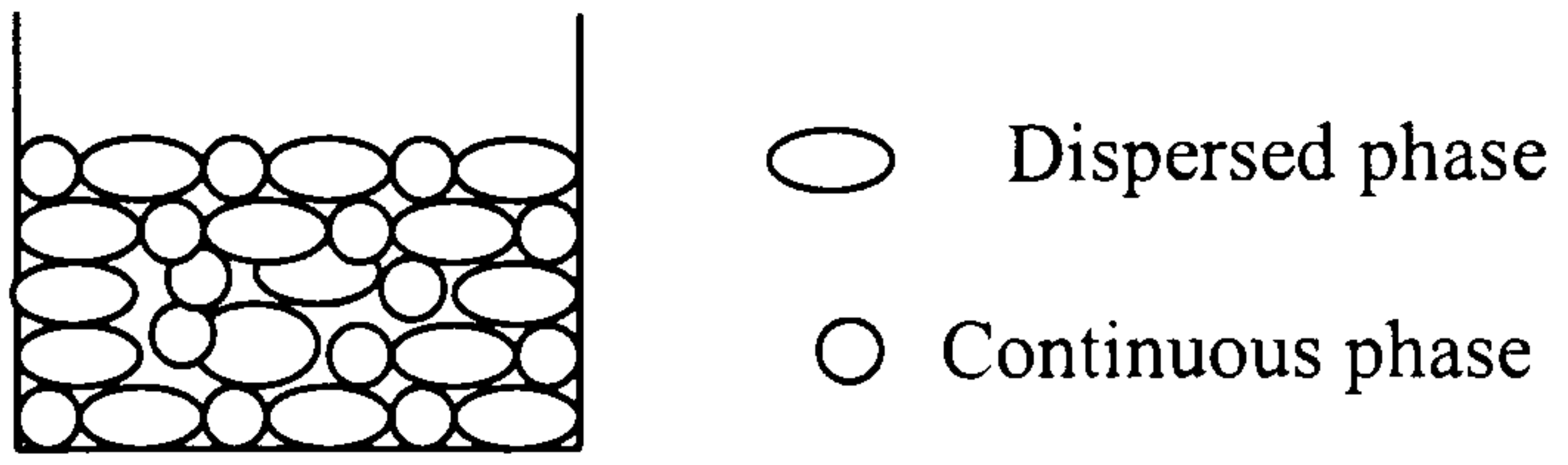
1.10.1.1 Drop-interface coalescence

Phase disengagement, or phase coalescence, can be divided into two stages; a primary break and a secondary break. The time required for the two phases to meet at a sharply defined interface after mixing is termed the primary break time. Both phases may be clear at this time, but occasionally, due to the dispersion of very small droplets of one phase in the other, one or both of the phases may be cloudy. The time required for this cloudy effect to clear is called the secondary break time.

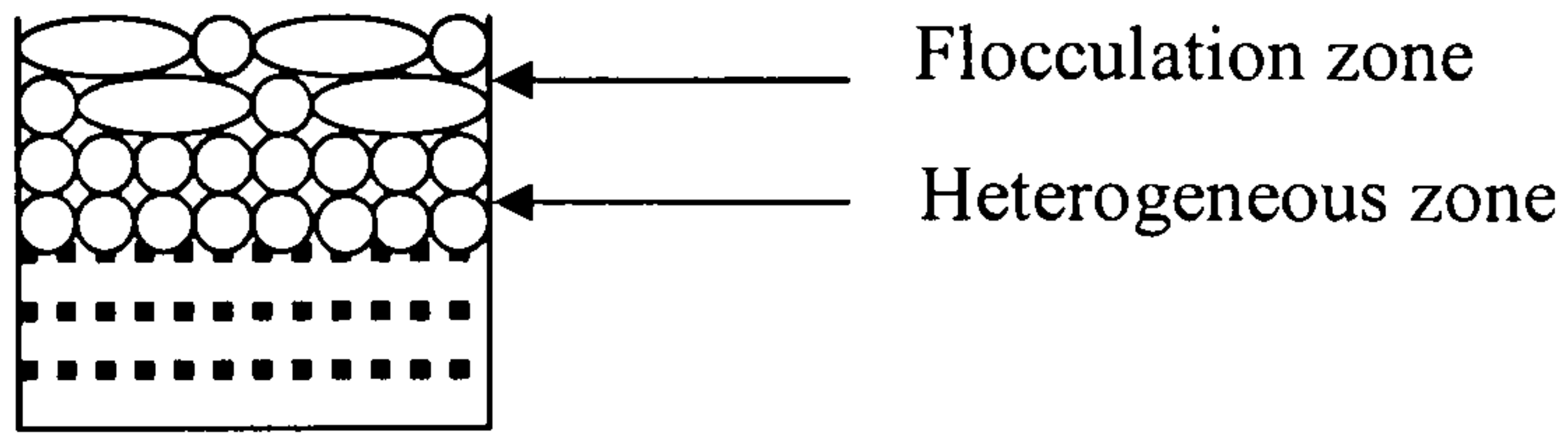
Generally, the primary dispersion, which gives rise to the primary break time, is assumed to involve a mean droplet size of greater than about 150µM, and the secondary dispersion to involve a mean droplet size of less than 100µM. If the droplet size is much less than 100µM coalescence will be very slow. This latter effect is the primary cause of loss of solvent to the aqueous phase by entrainment. Coalescence is considered to occur through five consecutives stages (37) (Fig. 1.18, Table 1.3).

(i) Approach of a drop towards the interface, which causes both drop and interface deformation.
(ii) Damped oscillation at the drop near the interface.
(iii) Formation of a film of the continuous phase between the drop and its bulk phase.
(iv) Drainage of the film, its rupture and removal, with the initiation of the process of coalescence.
(v) Transfer of the contents of the drop into bulk phase.

It is accepted that stages (i) and (ii) are very fast, and that (iii) through (v) constitute the time of coalescence. Step (v) is reported to occur in 0.06 to 0.08 seconds, (38) thus stages (iii) and (iv) represent the rate determining steps.



Mixing random motion
of drops, heavy phase dispersed



Mixing stop

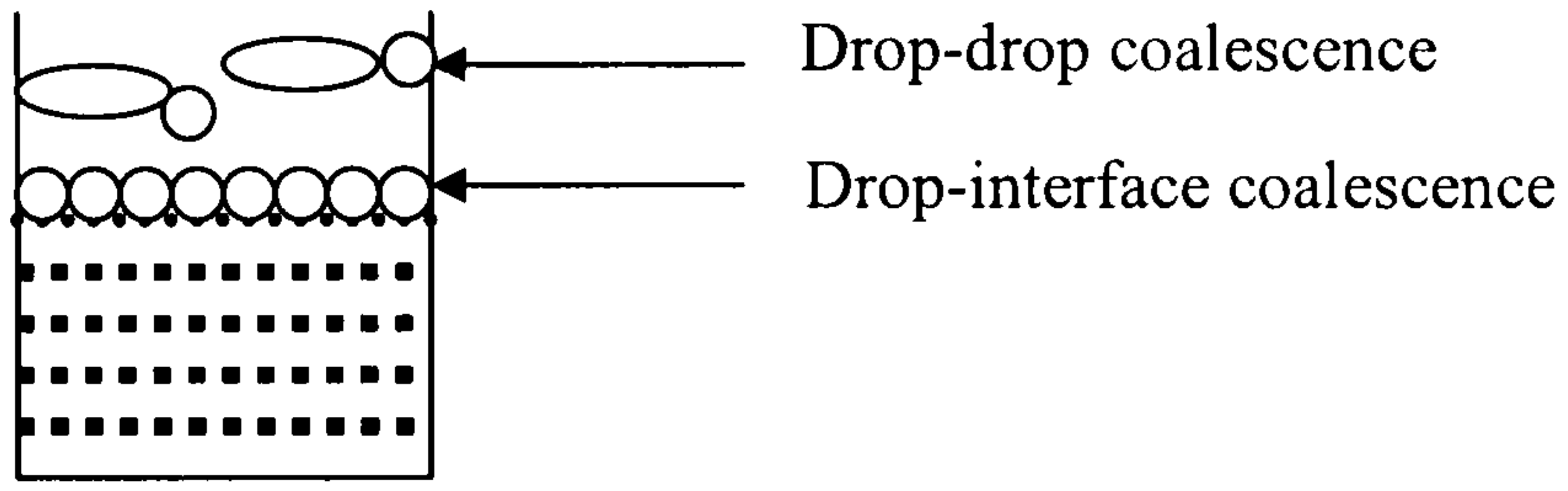


Figure 1.18: Some of the various stages from mixing to phase disengagement of two immiscible liquids. (39)

The process of drop coalescence may be illustrated schematically as shown in Table 1.3 as a function of time.

Table 1.3: The process of drop coalescence in a binary dispersed system. (37)

Drop moves towards interface Oscillates	Pre-drainage Time	Rest Time	Coalescence Time	Time Increased
Oscillations damped out Film forms Film thins	Drainage Time			
Film rupture Film removal complete	Film removal Time			
Drop content deposited	Deposition Time			

1.10.1.2 Dispersion, coalescence, and the solvent extraction process.

A more important phenomenon as far as liquid-liquid extraction is concerned is coalescence. Much of the work on coalescence has been carried out under (more or less) ideal conditions. In fact, many investigators (40) take particular care in the preparation of solutions and design of equipment used in their studies. The fact which emerges from the published data on the dispersion and coalescence of a system involving two immiscible phases is the strong dependence of these phenomena on the absence or presence of mass transfer, and on the presence of surface active materials. All solvent extraction processes involve mass transfer, thus knowledge of the factors affecting dispersion and coalescence in the presence of mass transfer should be known if the effects are to be useful in making quantitative predictions in an actual process.

In addition to chemical and physical properties of the aqueous phase influencing phase disengagement rates, we must also consider the possible influence of the solvent phase and its composition. Research by the Oak Ridge Laboratory has been reported by Moyer and McDowell on the effects of amine size and structure on phase disengagement in the AMEX process for uranium recovery from sulfate liquors. (41) The tests were conducted with 9 commercial and 4 laboratory amines in contact with either synthetic solutions containing silica or with typical uranium leach solutions as found in the mills in New Mexico. Their data indicated that there were differences in phase disengagement rates depending whether the system was under aqueous or organic continuous. The low molecular weight amines resulted in slow phase disengagement rates. The conclusion was that the higher molecular weight amines may offer advantages in aqueous continuous processing to result in faster disengagement, decreased emulsion and crud tendency, and decreased third phase formation.

1.11 Kinetics of extraction.

The kinetics of liquid-liquid extraction is complex, involving mass transfer with chemical reaction in a heterogeneous system. However, it is important to elucidate the kinetic behaviour of an extraction system because it influences such important economic parameters as time spent in the mixer, the size of plant, and volume of reagent used. Being a heterogeneous process, one of the major factors covering the overall kinetics is the interfacial area, which depends largely on the degree of agitation, although other parameters such as interfacial tension are also involved. Metal extraction with a solvent extraction reagent involves three steps: Diffusion of reagents to the reaction zone; chemical reaction; and diffusion of products away from the reaction zone. Any one of these can be slowest step and hence rate determining. This suggests that two limiting cases exist, involving diffusion and chemical reaction control. (2) The former depends on the interfacial area and the concentration of the slow-diffusing species. In the latter it is important to determine the site of reaction, that is, within the bulk phase or at the interface, or more likely in the interphase region.

For bulk phase reactions the important kinetic parameters are reactant solubility, their distribution coefficients, ionisation constants and phase volumes. On the other hand, for interfacial chemical control the interfacial area will be important, together with the interfacial activity of the species involved, which in turn are influenced by the molecular geometry of the reagent. The study of extraction kinetics has attracted considerable attention, especially for acid chelating extractants. Two limiting models have been proposed to explain the observed results. The first (42) was concerned with the influence of the liquid-liquid interface and diffusion processes on the extraction rate. The second model considered that the bulk aqueous phase was the site of the chemical reaction. (43) Thus, it is very important in studies of kinetics of mass transfer to distinguish between chemical reaction and diffusion control. This can be achieved by using several techniques; the stirred quiescent interface cell as originally designed by Lewis has undergone many modifications and provides one of the simplest devices to operate. But as indicated, (44) there are still many limitations, which need to be recognized. On the other hand a considerable number of earlier studies used single-drop methods.

Studies on the kinetics of metal extraction using both Lewis-type cells and single-drop methods have been published. (45, 46) Extraction reagents all exhibit interfacial activity arising from the presence of both polar groups and non-polar alkyl carbon chains. This activity can be explained by the lowering of the interfacial tension caused by the penetration of the interfacial surface by the hydrophilic groups. The extent of this lowering depends on reagent type and geometry, bulk phase concentration, diluent and water solubility of the reagent. Values of interfacial concentration that feature in the kinetic equations can be obtained from interfacial tension measurements by the applications of the Gibbs isotherm. Because the nature of the diluent will influence the interfacial properties of the extractant and extracted metal complex it follows that it will also affect the rate of extraction. Thus the use of an aromatic diluent will decrease the rate of extraction when compared with an aliphatic hydrocarbon diluent.

The interfacial area can also be increased by the addition of surfactants that reduce the interfacial tension of the diluent/aqueous interface. These compounds are normally more surface active than the metal extractants and so, for extraction systems without chemical reaction, addition of surfactants normally reduces the rate of extraction. For systems with chemical reaction either an enhancement or reduction of rate is observed, depending on the sign of the charge developed at the interface by the adsorbed surfactant molecules. Thus the adsorption of a positively charged species will reduce the rate of cation extraction, whereas adsorption of negatively charged species would enhance this extraction rate. (47, 48) For anion extraction the opposite conditions would apply. The reduction in the rate can be explained by postulating a mechanism of mutual charge repulsion, or a reduction in interfacial area available for the extractant by blocking with adsorbed surfactant molecules. The enhancement is achieved by electrostatic interaction between the surfactant and the transferring species to form a compound or ion-pair is then rapidly desorbed into the organic phase where it can undergo fast ligand exchange reactions to give the expected product in the absence of surfactant. Several examples of this type of behaviour have been investigated including copper extraction by hydroxyoxime extractants, (49) di-2-ethylhexylphosphoric acid, (50, 51) and carboxylic acids. (52)

With the addition of modifiers such as *iso*-decanol, a variation in extraction rate can also occur. This was attributed to the modification of the extraction chemistry by hydrogen bonding between the modifier and extractant or extracted complex. This leads to a reduction in the rate by the formation of kinetically inactive modifier-extractant complexes. (53, 54) A number of compounds have been shown to act as accelerators for the extraction rate. The mechanism of this acceleration process depends on the nature of the extractant and sometimes upon the nature of the metal ion. From the above it is obvious that the kinetics of metal extraction are complex and involve both diffusion and chemical reaction processes. It is now generally accepted that, except under the most extreme conditions, the chemical reactions are interfacial in nature. This poses the question of definition for a liquid-liquid interface in this situation. Some workers consider this to be a defined boundary with a thickness of a nanometre, whereas other prefers an interfacial zone of the order of a micrometer. Perhaps, until the picture is clear, the term interphase reaction might be more suitable, implying reactions in a region in which the properties are different from either of the bulk phases.

Certainly the presence of adsorbed extractant molecules will modify this interphase region from that found in the absence of any adsorbed species, and the thickness of any boundary layer will vary according to the adsorbed species. However, as the interfacial/interphase nature of such processes is now accepted, little is to be gained from establishing more examples of the same. In the investigation of interfacial reactions more effort is required to see if these can be used as a basis for metal separations. Generally it is found that mass transfer rates for ionic systems, for example, simple acid and amine salt extractants, are faster than the chelating acids. Finally, can kinetic accelerators, like synergistic extractant mixtures, provide an additional means of developing new processes?

1.12 Aims of the project.

The main objective of this study is oriented towards the detailed study of the different variables, which affect the liquid-liquid extraction of Y, Ce and La as single rare earth elements from sulfuric acid solution. In order to obtain an efficient and economic separation of these elements, it has been found necessary to study the relevant factors affecting the extraction process to determine the optimum conditions for extraction. These factors include extractant concentration, equilibration time, pH value, diluent, temperature, solvent saturation and construction of McCabe-Thiele diagrams, in addition to elucidation of the extracted species. Following these initial studies, the use of liquid-liquid extraction for separation and purification of mixtures of two lanthanides such as Y-La will also be described.

Next, liquid-liquid solvent extraction for separation of ternary mixtures of three rare earth elements, such as Nd-La-Y using different acidic (e.g. D2EHPA), basic (e.g. TiOA and Primene JMT), and solvating extractants, (e.g. TBP and TOPO) will be reported. Also, use of combinations of two extractants as TiOA/TBP, TiOA/TOPO and TiOA/D2EHPA to enhance the separation process synergistically will be discussed. Moreover the use of water-soluble complexing agents such as EDTA (ethylene diamine tetraacetic acid) to increase the separation factor and purification process will be considered. Finally, the synthesis of some novel amide ligands from piperazine and piperidine derivatives and the testing of these ligands in extraction equilibrium experiments will be reported.

1.13 References.

1 M. Berthelot and J. Jungfleisch, *J. Ann. Chem. Phys.*, (1872) **26**, 396.

2 J. D. Thornton, *Science and Practice of Liquid-Liquid Extraction*, Clarendon Press, Oxford (1992), **2**, 28.

3 www.uic.com.au/uicchem.htm.

4 M. Streat, and D. Naden, *Ion Exchange and Sorption Processes*, CRAC, (1987), **19**, Soc. Chem. Ind./Wiley.

5 R. Price, and J. A. Tumilty, *Symp. Ser. No* 42, (1975), 19.

6 D. S. Flett, J. Melling, and M. Cox, *Handbok of Solvent Extraction*, Wiley, New York, (1983) Chapter 24, 629.

7 F. Habashi, *Miner. Eng.*, (1994) **7**.

8 J. Szymanowski, *Hydroxyoximes and Copper Hydrometallurgy*, CRC Press, Inc. London, (1993).

9 S. G. Galbraith, and P. A. Tasker, *Supramolecular Chemistry*, (2005) **7**, 191.

10 G. Vassalo, (1981), EUR 6996.

11 A. L. Mills, Insititution of Chemical Engineers Symposium Series 88, (1984), 245.

12 G. M. Ritcey, "Solvent Extraction Contactors", *in Proceedings of AIChE Symosium on Solvent Ion Exchange*, Arizona, (1973).

13 G. M. Ritcey and A.W. Ashbrook "*Solvent Extraction Principles and Applications to Process Metallurgy*" Part II, Elsevier, Amsterdam, (1979).

14 M. Ritcey, "Crud in Uranium Solvent Extraction", *in Proceedings of International Mineral Processing Congress*, Toronto, Vol. 1, Pub.CIM, (1982).

15 D. A. Orth, J. M. Mckibben and W. C. Scotton, *Proceedings of International Solvent Extraction Conference, ISEC'74 Lyon*, Soc. Chem. Industry, London, (1971), 433.

16 Z. Fijal, C.Loukeris, Z. nagibzadeh, J. Walsdorf, A. Linninger, "Liquid-Liquid Extraction", Senior Design CHE 396,

17 J. D. Seader, and E. J. Henley, "*Separation Process Principles*", John Wiley and Sons, New York, (1999).

18 www.sxkinetics.com technology.htm.

19 R. F. Strigle, Packed Tower Design and Applications, Gulf Publishing Company, Houston, (1994).

20 www.liquidextraction.com/packed-column-random.htm.

21 www.liquidextraction.com/karr-column.htm.

22 W. Nerst, Z. *Physik. Chem.*, (1891) **8**,110.

23 F. Basolo and R. G. Pearson, "*Mechanisms of Inorganic Reactions*" 2nd Edition, John Wiley and Sons, Inc., New York, N. Y., (1967).

24 F. A. Cotton, and G. Wilkinson, "*Advanced Inorganic Chemistry*", 3rd Edition, Interscience, New York, N. Y., (1972).

25 G. M. Ritcey and A. W. Ashbrook, "*Solvent Extraction Principles and Applications to Process Metallurgy*" Part I, Elsevier Science Publishers B.V., (1984).

26 C. M. Guldberg, and P. Waage, *J. Prakt. Chem.*, (1879) **19**, 71.

27 R. W. Cattrall, and S. J. E. Slater, *Coord. Chem. Revs.*, (1973) **11**, 227.

28 G. M. Ritcey, A.W. Ashbrook, and B. N. Lucas, "Development of a Solvent Extraction Process for the Separation of Cobalt from Nickel", Presented at the Annual AIME Meeting, San Francisco, Feb. 1972, CIM Bulletin, (1975) **63**, 1.

29 R. S. Long, and D. A. Ellis, U.S. Patent 3,072,461.

30 D. S. Bunin, F. J. Kelso and R. A. Olsen, U.S. Patent 3,410,656.

31 M. Martin, and L. Winand, U.S. Patent 3,366,448.

32 Tachnical Editor, *Eng. Min. J.*, (1960) 161,78.

33 W. L. Hunter, and K. B. Higbie, USBM RI-5918 (1961).

34 Y. Marcus, and A. S. Kates, *Ion Exchange and Solvent Extraction of Metal Complexes*, Wiley-Interscience, New York, N. Y. (1969), 537.

34 H. A. C. McCkay, *Solvent Extraction Chemistry of Metals* Ed., Macmillan, London, 1966.

36 G. V. Jeffreys, and G. A. Davies, in *Recent Advances in Liquid-Liquid Extraction*, ed. C. Hanson, Pergamon, (1971), 495.

37 G. A. Davies, Inst. Chem. Engrs., Course on Solvent Extraction, Bradford University, Bradford, U.K., (1972).

38 L. M. Gindin, P. I. Bopikov and A. M. Rozen, *Russ. J. Inorg. Chem.*, (1960) **5**, 1146.

39 H. C. Pich, C. S. Santos, J. T. Elias, M. F. Alves, E. H. Conceicao, and H. X. Viera, *Proc. Symp. on Recovery of Uranium*, IAEA, Vienna, (1971), paper IAEA-SM-135/17.

40 P. R. Kiezyk, and Mackay, *Can. J. Chem. Eng.*, (1971) **49**, 747.

41 B. A. Moyer and W. J. McDowell, *J. Separation Science and Technology*, (1981) **16**(9), 1261.

42 D. S. Flett, *Acc. Chem. Res.*, (1977) **10**, 99.

43 H. Freiser, *Acc. Chem. Res.*, (1984) **17**, 126.

44 G. J. Hanna and R. D. Noble, *Chem. Rev.*, (1985) **85**, 583.

45 C. Hanson, and R. Whewell, *Solv. Ext. Ion Exch.*, (1981) **8**, 1.

46 A. Danesi, and R. Chiarizia, *Crit. Rev. Anal. Chem.*, (1980) **10**, 1.

47 Th. Michel and W. Nitsch, *Proc. ISEC 88*, Moscow, Vernadsky Inst. Geochem. and Anal. Chem., Academy of Sciences, Moscow, (1988) **11**, 20.

48 V.V. Tarasov and G. A. Yagodin, *Ion exchange and Solvent Extration* (ed. J. A. Marinsky and Y. Marcus), Marcel Dekker, New York, (1988) **10**, 141.

49 E. A. Morin, and H. D. Peterson, (1975), US patent 3878286.

50 E. G. Joe, G. M. Ritcey, and A. W. Ashbrook, *J. Metal*, (1966), 13.

51 W. C. Hazen, and E. L. Coltrinari, (1975), US Patent 3872209.

52 A. J. Vander Zeeuw, and R. R. Kok, *Proc. ISEC77*, Toronto, CIM Spec. Pub.21, (1979), **1**, 17.

53 C. Hanson, M. A. Hughes, J. S. Preston, and R. J. Whewell, *J. Inorg. Nucl. Chem.*, (1976) **38**, 2306.

54 R. F. Dalton, *Proc. ISEC77*, Toronto, CIM Spec. Pub. 21, (1979) **1**, 40.

Chapter Two

Liquid-liquid extraction of yttrium.

2.1 Introduction to yttrium chemistry.

Yttria (yttrium oxide, Y_2O_3), was discovered by Johann Gadolin in 1794 in a mineral called gadolinite from Ytterby, which is the site of a quarry in Sweden which produces many unusual minerals containing erbium, terbium and ytterbium, as well as yttrium. Friedrich Wöhler obtained the impure element in 1828 by reduction of the anhydrous chloride YCl_3 with potassium.

2.1.1 Natural abundance.

Yttrium is more abundant than the heavy lanthanides, resembles them in properties, and occurs with them in nature (Table 2.1). Values for the abundances of trace elements are difficult to determine with much certainty, so all values in Table 2.1 should be treated with some caution. The local concentration of any elements can vary from those given here by orders of magnitude.

Yttrium is never found in nature as the free element. It is found in the two main minerals supplying lanthanides, monazite [$(Ln)PO_4$] and bastnaesite [$(Ln)(CO_3)F$], as well as other ores containing small amounts of all the rare earth metals (Table 2.2). It is difficult to separate from other rare earth elements. Lunar rock samples show a relatively high yttrium content. Other potential sources of yttrium include a brannerite–type mineral derived as a uranium–mining byproduct concentrate, and the mineral eudialyte, a complex silicate, found in several locations, such as Russia, in large quantities.

Table 2.1: Natural abundance of yttrium from different sources.

Abundances	**ppb by weight**	**ppb by atoms**
Universe	7	0.1
Sun	10	0.1
Meteorite (carbonaceous)	1900	430
Crustal rocks	29000	6700
Sea water	0.013	0.0009
Fresh water	50	0.6
Human	no data	no data

Table 2.2: Yttrium content as weight % of total Ln concentration in minerals.

Bastnaesite	0.1 %
Monazite	2.1 %
Xenotime	~ 60 %

Yttrium has silvery–metallic lustre, spontaneously igniting in air, and is used as a "phosphor" to produce the red colour in television screens. Separation of yttrium by a single discrete process is not possible. It needs to be recovered by liquid–liquid extraction processes that rely on the differential partitioning of complexes between an organic phase and an aqueous phase.

2.1.2 Recent developments in yttrium extraction chemistry.

Several investigations have been reported in the literature to study the extractability of yttrium by different organic solvents. The most important solvents studied include di(2-ethylhexyl)phosphoric acid (D2EHPA), tributyl phosphate (TBP) and tri*iso*octylamine.

Antico *et al* (1) studied the distribution of yttrium between acidic aqueous solutions and kerosene solutions of D2EHPA. This was examined as a function of various chemical parameters at constant aqueous ionic strength 2.0 M and different ranges of metal concentrations. For low and medium concentrations, 1.5×10^{-4} - 2.6×10^{-2} M (13-2300 mg /L), the distribution of yttrium was examined as a function of extractant concentration at a fixed [H^+] of 1.0M. The distribution data were analysed by both graphical and numerical methods. The results for the low metal concentration may be explained by the formation of the two organic metal species, $YA_3.2HA$ and $YA_3.HA$ (HA refers to D2EHPA). Equilibrium constants for these reactions were determined and they are compared with corresponding constants in nitrate media and with results reported in the literature.

Numerical calculations rejected the possibility of mixed extracted complexes containing chloride. This prediction was confirmed by separation analysis of the chloride content in the organic phase. When the metal concentration is increased, the system becomes more complex, which is attributed to the formation of aggregates in the organic phase. For the highest metal concentration a gel forms under some of the experimental conditions. These results are discussed in terms of polymeric metal complexes.

Takahashi ***et al*** (2) studied the equilibria and kinetics for the extraction of yttrium from hydrochloric acid solution by EHPNA (2-ethylhexylphosphoric acid mono–2–ethylhexyl ester, PC–88A) in *n*-heptane as the diluent. It was found that the extracted species in this system is YCl_3-HR and the equilibrium constant $K_{ex} = 3.80 \times 10^3$ mol m^{-3}. Initial rates of extraction and stripping for the EHPNA–Y system were determined with a stirred transfer cell, and the rate data were correlated as a function of the concentration of relevant species. The concentration dependencies of both the initial rates satisfy the assumption that a reaction between Y^{3+} and the ionic extractant adsorbed at the liquid–liquid interface is likely to be the rate-controlling step.

Iglesias ***et al*** (3) have studied the solvent extraction process of yttrium from nitrate media by D2EHPA as a first step to accomplish the homogenous precipitation of yttrium oxalate from metal loaded D2EHPA solution. The analysis of liquid–liquid distribution data at low metal concentrations determined $Y(NO_3)_3.2HA$ as the only metal species formed during the extraction with a formation constant of $\log \beta = 16.410 \pm 0.055$. Polymerisation of this metal-organic species was observed at high metal loadings of the organic phase. A comparison of these results with previous studies carried out in chloride or perchlorate media reveals a strong influence of the aqueous medium on the metal species formed in the organic phase, affecting particularly the stoichiometry of such species. The homogeneous precipitation of yttrium as yttrium oxalate using oxalic acid was carried out as a direct recovery of the metal from the organic solution.

The kinetics of precipitation and stripping was related to the formation of organic yttrium species. The acidity of the stripping solution and the oxalic acid concentration also affected the kinetics and yield of the precipitation process. The particle size distribution of the yttrium oxalate powders support the aforementioned influence of the precipitation–stripping kinetics.

Konishi, Yasuhiro, ***et al*** [4] studied precipitation-stripping of yttrium leaches, which are a combination of the stripping and precipitation stages in a conventional solvent extraction process for separation and purification of rare earths. Crystalline yttrium oxalate powders were precipitated by emulsifying yttrium–loaded carboxylate solutions with aqueous oxalic acid solutions at 30°C. Yttrium in the organic solution was completely stripped and precipitated within the first 5 minutes of mixing with aqueous solution. The particle size distributions of the oxalate powders in this study were markedly dependent on processing parameters, such as mixing time, liquid–phase stirring speed, initial organic phase concentration of yttrium carboxylate, and ionic strength of the aqueous oxalate solution. However, the nature of the two solvent extractants, carboxylic acid and phosphoric acid systems had little effect on the size distribution of yttrium oxalate.

Combes ***et al*** [5] have studied the influence of several parameters on the precipitation yield, the solubility of yttrium in the aqueous phase, and the nature and size distribution of the precipitated salt. The parameters varied were: the initial concentrations of nitric (0–5 mol L^{-1}) and oxalic (0.15–0.75 mol L^{-1}) acids in the aqueous phase, the initial concentrations of $Y(HL_2)_3$ (0.075–0.10 mol L^{-1}) and HL (0.8–2.2 mol L^{-1}) in the organic phase, the nature of the organophosphorous acid solvent used [$(RO)_2PO_2H$ or $R(RO)PO_2H$ with R =2-ethylhexyl], temperature (24–60°C), and the ratios of the volumes of phase (Vo/Va varying from 0.5 to 4). The nature of the precipitated salt depended on the concentrations of oxalic and nitric acid. At ambient temperature, the neutral salt $Y_2(C_2O_4)_3.10H_2O$ was precipitated as aggregated platelets, the median diameter of which could vary from 1 to 4 μm depending on the experimental conditions. The acidic salt $YH(C_2O_4)_2.3H_2O$ was precipitated in concentrated acidic aqueous media as platelets with a median diameter which could vary from 4 to7 μm.

Wang ***et al*** [6] studied the selective extraction of yttrium from heavy lanthanides by liquid-liquid extraction using CA-100 (s-nonylphenoxy acetic acid) in the presence of a complexing agent such as EDTA, DTPA, and HEDTA. The extraction of heavy lanthanides in the present of the complexing agent was suppressed when compared to that of Y because of the masking effect, but the selective extraction of Y was enhanced. All complexing agents formed 1:1 complexes with rare earth elements, and only free rare earth ions could take part in the extraction. The condition for separation was obtained by exploring the effects of the complexing agent concentration, the extractant concentration, pH and the equilibration time on the extraction of the heavy rare earth elements.

2.2 Extraction coefficient.

The extraction coefficient, E, is a measure of how well a solvent will extract a metal. That is, it is a measure of the overall driving force of the solvent extraction system, and is therefore concentration dependent. As defined, E is the ratio of the total analytical concentration of element in the organic phase, to the concentration of element in the aqueous phase (equ. 16). Hence, it is a number with no units, and is not constant. The value of E depends on many factors, such as the aqueous: organic phase ratio A/O, extractant concentration, temperature, pH, metal complexation in the aqueous and organic phases, and metal concentration in the aqueous phase.

Consider the variation of E as a function, of A/O ratio. This is illustrated graphically in Fig. 2.1 for the extraction of cobalt from an acid solution (pH 6) using D2EHPA as the extractant. (7) In these experiments the cobalt concentration in the feed, the extractant concentration in the solvent, and the equilibrium pH were kept constant, only A/O ratio was varied. Values of E vary from about 100 at an A/O ratio of 1/2 to about 1.9 at an A/O ratio of 10/1. Similar wide variations can result from changes in the other factors noted above.

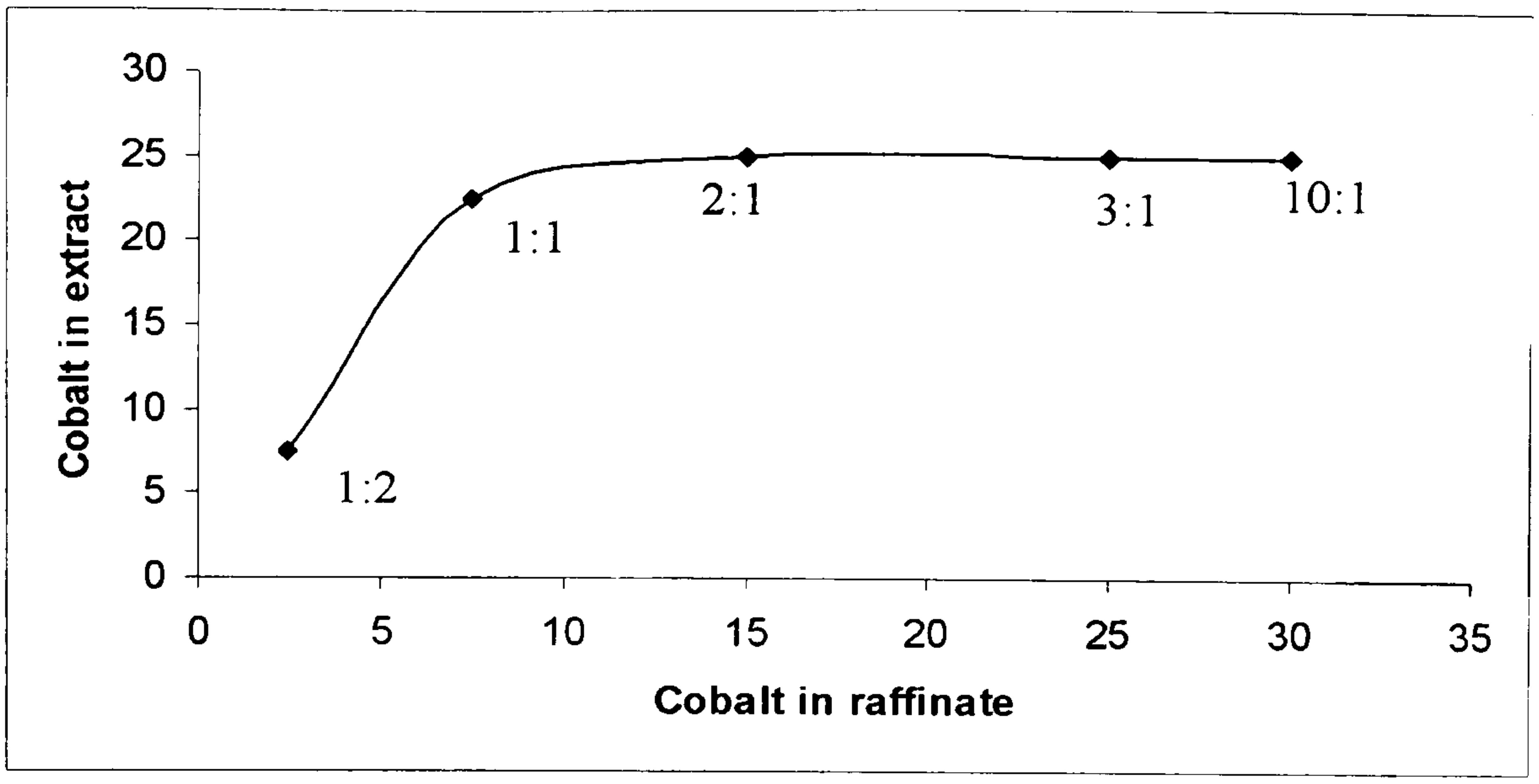


Figure 2.1: Variation of partition of cobalt in extract and raffinate by changing of A/O ratio. [(8)]

The value of E, by itself, has really no meaning, simply because it is dependent on the variables noted above. Thus, to say that an extraction system is good because the extraction coefficient is high, without giving the conditions under which the result was obtained is meaningless. Similarly, a comparison of different systems using only E values is again an exercise in futility. It cannot be emphasised too strongly that values of E are unique to a particular system, and comparisons of different systems should be done only when the experimental conditions are identical for each.

In spite of these restrictions, the extraction coefficient, or logE, is the most used parameter in solvent extraction studies. Together with the loading capacity of a solvent it is fundamental to the design of a solvent extraction process. For the situation where the separation of the two metals is to be made (from the same solution) a useful indication as to whether this can be achieved is given by the so-called separation factor. This was defined in terms of the extraction coefficients for each of the two metals in similar systems, by:

$$SF = E_A/E_B \qquad (28)$$

where E_A and E_B refer to the E value for metals A and B respectively. Separation factors of greater than one indicate that the two metals can be separated, but this gives no indication of the ease of separation or the number of stages, which may be required. For example, the separation factor for the extraction of cobalt from an aqueous phase contains both cobalt and nickel at pH 5-6, using D2EHPA as the extractant, is about 1.6. Generally, the higher the separation factors, the less the number of stages required to achieve a given metal ratio in the loaded solvent.

2.3 Extractant concentration.

For a given metal ion concentration in the aqueous phase the extraction coefficient will increase with an increase in extractant concentration, if all other factors are constant. As the extractant concentration is increased, the distribution curve for a metal, as a function of pH, will shift towards lower pH values as predicted by Equation (29).

$$pH = \frac{1}{n}\log E - \frac{1}{n}\log K_E - \log\left[\overline{HA}\right] \tag{29}$$

Thus for a fixed metal ion concentration, pH, and phase ratio, the amount of metal extracted will increase with an increase in extractant concentration. Plots of extractant concentration versus E generally show a linear relationship provided that the concentration of metal is not too high. The slope of the line is equal to the number of extractant molecules, n, associated with the metal atom in the extracted species. This number may or may not an integer. That the slope of extractant concentration versus E gives the values of n is shown by the following:

$$M^{n+} + \overline{nHA} \Leftrightarrow \overline{M.nA} + \mathrm{nH}^{+} \tag{30}$$

$$K_E = \frac{\left[\overline{M.nA}\right]\left[H^{+}\right]^{n}}{\left[M^{n+}\right]\left[\overline{HA}\right]^{n}} \tag{31}$$

at constant pH

$$K_E = \frac{E}{\left[\overline{HA}\right]^{n}} \tag{32}$$

and $E = K_E\left[\overline{HA}\right]^{n}$ (33)

taking logarithms

$$\log E = n\log\left[\overline{HA}\right] + \text{constant} \qquad (34)$$

which is the equation of a straight line of slope n.

2.4 Extraction experiments.

Generally a known volume of tri-*iso*octyl amine (TiOA) was diluted with carbon tetrachloride and mixed with an equal volume of the sulfate liquor shaken for a specific time using a mechanical shaker. After the equilibrium was reached, the contents were transferred to a separation funnel where the solutions were left for 30 seconds, the time necessary to separate the layers. The concentration of the element of interest remaining in the aqueous phase was determined by three different methods: UV/VIS using the Arsenazo III indicator, (9) Inductively Coupled Plasma Atomic Emission Spectroscopy (ICPAES), and Atomic Absorption Spectroscopy (AAS). Quoted data represent the averaged results from these three different measurements. Errors in the measured concentrations can be estimated as ± 0.7 ppm from UV/VIS determinations, ± 0.1 ppm from ICP and ± 0.5 ppm from AA. Each measurement was performed in triplicate to check for reproducibility, the amount of metal extracted into the organic phase being determined from the mass balance.

2.5 Instrumentation.

All samples were weighed using an analytical balance having a maximum sensitivity of 10^{-5}g; the hydrogen ion concentration of the different solutions was measured accurately using a JENWAY 350 digital pH-meter, within an error of ± 0.01; for the equilibration experiments, a good mixing for the two phases was achieved using a VIBRAMAX100/ROTAMAX120 mechanical shaker; complete phase separation of the two phases was attained by using separation funnel; yttrium, cerium and lanthanum concentrations were determined spectrophotometrically using double beam UV-Visible spectrometry using a PERKIN- ELMER UV/VIS/NIR Lambda 900 spectrometer, in all measurements, two matched 5cm^3 quartz cells with a path length of 1cm were used for sample and blank measurements. All measurements were carried out at laboratory temperature; Inductivity Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) analysis was performed on a Thermo Jarrell Ash IRIS ICP-

EAS spectrometer; and Atomic Absorption Spectroscopy (AAS) analysis was performed on PERKIN-ELMER AAnalyst 100.

2.6 Spectrophotometric determination of yttrium using Arsenazo III.

This is a very useful spectrophotometric reagent. (10) Arsenazo III (Fig. 2.2) is a bisazo dye based on chromotropic acid and *o*-aminophenyl arsenic acid. It is moderately soluble in neutral and acid solutions, and readily soluble in slightly alkaline solutions. The reagent is stable in the solid state and in aqueous solution although strong oxidizing (H_2O_2, Cl_2 and Br_2) or reducing ($TiCl_3$) agents cause decomposition. The use of Arsenazo III in strongly acidic media overcomes difficulties connected with the hydrolysis of some multivalent metals (e.g. Zr, Th, and U). In the determination of these metals, the high acidity enhances the selectivity of the reagent. Interference from sulfate and phosphate is considerably reduced in strongly acid solution.

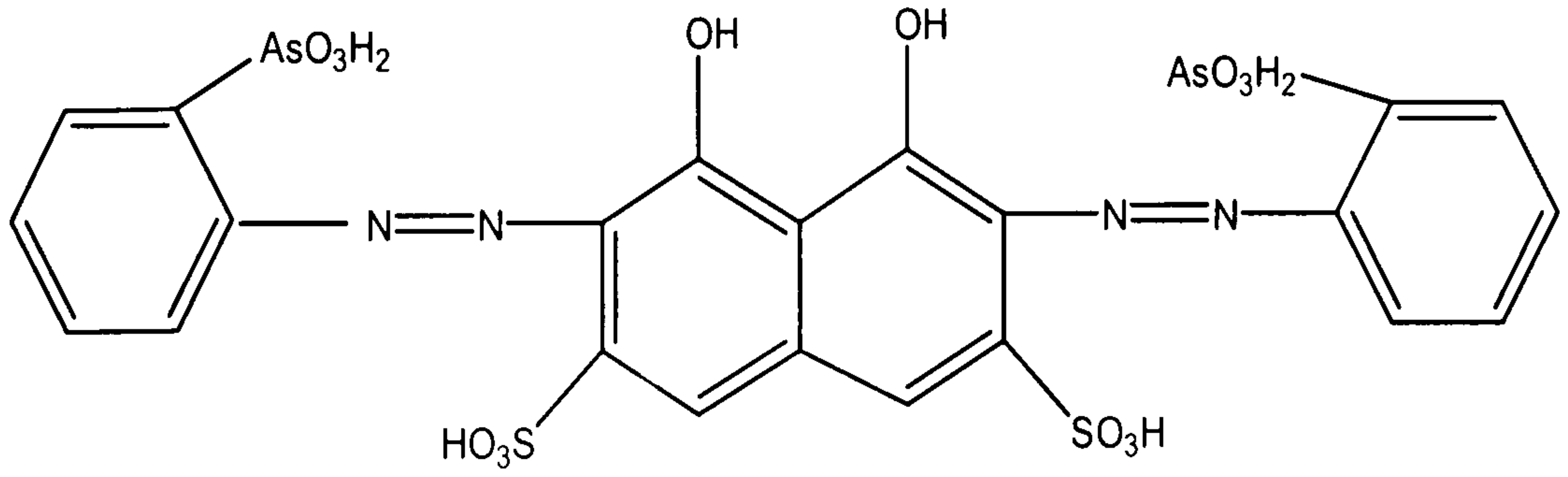


Figure 2.2: Chemical structure of Arsenazo III

In weakly acidic media the lanthanides and yttrium react with Arsenazo III to form coloured complexes which are the basis of this sensitive method. The reagent is violet, whereas its complexes with the rare-earth elements are green.

Reagents.

- Arsenazo III: 0.05% aqueous solution.
- Standard yttrium solution: 1mg/ml: dissolve 0.1270g of yttrium oxide in 5ml of hot HCl (1:1). Dilute the solution to volume with water in a 100-ml standard flask.
- Formate buffer: pH 3.5, dissolves 60ml of formic acid and 28g of NaOH in water, and dilutes the solution with water to 1 litre.

Procedure.

- A 1ml sample from the analyte solution was taken in 25ml volumetric flask.
- 1ml of 1% ascorbic acid solution was added, and the solution left to stand for few minutes.
- 1ml of the formate buffer was added.
- 2ml of the Arsenazo III solution was added, and the resultant solution was diluted to approximately 20ml volume.
- The coloured solution was adjusted to pH 2.6(± 0.1) with 0.1M NaOH and dilute H_2SO_4.
- The solution was transferred to a 25ml standard flask, make up to the mark with water.
- The absorbance was measured at 650nm against a reagent blank solution.
- Calibration curves for different Y(III)-Arsenazo III complexes were obtained at different concentrations of yttrium.

2.7 Error calculation.

The two principal types of the experimental errors, errors on stock solution, and errors on the three different techniques used in the determination of concentration of rare earth elements. The best way for reduction of experimental error is to repeat the measurement a number of times. Making several (three) repetitions of measurement will reduce "random errors" to improve accuracy. Also, repeating the measurement with three different techniques can minimize "systematic errors".

2.7.1 Error on stock solution.

Error on of [Y] on four-figure balance = ± 0.0001 g

Error on volume of solvent = ± 0.02 cm^3

Then error of stock [Y] = $\frac{0.0001}{0.2} + \frac{0.02}{100} \times 0.005222 \approx \pm 0.000004\ \text{Mol.dm}^{-3}$

So stock [Y] = 0.005222± 0.000004 Mol.dm^{-3}

2.7.2 ICP error on measurement = ± 0.1 ppm.

[Y] in organic = [Y] in stock – [Y]in aqueous

Error on [Y] in organic = $\sqrt{(0.000004)^2 + (10^{-7})^2}$ = 0.000004

Then error on % extraction = $\dfrac{0.000004}{[Y]organic} + \dfrac{0.000004}{[Y]stock} \times$ %E

Error on % E = $\dfrac{0.000004}{0.0045} + \dfrac{0.000004}{0.00522} \times 90 = \pm\, 0.152\ \%$

Error on distribution coefficient (D)

$$= \frac{0.000004}{0.0045} + \frac{0.000004}{0.00522} \times 10 = \pm\, 0.\ 0166$$

2.7.3 AA error on measurement = ± 0.5 ppm.

Error on [Y] in organic = $\sqrt{(0.000004)^2 + (5 \times 10^{-7})^2}$ = 0.000004

Error on % E = $\dfrac{0.000004}{0.0045} + \dfrac{0.000004}{0.00522} \times 90 = \pm\, 0.152\ \%$

Error on distribution coefficient (D)

$$= \frac{0.000004}{0.0045} + \frac{0.000004}{0.00522} \times 10 = \pm\, 0.\ 0166$$

2.7.4 UV/VIS error on measurement = ± 0.7 ppm

Error on [Y] in organic = $\sqrt{(0.000004)^2 + (7 \times 10^{-7})^2}$ = 0.000004

Error on % E = $\dfrac{0.000004}{0.0045} + \dfrac{0.000004}{0.00522} \times 90 = \pm\, 0.152\ \%$

Error on distribution coefficient (D)

$$= \frac{0.000004}{0.0045} + \frac{0.000004}{0.00522} \times 10 = \pm\, 0.\ 0166$$

These are the three major errors in measurement of yttrium by taking the average; the error on the distribution coefficient is estimated ± 0.02 and percent extraction ± 0.15 %. Data in Tables are averaged values from data measured by all three techniques from the same sample.

Error on D = $\sqrt{\sigma(D_{ICP})^2 + \sigma(D_{AA})^2 + \sigma(D_{UV/Vis})^2} = \pm\, 0.035$

Error on % E = $\sqrt{\sigma(D_{ICP})^2 + \sigma(D_{AA})^2 + \sigma(D_{UV/Vis})^2} = \pm\, 0.26\ \%$

2.8 Effect of different concentrations of tri*iso*octylamine (TiOA) in carbon tetrachloride on the distribution coefficient of yttrium.

Firstly the solvent must be equilibrated by contacting it with 0.5M sulfuric acid for 5 minutes. To 5 ml of the sulfate liquor (yttrium sulfate), 5 ml of a solution of TiOA in CCl_4 was added with concentration ranging from 0.01 to 0.1M, and then the solution was shaken for 10 minutes at room temperature to attain equilibrium state. The optimum value of a 0.08M solution of TiOA in CCl_4 was chosen from the data reported in Table 2.3 and presented in Fig. 2.3. The decrease on the distribution coefficient above 0.08M probably due to the increase in the viscosity of extractant (TiOA) that causes a decrease in the mass transfer of yttrium from aqueous to organic phase.

Table 2.3: Effect of different concentrations of solvent/carbon tetrachloride on the distribution coefficient of yttrium.

[TiOA]/M	% Extraction	Distribution Coefficient
0.01	89.78	8.76
0.04	89.84	8.84
0.06	90.13	9.13
0.08	90.50	9.54
0.10	89.29	8.33

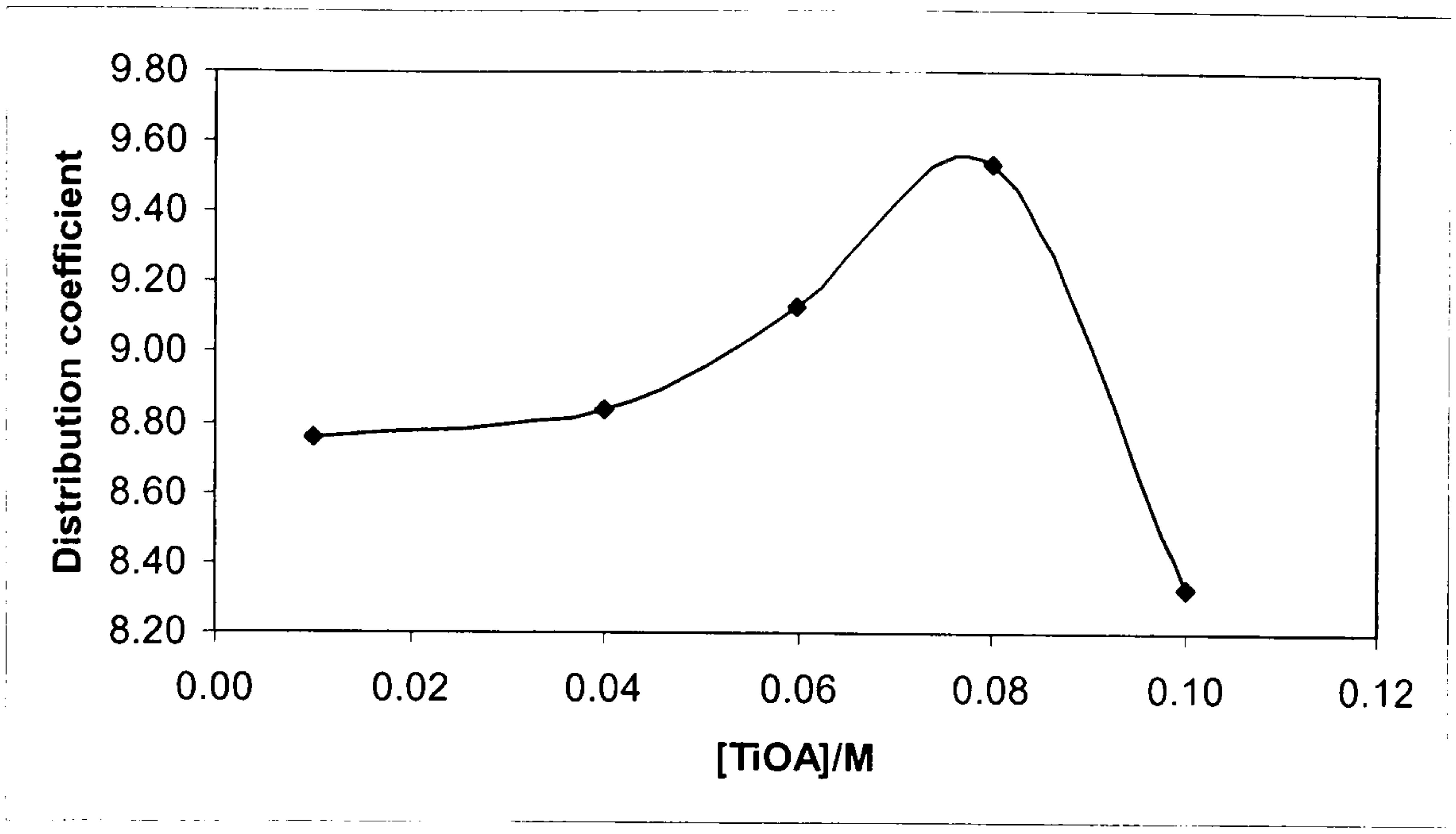


Figure 2.3: The effect of different concentrations of TiOA on the distribution coefficient of yttrium.

2.9 Effect of contact time on the distribution coefficient of yttrium.

The effect of contact time on the attainment of an equilibrium state was studied at intervals between 1–30 minutes, while the other factors were kept as mentioned before. The results obtained are given in Table 2.4 and shown in Fig. 2.4. It is obvious that contact time of 5 minutes is quite adequate for efficient yttrium extraction. The distribution coefficient was increased from 1-5 minutes and after that slightly decreased, probably due to the entrainment of some organic phase droplets into aqueous phase, which causes a slight decrease in the extractive power of extractant.

Table 2.4: Effect of contact time on the distribution coefficient of yttrium from 0.08M solvent/carbon tetrachloride.

Time/minutes	% Extraction	Distribution Coefficient
1	85.00	5.67
5	90.54	9.53
10	89.67	8.64
20	89.67	8.64
30	89.65	8.62

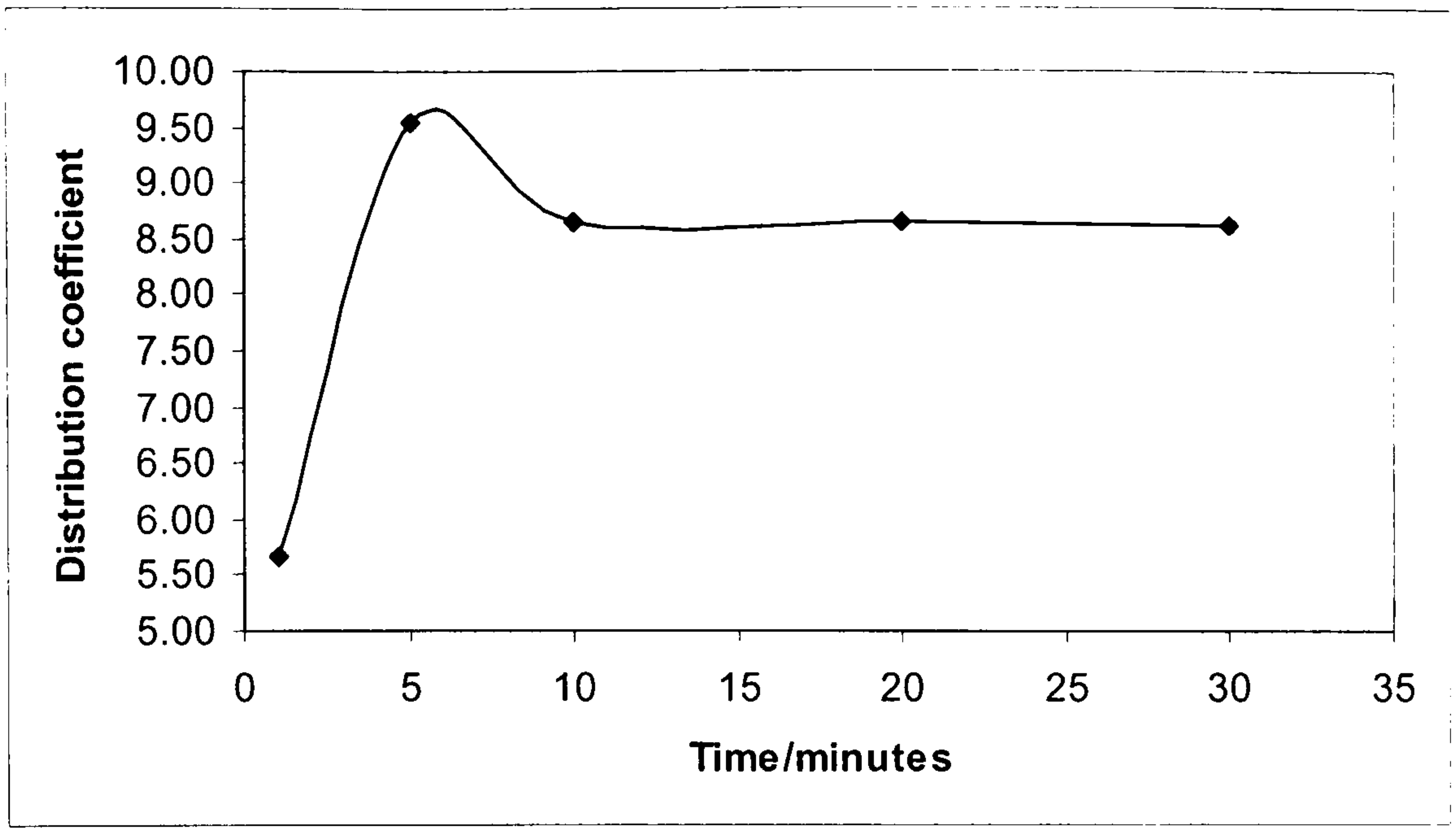


Figure 2.4: The effect of shaking time on the distribution coefficient of yttrium.

2.10 Effect of pH.

All extractants of the chelating or acidic types used in solvent extraction processes liberate hydrogen ions on the extraction of a metal:

$$M^{n+} + \overline{nHA} \Leftrightarrow \overline{MA_n} + nH^+ \qquad (35)$$

The greater the amount of metal extracted (that is, the higher the solvent loading) the more hydrogen ions are produced. These result in a decrease in pH of the system and consequently a decrease in the amount of metal extracted. From Equation (35) it follows that the higher the equilibrium pH of the system, the lower will be the extractant concentration needed to achieve a given percent metal extraction, and vice versa. At constant concentration, E will increase as the pH is raised, unless other factors such as metal complexation or hydrolysis occur in the aqueous phase. For example, at a phase ratio of 1, increasing the pH by one unit will increase E by an order of magnitude for n = 1. For n = 2 an increase of 10 orders of magnitude is predicted and so on. This is shown in Fig. 2.5. For metal ions having values of n from 1 to 4, the curves each have a linear portion, the slope of each being equal to the number of hydrogen ions released in the formation of the extractable species.

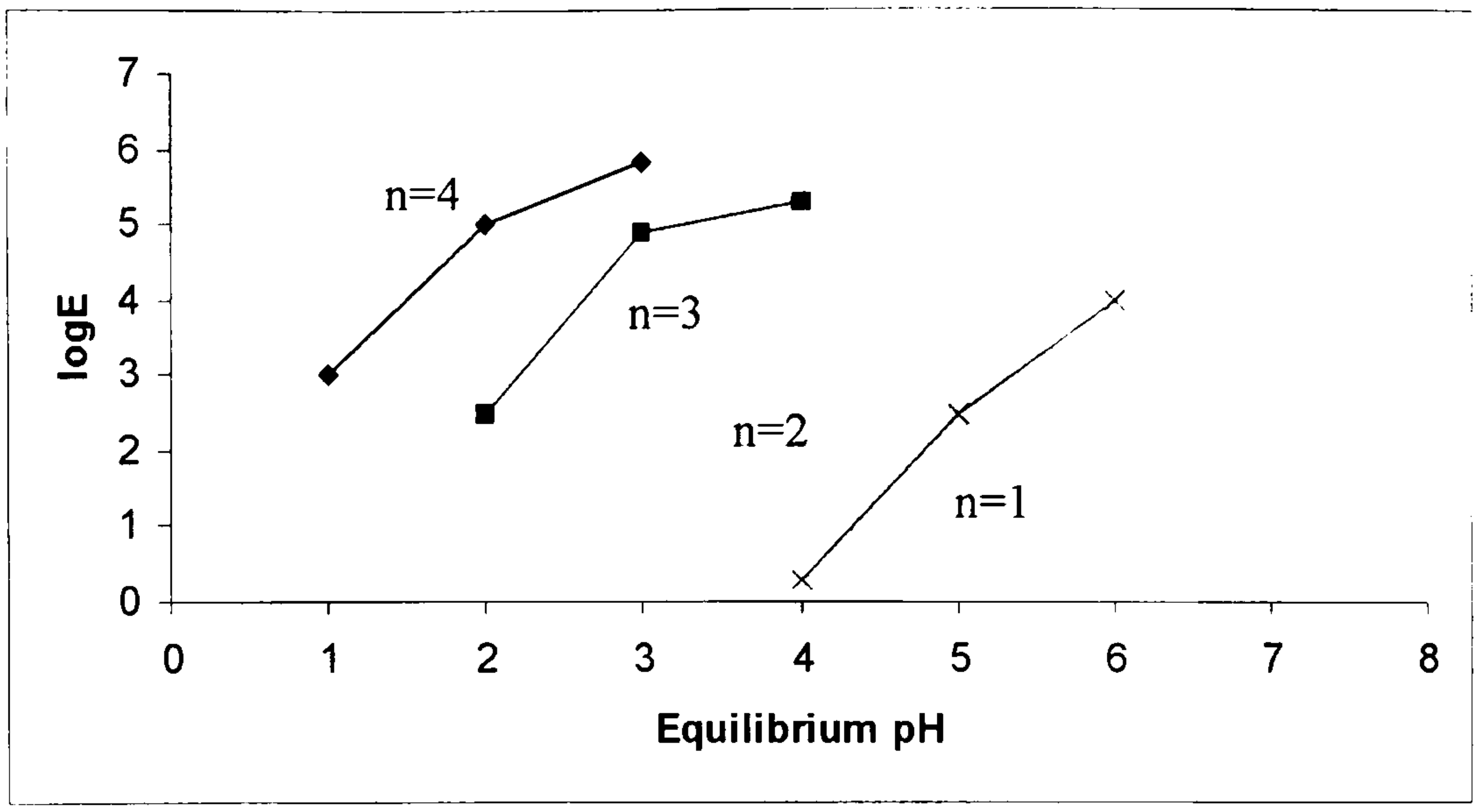
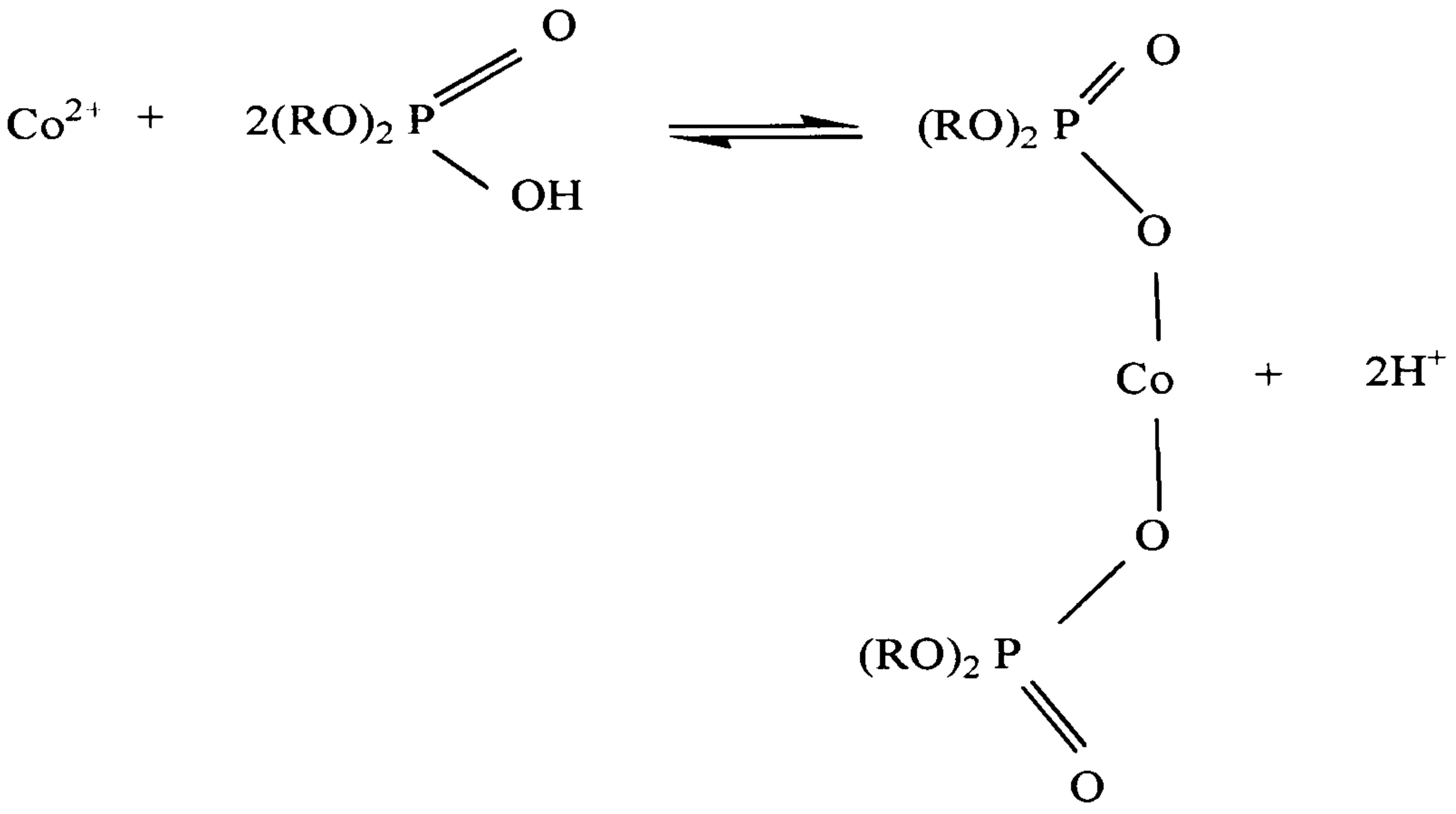


Figure 2.5: Effect of equilibrium pH on the extraction coefficient. (8)

It should be pointed out that the number of hydrogen ions and molecules of extractant involved in the formation of extractable species depends on the type of extractant. All extractants of the chelating or acidic type available are monobasic in nature, and thus release one hydrogen ion for every molecule, which combines with a metal. The number of molecules of extractant involved in the formation of an extracted species depends on the oxidation state or coordination number of the metal ion, and the number of places at which bonding can occur to the extractant. For example D2EHPA, is a monobasic extractant and forms complexes with metal atoms shown in Scheme 2.1:



Scheme 2.1: D2EHPA, monobasic extractant and complexes with Co^{2+}.

These complexes depend on the oxidation state of the metal ion. Thus for Co^{2+}, two molecules of D2EHPA are involved; for Fe^{3+}, three molecules are involved; for Th^{4-}, four molecules are involved, all producing neutral species. (8) The pH of the system affects both the metal ion and the extractant. Thus if the pH is increased, the metal complex will not extract.

A decrease in pH (increase in hydrogen ion concentration) may result in the formation of non-extractable metal species as a result of complexation with components of the aqueous phase. This occurs, for example, in systems, which involve sulfuric acid due to the equilibrium between SO_4^{2-}, HSO_4^-, and H_2SO_4, resulting in the formation of metal complexes with these anions. All extractants undergo protonation as the pH of the system decreases.

$$A^- \underset{-H^+}{\overset{H^+}{\rightleftharpoons}} HA \underset{-H^+}{\overset{H^+}{\rightleftharpoons}} H_2A^+ \tag{36}$$

If the extractant is unable to ionise as a result of the concentration of hydrogen ion, it may not be able to form a complex with a metal ion, and hence extraction will not occur. The general effect of pH is illustrated in Fig. 2.6 for the extraction of a metal.

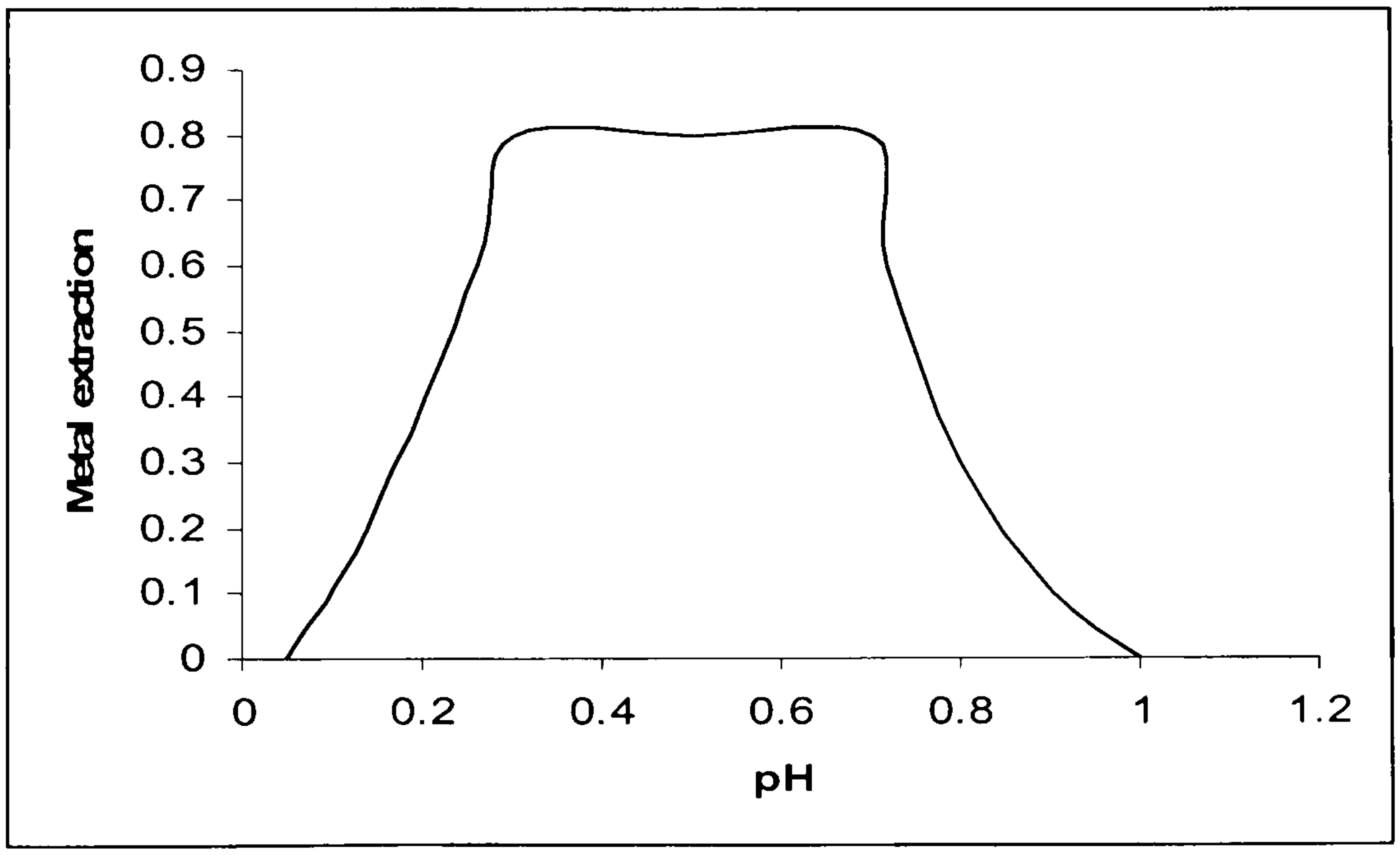


Figure 2.6: General effect of pH on metal extraction. (8)

At low pH values, extraction decreases as a result of protonation of the extractant, and at high pH values, extraction metal complex decreases. This generalisation does not hold for ion-association or solvating extractants because these are not primarily dependent on pH for metal complex formation, but rather on factors such as anion concentration in the aqueous phase. It should be apparent that pH is of prime importance in many solvent extraction systems, and also affects other variables significantly.

2.11 Effect of pH on the distribution coefficient of yttrium.

The distribution coefficient has been studied by varying the pH values of the sulfate liquor from 0.5 to 2.7, using either sulfuric acid or sodium hydroxide. Other factors were fixed at 1:1 (v/v) organic to aqueous phase ratio, 0.08M TiOA in carbon tetrachloride, contact time 5 minutes and the experiments were carried out at room temperature. The results obtained are given in Table 2.5 and shown in Fig. 2.7. It is clear that the pH 0.97 of the sulfate liquor can be taken as an optimum pH value. Fortunately, that is the same pH of the parent sulfate liquor under examination. However, by increasing pH above 1.1 there is a decrease in the distribution coefficient, which may result from the formation of non-extractable metal species as a result of complexation with components of aqueous phase. This occurs, in sulfate media due to equilibria between SO_4^{2-}, HSO_4^-, and H_2SO_4 resulting in the formation of yttrium complexes with these species. (8)

Table 2.5: Variation of yttrium distribution coefficient with the pH of the sulfate solution.

pH	% Extraction	Distribution Coefficient
0.50	90.03	9.03
0.97	90.50	9.53
1.10	89.50	8.52
1.20	89.25	8.30
1.80	88.75	7.89
2.70	88.25	7.50

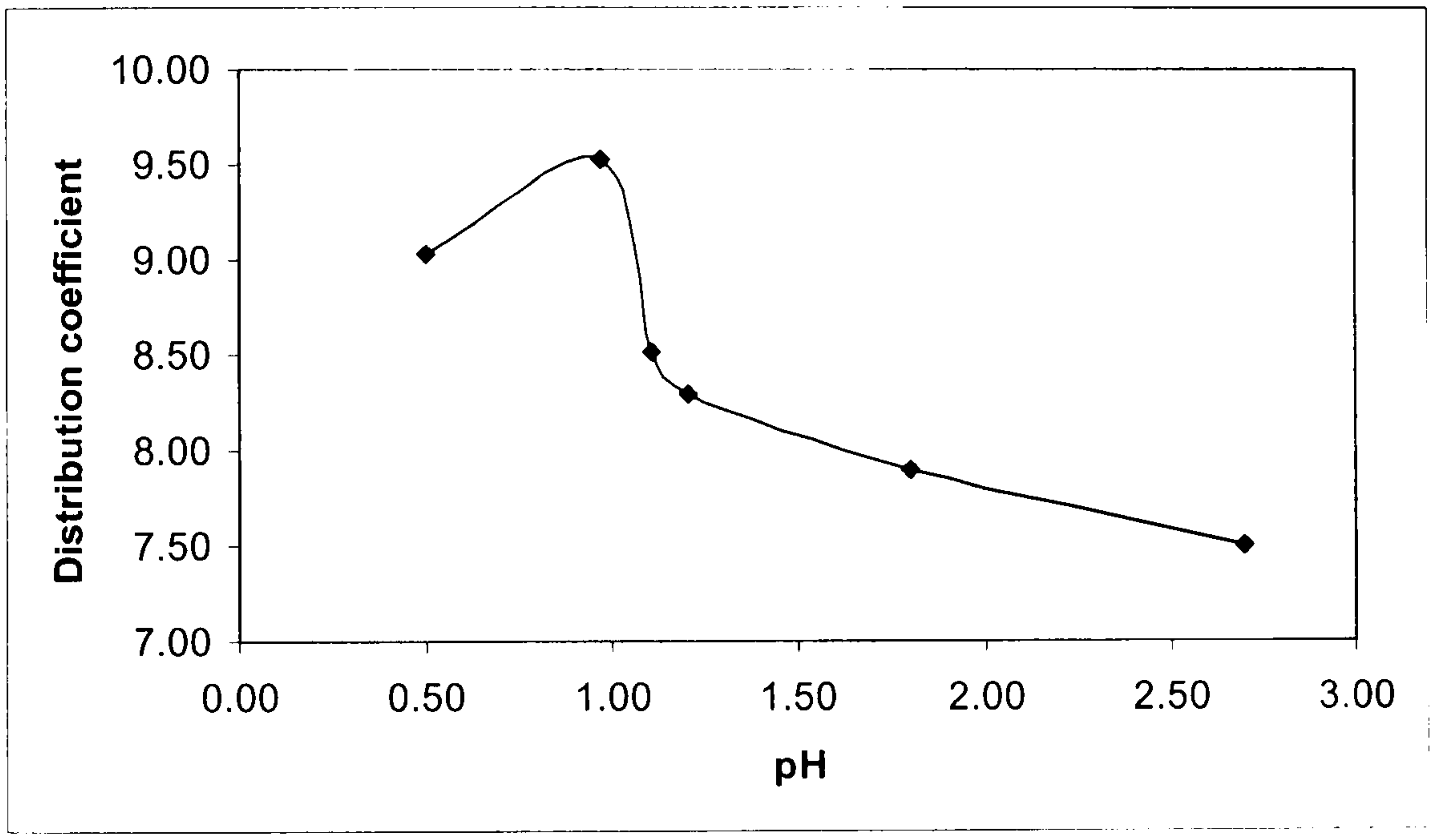


Figure 2.7: The effect of pH on the distribution coefficient of yttrium.

2.12 Effect of temperature on the distribution coefficient of yttrium.

For studying the effect of temperature on distribution coefficient and extraction percent, experiments were carried out in oil bath using an electric thermostat, the temperature of which was regulated from 25–50°C. The following factors were kept constant at 1:1 (v/v) organic to aqueous phase ratio, pH 0.97, and a contact time of 5 minutes and 0.08M TiOA in carbon tetrachloride. From the results in Table 2.6 and Fig. 2.8 it is clear that room temperature can be considered as the best temperature for the extraction process. It is obvious from the data obtained, that distribution coefficient decreases with increasing temperature. This means that the extraction of yttrium is exothermic. This behaviour is similar to that reported by previous investigators. (11, 12)

Table 2.6: Distribution coefficient of yttrium at different temperatures.

Temperature, °C	% Extraction	Distribution Coefficient
25	90.50	9.53
30	89.75	8.76
35	89.25	8.50
40	89.00	8.20
46	88.75	7.88
50	88.50	7.69

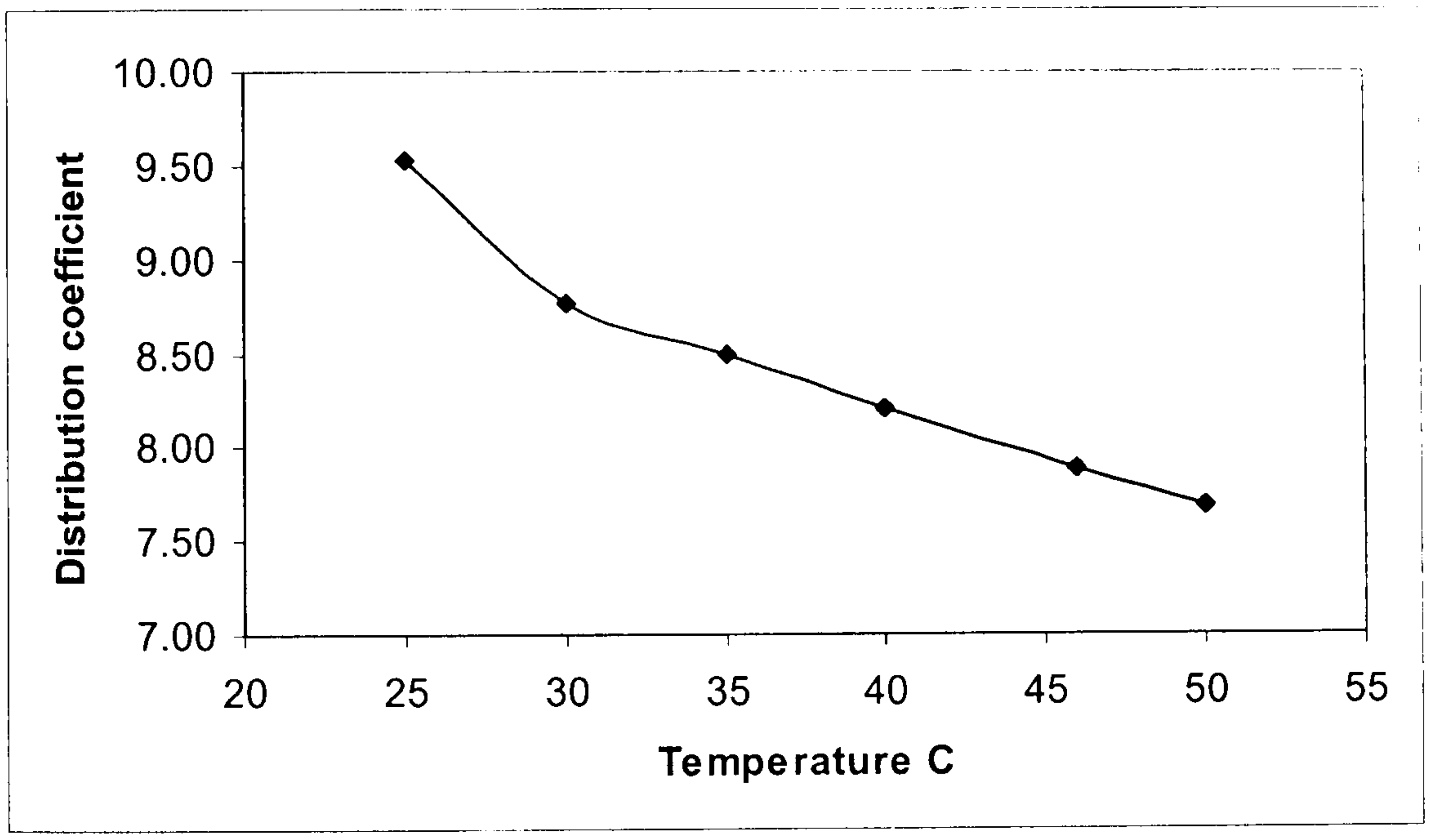


Figure 2.8: Effect of temperature on the distribution coefficient of yttrium.

2.13 Effect of aqueous phase composition on the extraction of metals.

The type and concentration of any anionic species present in the aqueous phase affects the extraction of metals. It can generally be expected that when a metal complex in the aqueous phase has stability greater than that of the metal-extractant complex, it will not be extracted. For example, hydrolysed and ion-association metal species can drastically affect the extraction of a metal by some extractants. The extraction of cobalt and nickel by D2EHPA from ammonia solution is shown to be affected by the concentration of sulfate ion in the aqueous phase. The formation of ion-association complexes, such as $[Co(NH_3)_6.SO_4]^+$, inhibits metal extraction because the stability of such complexes is greater than those of the extractable species $[Co(NH_3)_6]^{3+}$. (13) Also, in the extraction of uranium from acidic sulfate solution by tri-n-octylamine, uranium extraction decreases with increasing concentration of other anions, and the effect varies with the anion. (14) On the other hand, the extraction of metals by neutral extractants can be enhanced by increasing the salt concentration, probably reflecting a salting-out effecting by which the dissociation of the extractable neutral species is depressed.

Complexation of a metal in the aqueous phase can be used to advantage in the separation of metals. In a process for the separation of zirconium and hafnium, neutral metal thiocyanate complexes are formed by the addition of ammonium thiocyanate, which allows the extraction of hafnium from zirconium by methyl isobutyl ketone. The extraction of metals by amines (anionic exchange) generally requires the formation of anionic metal species in the aqueous phase, which is achieved by the use of high salt or acid concentration.

2.14 Distribution coefficients of yttrium as a function of aqueous H_2SO_4 concentration.

Fig. 2.9 shows the effect of different concentrations of H_2SO_4 on the distribution coefficients of yttrium in the two phases. The distribution coefficient of yttrium increases as the concentration of H_2SO_4 increases from 0.1-0.5M, but then decreases as the acid concentration is increased further. The reason for the initial increase in distribution coefficient may be caused by the salting-out effect of sulfuric acid. With further increase in H_2SO_4 concentration, the concentration of free extractant decreases probably as a result of sulfuric acid co-extraction. However, the best concentration of H_2SO_4 to use for yttrium highest distribution coefficient is clearly 0.5M. Other factors in this experiment were fixed at 1:1 v/v organic to aqueous phase ratio, 0.08M TiOA in carbon tetrachloride, mixing time 5 minutes and the experiments were carried out at room temperature. The results obtained are given in Table 2.7.

Table 2.7: Variation of yttrium distribution coefficient with the concentration of sulfuric acid solution.

$[H_2SO_4]$/M	% Extraction	Distribution Coefficient
0.1	89.13	8.19
0.25	89.58	8.59
0.5	90.50	9.35
0.75	89.18	8.24
1.0	88.80	7.93

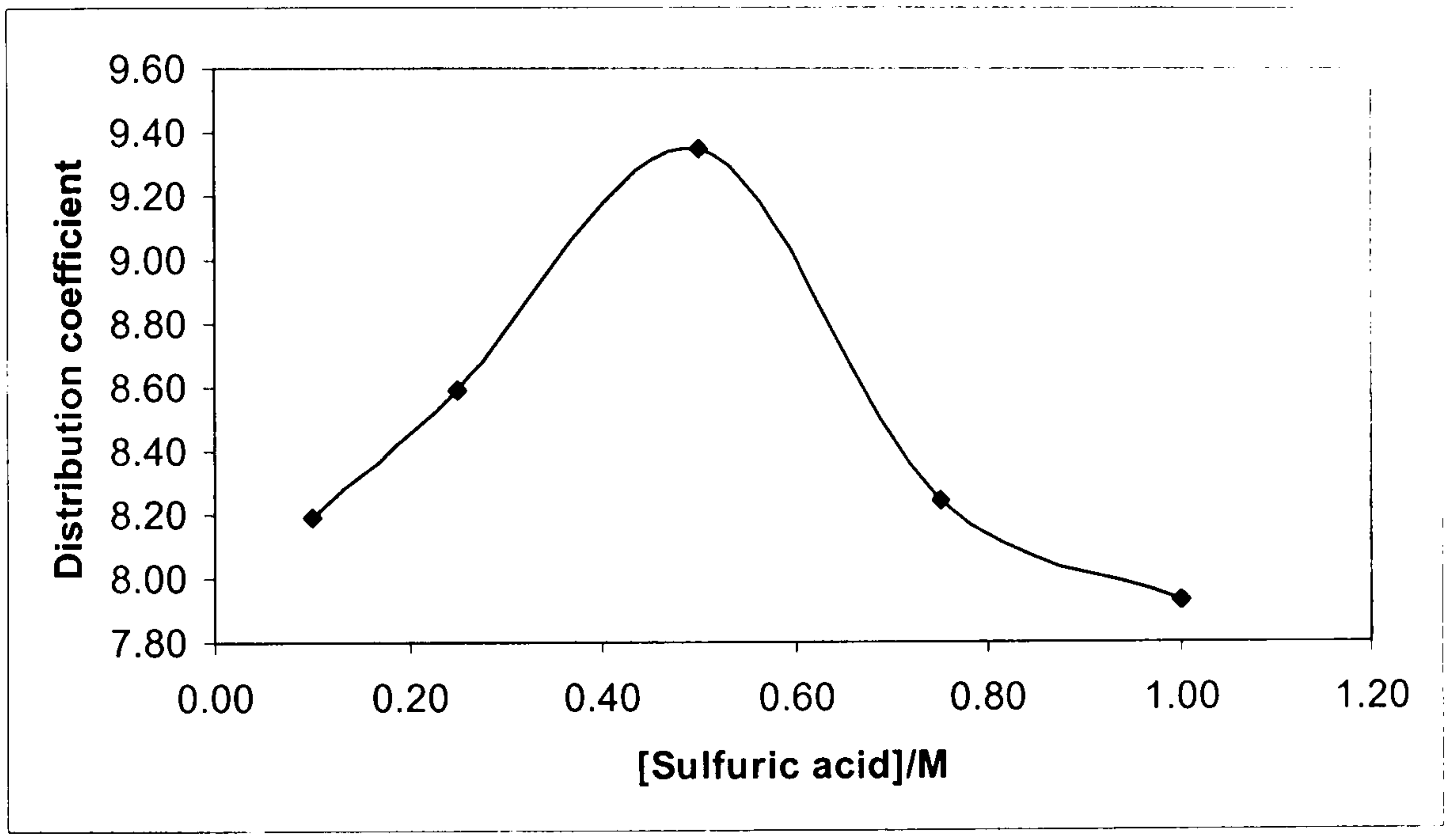


Figure 2.9: The effect of sulfuric acid concentration on the distribution coefficient of yttrium.

2.15 McCabe-Thiele Diagram.

Predicting the number of counter-current stages required for a metal extraction system can be accomplished by the use of a McCabe-Thiele diagram, an example of which is shown in Fig. 2.10. In constructing this diagram, the extraction isotherm is first drawn. A vertical line is then drawn from the concentration of metal in the feed solution at the x-axis. The operating line (a graphical representation of the mass balance of the system) is next inserted, the slope of which is equal to the phase ratio

(A/O) to be used. This line may be considered as representing the fact that in any extraction stage, the increase in metal concentration in the organic phase is equal to the decrease in metal concentration in the aqueous phase multiplied by the phase ratio. It may or may not pass through the origin, depending on how low a metal concentration in the raffinate is desired, or on the shape of the extraction isotherm. Finally, lines representing the theoretical extraction stages are drawn. Starting from the intersection of the operating line and the vertical line representing the metal concentration in the feed solution, a horizontal line is drawn to intersect the extraction isotherm. At this point, a vertical line is dropped to intersect the operating line. These lines then represent the conditions in the first extraction stage, namely the metal concentration in the feed, in the solvent, and in the raffinate.

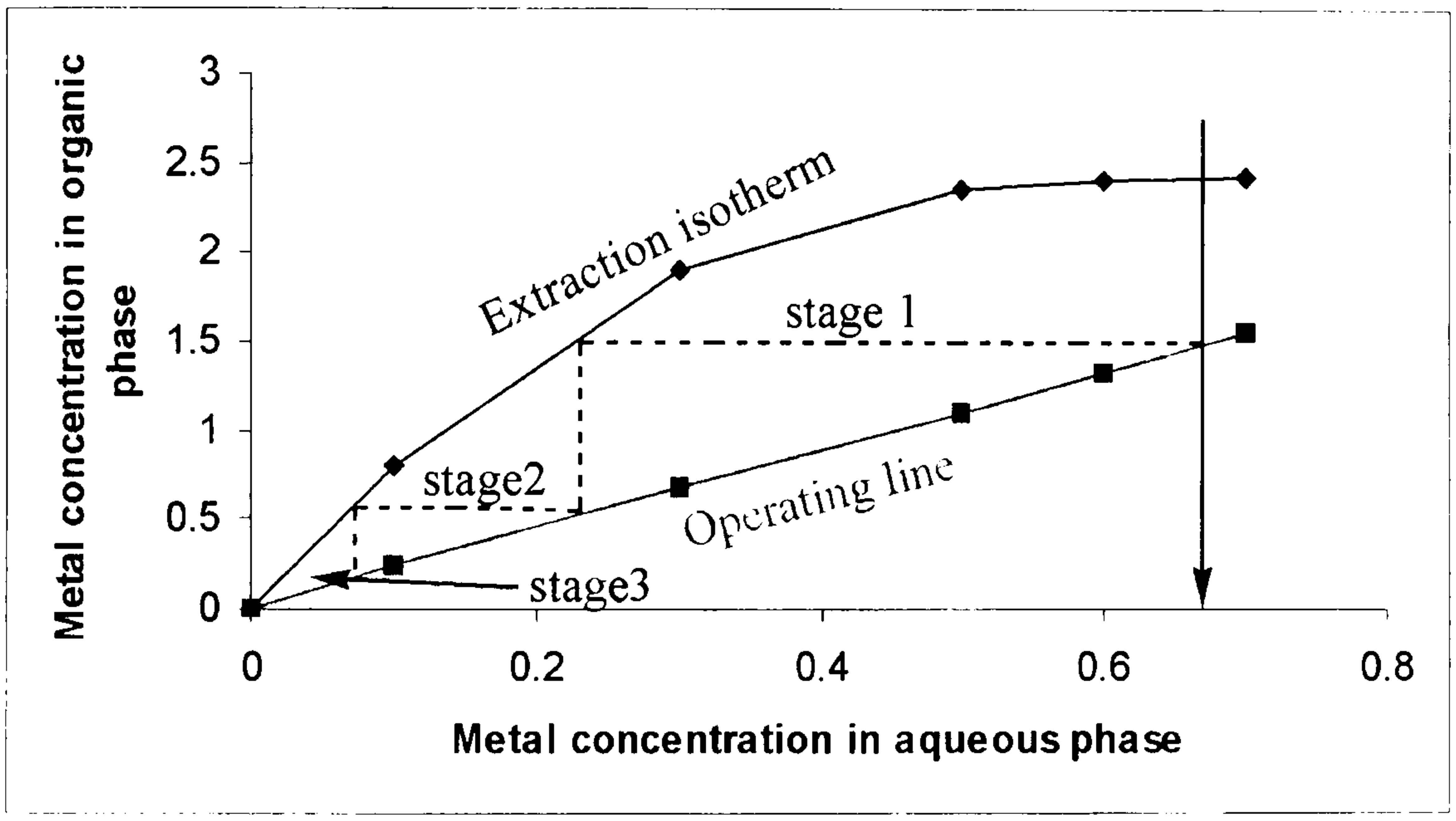


Figure 2.10: McCabe-Thiele diagram for the extraction of a metal.

2.15.1 Equilibrium line and construction of McCabe-Thiele diagram for yttrium extraction.

20 ml of each of the organic phase (0.08M TiOA in carbon tetrachloride) and aqueous phase were contacted for 5 minutes until equilibrium was obtained. The phases were allowed to separate and the aqueous phase was removed and analysed. A measured portion of the organic phase was also taken for analysis. Fresh aqueous solution was then added to the organic phase to give the same phase ratio as that originally used.

The phases are again contacted until equilibrium was obtained, and the procedure repeated. This process was carried out until saturation of the solvent with yttrium was obtained. Care must be taken to keep the same pH value of 0.97 throughout the series of shake-outs. The data were used to obtain the equilibrium curve by plotting the yttrium concentration in the organic phase against its concentration in the aqueous phase. The next step is the construction of McCabe-Thiele diagram. From Fig. 2.11 we can see yttrium extraction under these conditions needs only two extraction stages for nearly complete recovery.

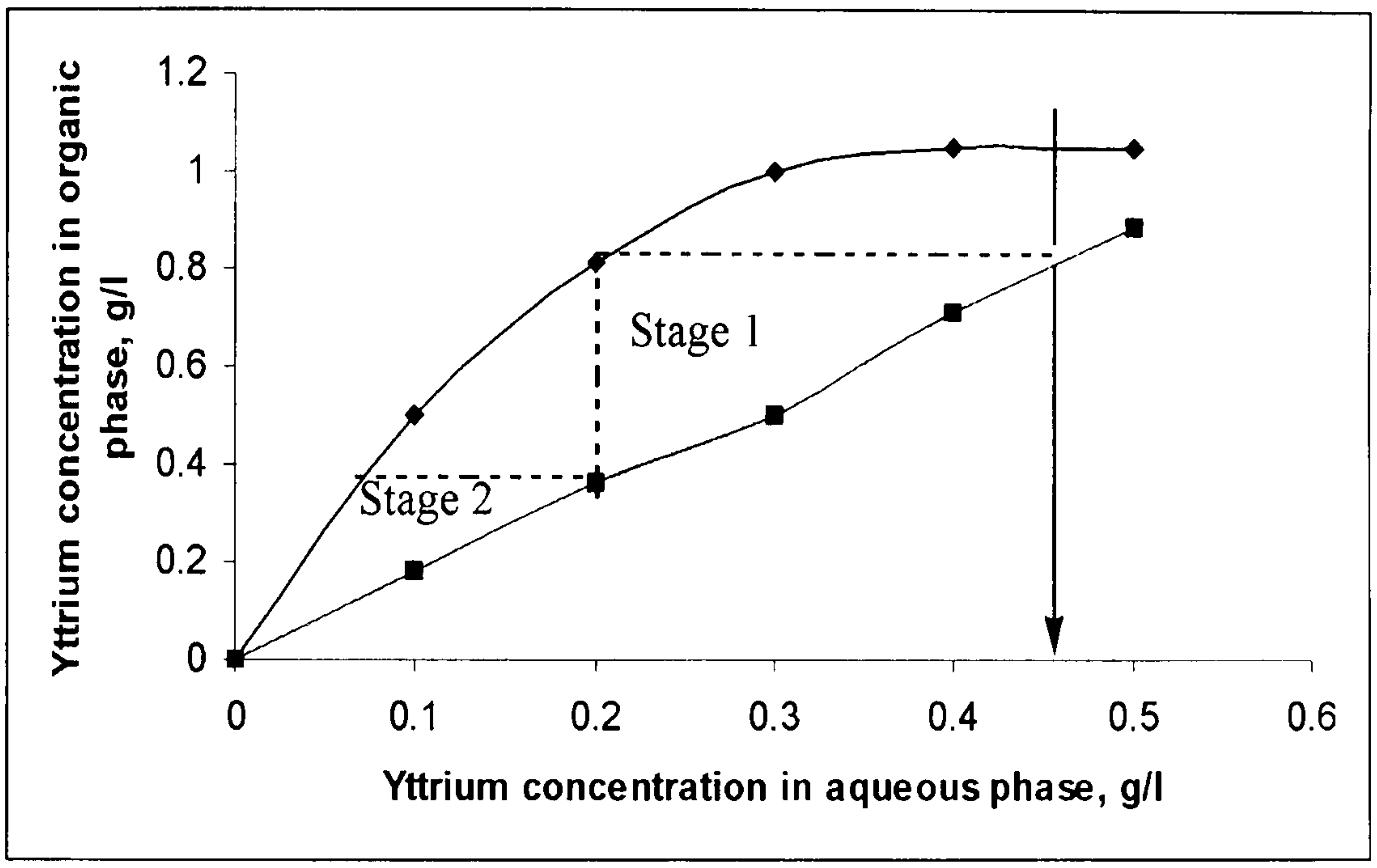


Figure 2.11: McCabe-Thiele diagram for yttrium extraction.

2.16 Diluents.

In solvent extraction, the term diluent refers to the organic liquid in which the extractant is dissolved to form the solvent. In the majority of cases, the diluent comprises the major portion of a solvent. Although there have been numerous studies undertaken on the evaluation of the most suitable extractant for a particular process, comparatively little attention has been directed towards optimising the solvent extraction process with respect to the diluent. (8) Proper selection of the diluent can be almost as important as selecting the extractant because of the physical and chemical effects that the diluent can exhibit, and also on the economics of a process.

Diluents were considered to have no effect on metal extraction characteristics, and were therefore “inert” to the process. But with the development of commercial copper solvent extraction plants came a new diluent, Napoleum 470, manufactured by Kerr McGee. This diluent, an essentially aliphatic hydrocarbon with a high, narrow boiling range was put to use in both copper and uranium plants. Since then, there have been more critical evaluations of diluents as related to performance and economics. Also, more diluents, both aliphatic and aromatic materials, are available for use in the solvent extraction process. Investigators have found that not only are diluents not “inert“ in the solvent extraction process, as previously thought, but that they can play a substantial role in determining the success of an operation.

The general requirements of a diluent are, in no particular order of preference: Mutual solubility with an extractant; high solvency for an extracted metal species, thus minimising both the problem of third phase formation and low loading capacity of a solvent; a low surface tension; it must be insoluble in the aqueous phase; low cost and ready availability; and low volatility and a high flash point, thus decreasing losses due to volatility as well as fire hazards.

The reasons for using a diluent in the make–up of solvent are: to decrease the viscosity of the extractant, as most of the extractants used in commercial solvent extraction process are viscous liquids; and to provide a suitable concentration of extractant. There is no point in using a high concentration of extractant if only a small portion is actually used for metal extraction. The unused portion is then recycled around the circuit for no reason. The diluent can also decrease any emulsion–forming tendencies of the extractant. Many of the extractants used in solvent extraction systems are surface–active and tend to emulsify in high concentrations, especially with high agitation; and to improve the dispersion and coalescence properties of the solvent. Much of the work done on the chemical role of diluents in solvent extraction has been directed towards the TBP–kerosene and amine– kerosene systems used in the nuclear (15) and uranium industries. (16, 17)

2.16.1 Properties.

Most of the diluents used today are fractions of crude oil, which may be produced in large quantities for reasons other than for use in solvent extraction processes and consequently are readily available in bulk and relatively cheap. As a result, the oil companies are the major suppliers of diluents.

2.16.1.1 Specific gravity.

In general, aromatic hydrocarbons have specific gravities higher than the aliphatics, which could inhibit the dispersion and coalescence of solvents containing them. For example, at high metal loading of the solvent, the difference in specific gravity of the loaded solvent and aqueous phase could be small, which might present problems in separating the two phases. Hence, aliphatic diluents are more often preferred to aromatic ones for solvent extraction. The density of solvent will usually increase as the concentration of extractant is increased, thus the density of the diluent can have a considerable effect on the rate of phase separation, especially at higher extractant concentrations and high metal loading.

2.16.1.2 Viscosity.

As the metal loading of a solvent increases, its viscosity is seen to increase markedly. For this reason, it becomes necessary to operate the solvent extraction system at elevated temperatures, both to reduce viscosity effects and to increase the rate of separation of the phases. It is advisable to use a diluent having a low density and surface tension.

2.16.1.3 Flash point.

In considering the diluents, which may be applicable to a particular process, the solubility in the aqueous solution and the flash point are important. Early work on the solvent extraction of uranium using long chain tertiary amines (18) used Esso JP–4 or BAT–2 as diluent. These have a very low flash–point (~ 32 °F) and presented a potential fire hazard. Today, diluents having much higher flash points are used.

2.16.1.4 Polarity.

In the extraction of rare earths with Aliquat336, (19) there was noted a decrease in the extraction of the metals with an increase in the polarity of the diluent. Also, the separation factor for La and Pr was decreased as the polarity increased. Similar effects are shown in the extraction of americium with a mixture of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone and TBP from nitrate solution. (20) The extraction constants decrease with increasing polarity of the diluent. The effects of variation of diluent on the extraction of molecules or anions such as $ZnCl_4^{2-}$ or $FeCl_4^{-}$ (21, 22) with tertiary amines gave similar results, showing the following trend in extractability: Cyclohexane ≈ *o*-xylene > toluene > benzene >>chlorobenzene.

One conclusion which may be drawn is that the diluent affects the solvation of the extractant and hence its extractive properties. Interaction of the diluent with the extractant can thus result in lower extraction coefficients for metal ions. Thus the formation of an extractant–diluent species in the organic phase produces a lower concentration of the "free extractant", with a consequent decrease in the extraction coefficient. (23) Although most of the normal diluents that would be considered for use in solvent extraction processing are kerosene–type materials, with a dielectric constant in the range 2-3, there is always the possibility of using a diluent with a higher dielectric constant.

Table 2.8: Effect of diluent on the distribution coefficient of uranium by alkylphosphoric acids. (8)

Diluent	Dielectric constant	Distribution coefficient, D, D2EHPA
Kerosene	**2.0**	**135**
Carbon tetrachloride	**2.2**	**17**
Benzene	**2.3**	**13**
Chloroform	**5.1**	**8**

Experimental conditions: aqueous phase; 0.5M SO_4^{2-}*, pH 1.0, 0.004M U (VI): organic phase; 0.1M D2EHPA in various diluents: aqueous/organic phase ratio = 1:1, temperature = 25 °C.*

Table 2.8 shows a comparison of the distribution coefficient, D, with various diluents in an alkyl phosphoric acid extraction of uranium. Kerosene was the best of those tested; that is, the diluent with the lowest dielectric constant resulted in the highest distribution coefficient. (24)

2.16.1.5 Solubility parameter.

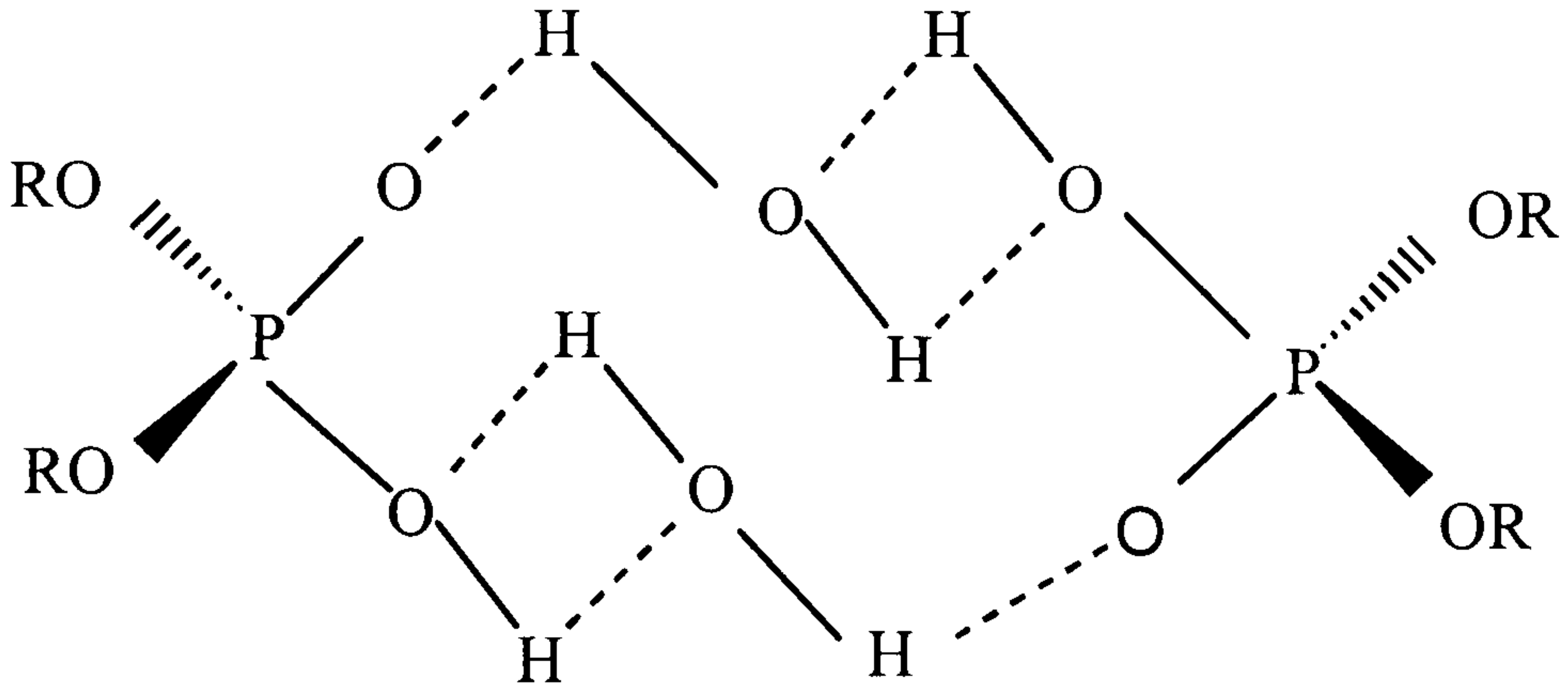
A measure of the solubility of a given solvent in the petroleum products used by oil companies is the solubility parameter δ. (25) The effect of δ on the extraction of metals by various extractants has been reported (26) and the following conclusions were noted. First, for LIX and Kelex extractants, the effect of increasing the solubility parameter is to decrease the extraction of copper. Second, there is some correlation between δ and the aromatic content of the diluent, ion association in the organic phase, and the solvation of the extractant by the diluent.

2.16.1.6 Heavy diluents.

Sporadic interest has been shown over the years in the use of heavy diluents (s.g. >1) in solvent extraction systems. The few data that are available indicate certain advantages in the use of such diluents over the regular light diluents. Tetrachloroethene appears to be the liquid of choice. Recently reported studies (27, 28) comparing tetrachloroethene with regular diluents in the system Cu–Fe–LIX 64N indicated that the use of this liquid provided somewhat better kinetics of copper extraction, faster phase disengagement, better discrimination for copper over iron, and improved stripping efficiency. The disadvantages in the use of tetrachloroethene are its relatively high cost, its high evaporation rate and high volatility. There appears to be no movement towards the use of heavy diluents in commercial operations.

2.16.1.7 Effects of diluent composition.

The effects of diluents on the form in which the extractant exists in the organic phase have received particular attention, especially in the case of organophosphate (29, 30) and amine extractants. (31, 32) It is observed that extractants are often polymerised or self–associated in non-polar reagents. In the case of organophosphate extractants, monobasic acids are polymerised to a large degree, depending on the polarity of the diluent. It is also interesting to note that water associated with the organophosphate species, using benzene as diluent, increases linearly as the sodium salt of D2EHPA increase in the organic phase. Such observations suggest the existence of dimer hydrates, (33) as shown in Fig. 2.12.



Or $\{(RO)_2PO.OH.H_2O\}_2$

Figure 2.12: Proposed structures of dimer hydrates formed by organophosphates in benzene diluent.

Formation of hydrated D2EHPA species in the organic phase is evident from the fact that, in the preparation of the sodium or ammonium salts of D2EHPA in a kerosene diluent, the addition of a stoichiometric amount of 50 wt% sodium hydroxide or 28-wt% ammonium hydroxide results in a single phase. That is, the water associated with the alkali salt solution is soluble in the solvent mixture. An equation can be written to represent this, which provides the same dimer hydrate:

$$2(RO)_2PO.OH + 2NH_4OH \rightleftharpoons \{(RO)_2PO.ONH_4.H_2O\}_2 \qquad (37)$$

The presence of polymeric forms of an extractant in a solvent will affect the distribution of the solvent between the aqueous and organic phases, and this distribution can affect the equilibrium distribution of a metal between the two phases. This situation is shown schematically (34) for the case of an alkyl phosphate (HA) in a diluent distributed between an aqueous and organic phases in Fig. 2.13.

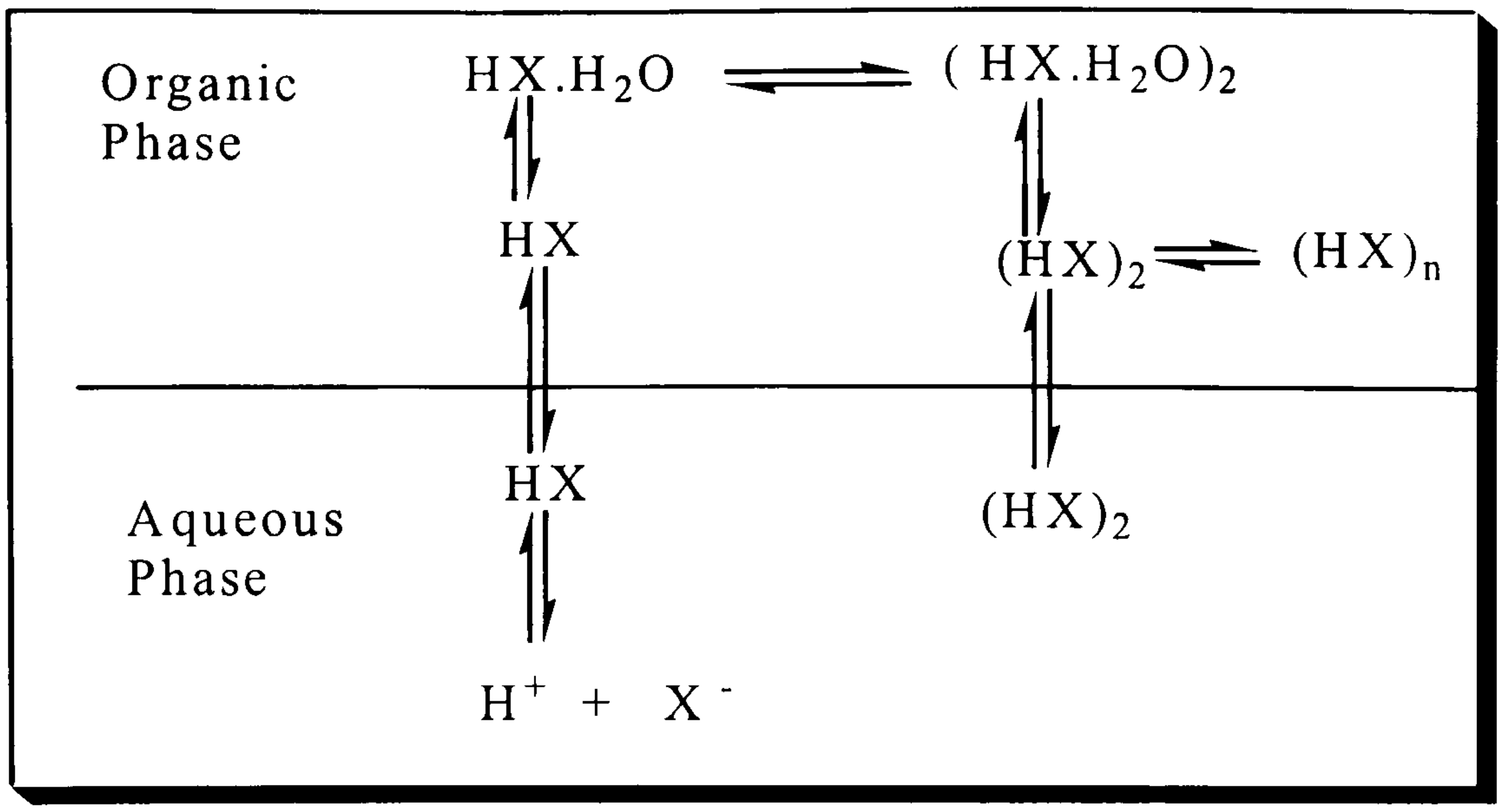


Figure 2.13: Some equilibria involved in polymerisation of an extractant in the organic phase.

As a result of the work done on alkyl amines, several general conclusions can be drawn with respect to their self–association or aggregation in organic diluents. Thus the nature of a diluent, together with its solvating power, are the two major factors which appear to affect the degree to which an amine is aggregated. These factors depend also on the concentration of the extractant in the diluent, and on the alkyl chain of the extractant. Increasing the chain length to a certain point increases the extent of amine self–association, after which the self–association decreases. Finally, the effect of increasing the temperature of the solvent is to decrease the degree of self–association.

Aggregation of amines in diluents is not simply related to one physical property of a diluent, such as dielectric constant. It has been found that aromatic and aliphatic hydrocarbons, having equally low dielectric constants and zero dipole moment, have markedly different effects upon aggregation. In polar diluents with high dielectric constants, aggregation seems to be insignificant, but it has been shown that some reagents, for example alcohols, form specific solvates with amine salts in the organic phase. (35) The aggregation of an extractant in the solvent phase affects the loading capacity of a solvent. For an extractant, which is polymerised, this can be expressed as:

$$M^{n+} + n\overline{(HA)_n} \rightleftharpoons \overline{M(A.HA)_n} + nH^+ \tag{38}$$

and for the case where the monomer is the predominant species:

$$M^{n+} + \overline{nHA} \rightleftharpoons \overline{MA}_n + nH^+ \tag{39}$$

Intermolecular hydrogen bonding can also give rise to self–association of extractants with acid functionalities. For carboxylic acids, self-association has been shown to decrease with increase in length of the alkyl chain. (36) It is found generally for acidic extractants that the extraction of MA_n is lower than for $M(A.HA)_n$. (37) Equations (38) and (39) represent two distinct extraction processes.

2.16.2 Effect of different diluents on the distribution coefficient of yttrium.

The distribution coefficient of yttrium has been studied using different organic diluents namely carbon tetrachloride, benzene, toluene, *o*-xylene, kerosene, and chloroform. The other studied factors were fixed at the values at which maximum distribution coefficient occurred i. e. 1:1 (v/v) organic to aqueous phase ratio, room temperature, 0.08M tri–*iso*octylamine in all diluents, contact time 5 minutes. Results are presented in Table 2.9. It is obvious that although benzene and toluene have dielectric constants of the same order of magnitude as that of CCl_4, both are less efficient at extracting yttrium. This is probably due to the lower solubility of the extracted species in these diluents as compared with CCl_4. This is probably a function of the different intermolecular diluent:diluent, and solvent:diluent, interactions that occur in aromatic and non-aromatic diluents. It is clear from Table 2.9 and Fig. 2.14 that CCl_4 is the best diluent from those studied.

Table 2.9: Effect of different diluents on the distribution coefficient of yttrium.

Diluents		% Extraction	Distribution Coefficient
Carbon tetrachloride	**(1)**	**90.50**	**9.54**
Benzene	**(2)**	**81.25**	**8.33**
Toluene	**(3)**	**81.75**	**8.48**
***O*-xylene**	**(4)**	**81.20**	**8.32**
Chloroform	**(5)**	**81.40**	**8.38**
Kerosene	**(6)**	**80.50**	**8.13**

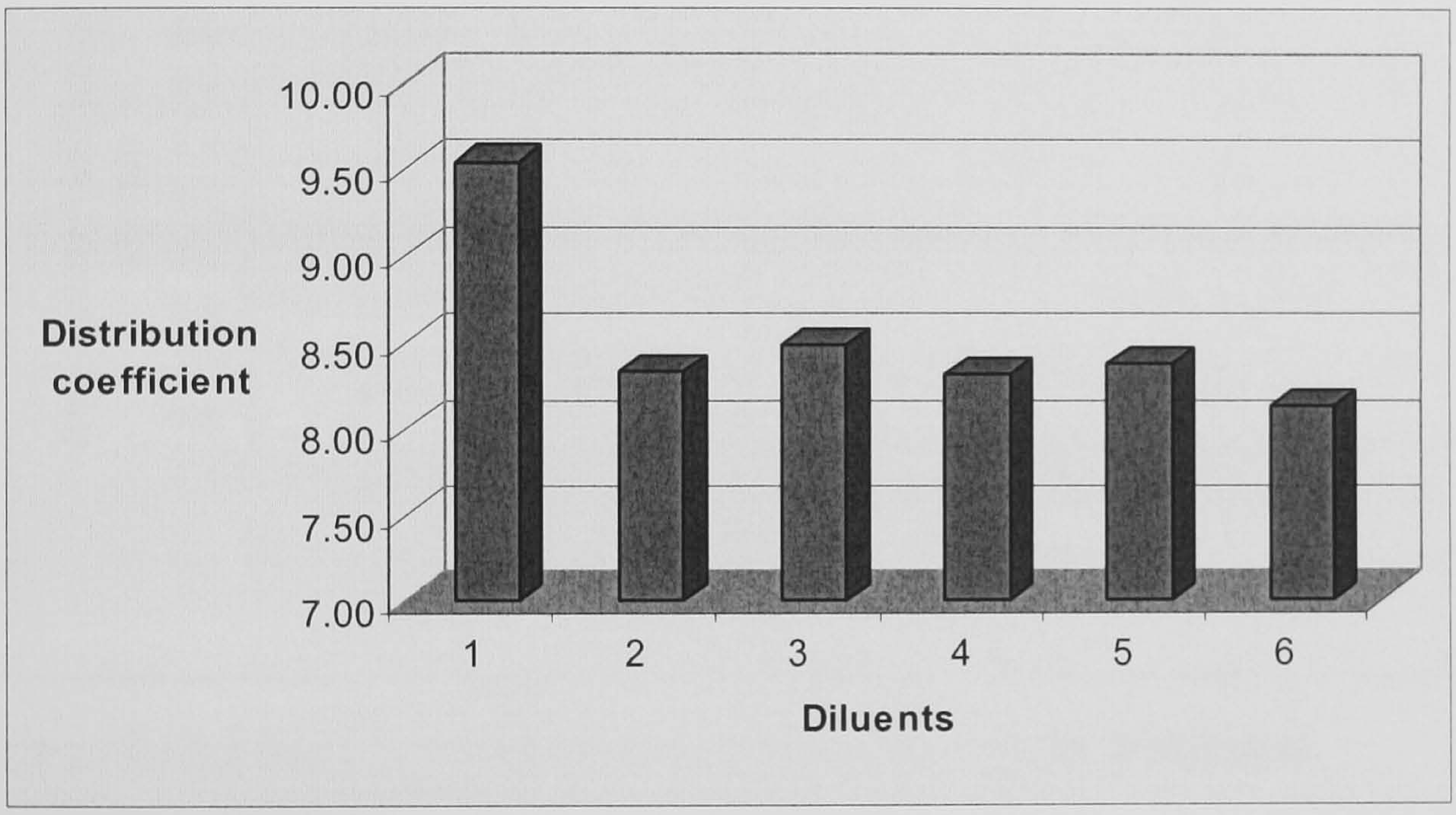


Figure 2.14: Effect of different diluents on the distribution coefficient of yttrium.

2.17 Effect of salting-out agent concentration on the distribution coefficient of yttrium.

Fig. 2.15 shows that the distribution coefficient of yttrium increases rapidly as the aqueous sodium sulfate concentration increases. The salting-out effect is supposed to be due to both to the increase in the thermodynamic activity of yttrium in the aqueous phase **(38)** and to the increase in SO_4^{2-} concentration.

Table 2.10: Effect of concentration of sodium sulfate on the distribution coefficient of yttrium

[Sodium sulfate]/M	Distribution Coefficient
0.10	7.60
0.35	7.63
0.60	8.23
0.85	9.12

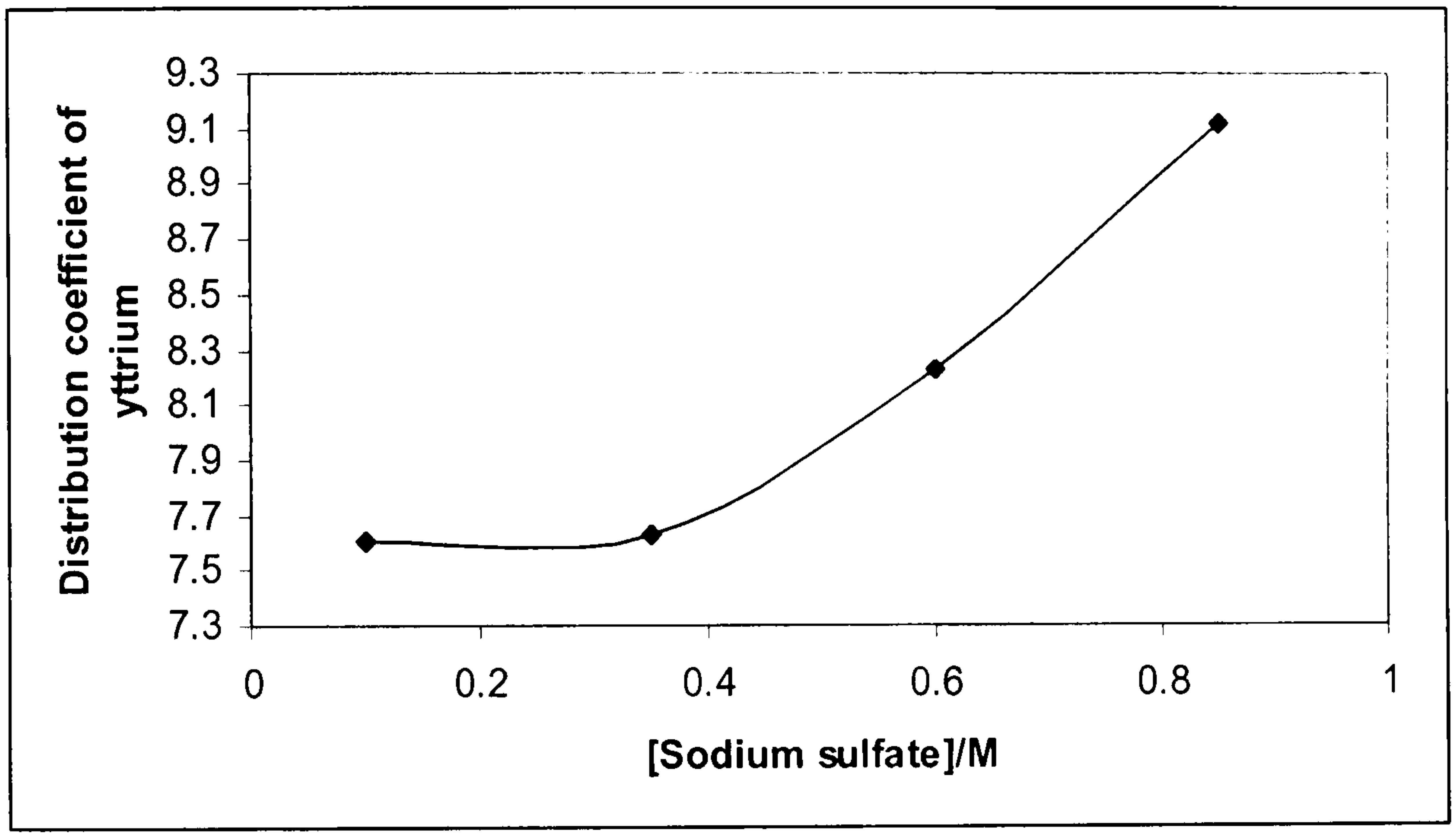


Figure 2.15: Effect of concentration of sodium sulfate on the distribution coefficient of yttrium

2.18 Synergism and mixed extractants.

The major objective in using mixed extractants for the extraction of metals is to take advantage of any synergism that may result. Synergism may be defined as "cooperative action of discrete agencies such that the total effect is greater than the sum of the effects taken independently". The converse of this effect is known as antagonism. Many mixed extractant systems have been studied in attempts to take advantage of this effect, especially for the extraction of actinide elements in the nuclear industry. Many striking examples of synergism have been found. For example, the addition of only 0.003M tributyl phosphate (TBP) to thenoyl trifluoroacetone (TTA) increases the extraction coefficient of U(VI) by a factor of

5000 from 0.01M nitric acid solution.(8) During the last decade, other mixed systems have also been studied, including LIX 63-carboxylic acids. LIX 63-amines, (39) LIX 63-D2EHPA, Kelex100-carboxylic acids, and many others.

The chemistry involved in most synergistic effects is complex, and not well understood. It certainly appears that mixed extractant systems can offer much in the way of enhanced separation of metals, and increase solvent loading. Another purpose for the use of mixed extractant systems is in the simultaneous extraction of both a cation and an anion.

2.18.1 Effect of TBP (tributyl phosphate) on the distribution coefficient of yttrium (synergistic effect).

A stock solution of TBP 0.08M in carbon tetrachloride was added to 0.08M TiOA/carbon tetrachloride in different amounts. Table 2.11 shows that upon increasing the percentage of TBP added there is a decrease in the distribution coefficient of yttrium, indicating that TBP is an antagonist in this system.

Table 2.11: Effect of TBP concentration on the distribution coefficient of yttrium (synergistic effect).

% TBP by volume	% Extraction	Distribution Coefficient
10	90.25	9.26
20	89.75	8.76
30	89.25	8.30
40	88.75	7.89
50	87.50	7.00

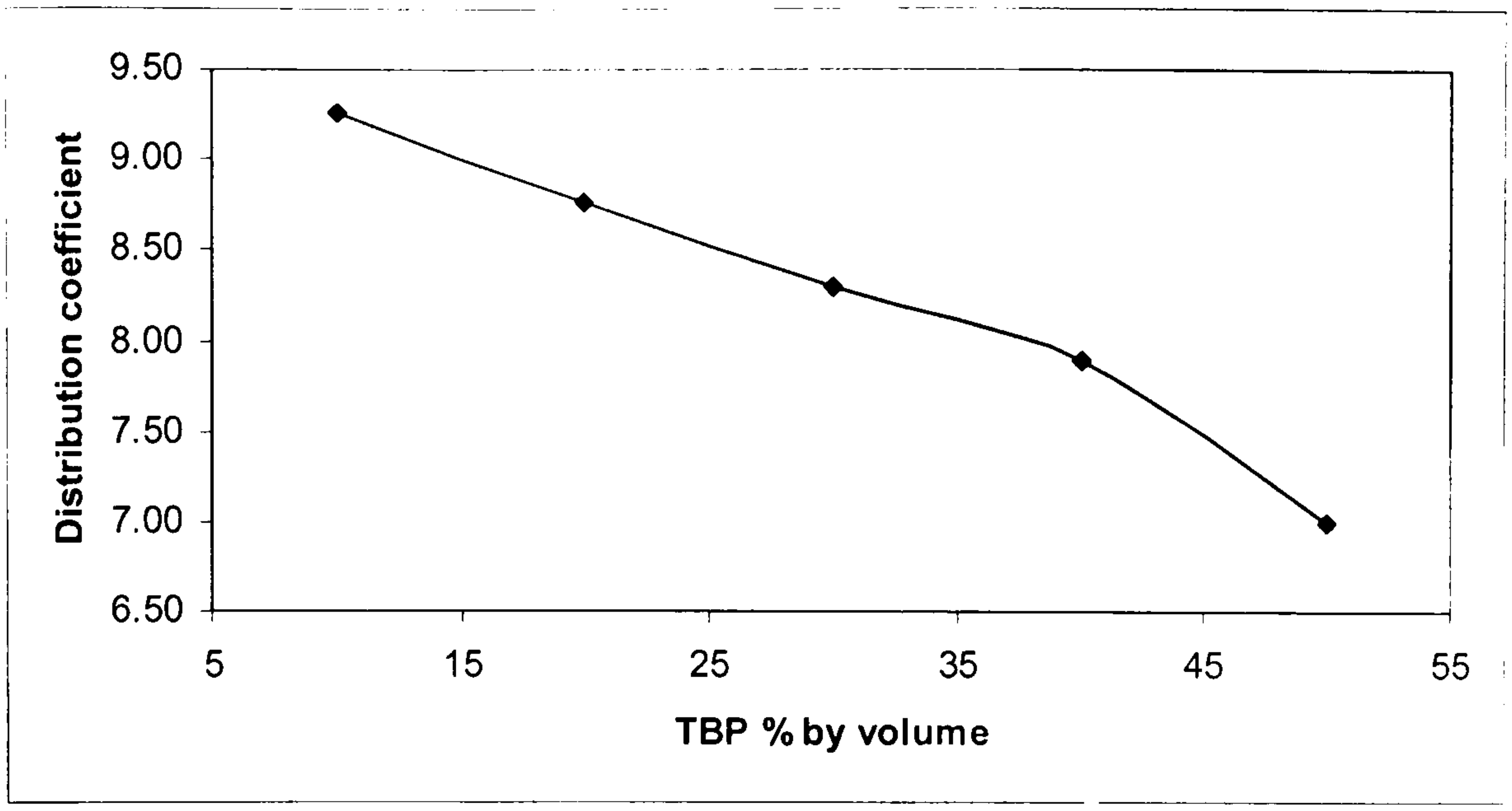


Figure 2.16: Effect of different TBP volume on the distribution coefficient of yttrium

2.18.2 Effect of TOPO (trioctyl phosphine oxide) on the distribution coefficient of yttrium (synergistic effect).

A stock solution of TOPO 0.08M in carbon tetrachloride was added to 0.08M TiOA/carbon tetrachloride in different amounts. Table 2.12 shows that by increasing the percentage of TOPO added there is a decrease in the distribution coefficient of yttrium, indicating that TOPO is an antagonist at lower concentrations. However, there is an enhancement in the distribution coefficient of yttrium when 40% volume of TOPO solution has been added, before another decrease at even higher added volume. This observation is reproducible but, as yet its origin is unknown.

Table 2.12: Effect of TOPO concentration on the distribution coefficient of yttrium (synergistic effect).

%TOPO by volume	% Extraction	Distribution Coefficient
10	90.38	9.39
20	90.38	9.39
30	90.25	9.26
40	90.50	9.53
50	90.13	9.13

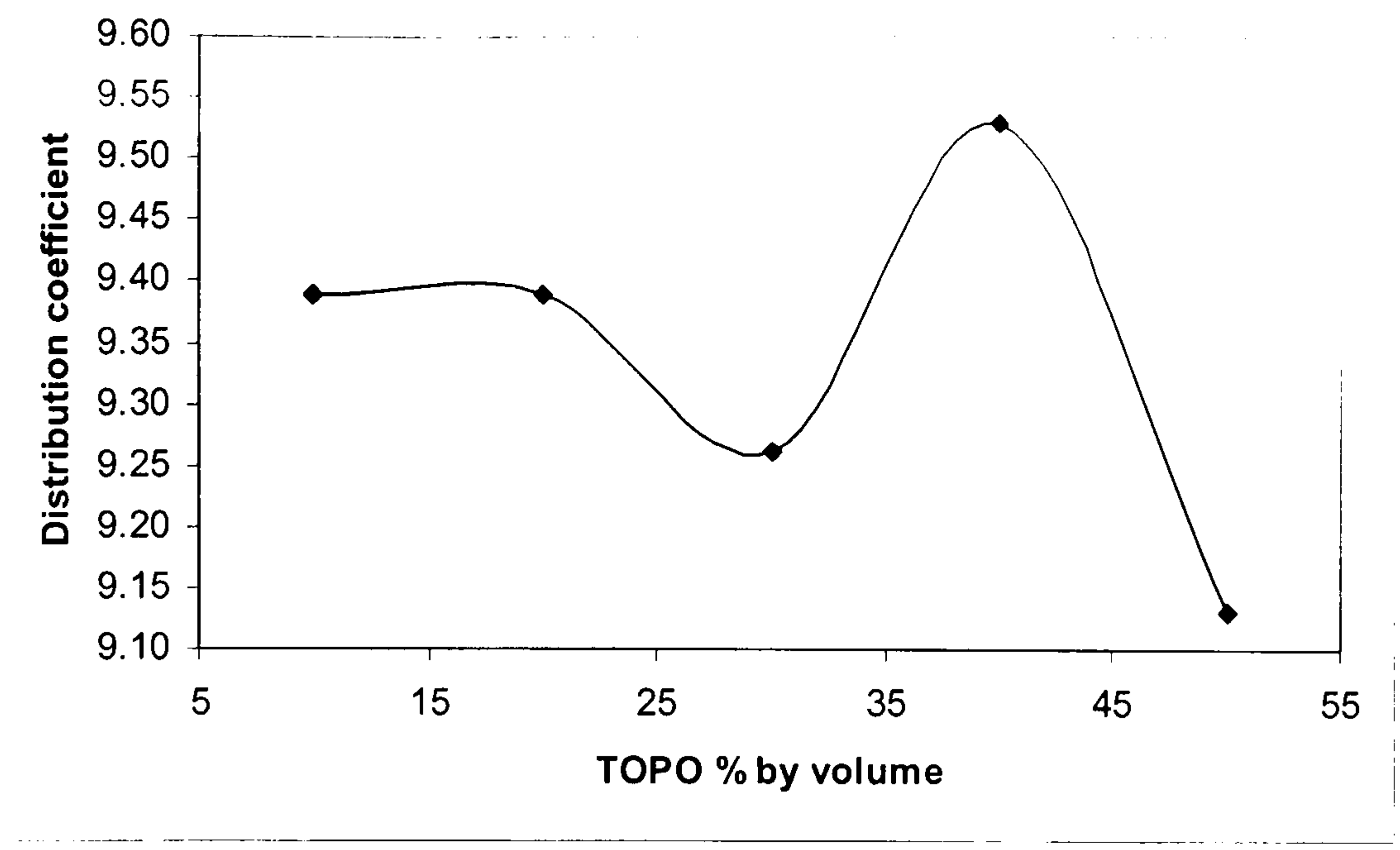


Figure 2.17: Effect of TOPO concentration on the distribution coefficient of yttrium (synergistic effect).

2.18.3 Effect of D2EHPA (di-2-ethylhexyl phosphoric acid) on the distribution coefficient of yttrium (synergistic effect).

A stock solution of D2EHPA 0.08M in carbon tetrachloride was added to 0.08M TiOA/carbon tetrachloride in different amounts. Table 2.13 shows that by increasing the percentage of D2EHPA added there is a decrease in the distribution coefficient of yttrium. This means that D2EHPA is antagonistic, but may be enhancing the distribution coefficient at lower concentrations.

Table 2.13: Effect of D2EHPA concentration on the distribution coefficient of yttrium (synergistic effect).

% D2EHPA by volume	% Extraction	Distribution Coefficient
10	91.60	10.90
20	91.20	10.36
30	91.20	10.36
40	91.20	10.36
50	90.80	9.45

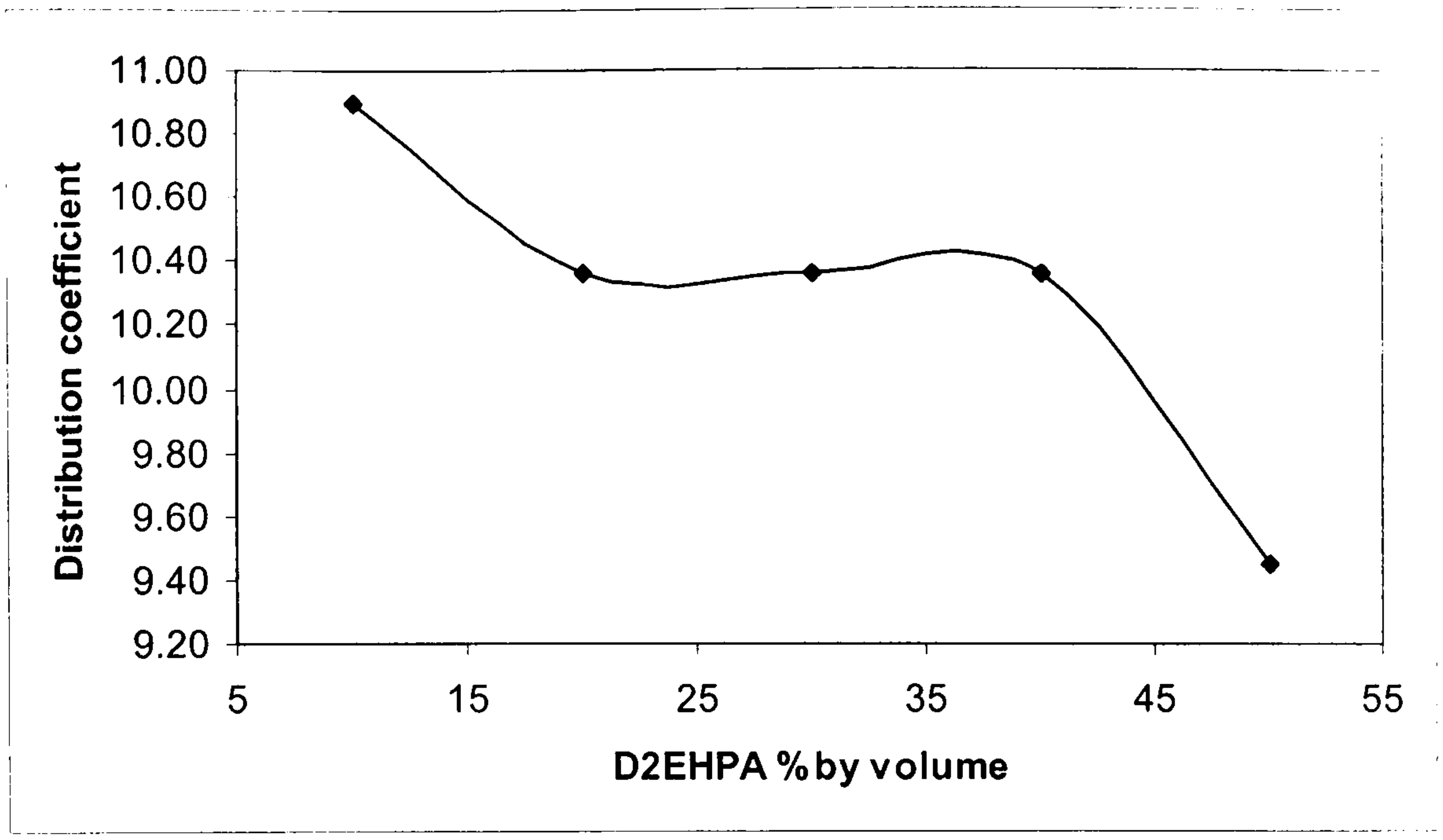


Figure 2.18: Effect of D2EHPA concentration on the distribution coefficient of yttrium (synergistic effect).

2.19 Scrubbing.

Scrubbing refers to the removal of unwanted co-extracted species in the metal-loaded solvent from the extraction stage of a process. There are many instances of the use of this technique in analytical chemistry, but relatively few in solvent extraction processes. Another well-used method is to remove co-extracted metals from the solution prior to solvent extraction, and a case in point here is iron, which can be precipitated. The specificity of an extractant for a particular metal depends on many factors, including pH, kinetics, complexation in the aqueous phase, metal and extractant concentrations, and so on. No extractant is entirely specific for one metal; hence co-extraction of other metals will occur to some extent, together with anionic species or acids.

Co-extraction may be physical or chemical in nature. For example, entrainment of aqueous phase may occur into the loaded solvent, especially if the feed contains high metal concentrations, and would show up as co-extraction from analysis of the loaded solvent. However, this situation can usually be overcome by scrubbing the loaded solvent with water, or some other suitable solution. Purification of the loaded solvent by scrubbing is more of a problem if the co-extraction is chemical in nature. There are essentially two ways of approaching this type of situation: use of acidic solution at a pH which is just sufficient to strip the unwanted metal and leave the metal of interest in the solvent phase; or use of a solution of a salt of the metal of interest which, by contacting with the loaded solvent, replaces the co-extracted (unwanted) metal by the metal required. The scrubbing technique thus provides a powerful technique for improving the quality of a loaded solvent prior to recovery of a metal by stripping.

2.19.1 Scrubbing the loaded solvent (yttrium).

Washing of the organic phase (loaded solvent) containing yttrium after the extraction is carried out for several times with deionised water to remove any possible impurities. After this process the organic phase is transferred into third stage, called re-extraction step (stripping).

2.20 Stripping.

Stripping, is the reverse reaction to extraction, and is really just the application of the law of mass action. From equation (35), the only variable, which can be changed to reverse the reaction, once the metal is extracted, is hydrogen ion concentration in the aqueous phase. Consequently, stripping in such cases requires the use of an acid solution of a concentration sufficiently high to shift the equilibrium to the left to drive the metal into the aqueous phase. With ion-association and solvating systems, where high salt or acid concentrations are required for metal extraction, stripping with water usually results in shifting the equilibrium to the left.

The stability of the extracted species will govern the type and concentration of strip solution required. For example, it should be evident that the lower pH at which metal extraction occurs, the higher must be the acid concentration of the strip solution. Problems can occur when the stability of the extracted complex is so great that even concentrated acids will not allow the metal to be stripped. This occurs, for example, in the case where cobalt is extracted by LIX extractants from ammonia solutions, and results from the oxidation of the Co(II) content of the solutions to Co(III). Co(III) amine complexes are very stable and are not readily decomposed by strong acids.

Hence, they are not amenable to stripping by acids. One alternative way in which cobalt has been stripped from such extractants is by precipitating it with H_2S. (40)

The general procedure for stripping yttrium in our experiments was as follows: the loaded solvent is contacted with a suitable acid or base strip solution, at an appropriate phase ratio, until equilibrium is attained. The aqueous phase was then removed and analysed for yttrium. The stripping process depends on a number of factors, which have to be studied in order to obtain the best stripping efficiency that matches at the same time with economic considerations. The factors under consideration were: the effect of different reagents in the strip solution, the effect of different reagent concentrations, the contact time and the organic/aqueous phase ratio.

2.20.1 Stripping (re-extraction) experiments.

A general procedure for this technique was as follows. The loaded solvent is contacted with a suitable strip solution, acid or base, at an appropriate phase ratio until equilibrium was attained. The aqueous phase was then removed and analysed.

2.20.1.1 Effect of different reagents.

The loaded TiOA/CCl_4 were mixed with different acidic, basic, or even neutral stripping aqueous solutions, to find out the most suitable reagent for re-extraction of yttrium.

2.20.1.2 Acidic stripping.

Three different acid reagents namely HCl, HNO_3 and H_2SO_4 in the same concentrations were tried to find out the most suitable reagent for stripping yttrium at an aqueous/organic phase ratio of 1:1. It is clear from the obtained result that H_2SO_4 is the best reagent for stripping yttrium, moreover it is cheapest.

Table 2.14: Effect of different acidic reagents on the stripping of yttrium

Stripping agents	% Stripping
6M HCl	6.90
6M H_2SO_4	18.61
6M HNO_3	18.33

2.20.1.3 Alkaline stripping.

Sodium hydroxide and sodium carbonate (0.1M) were chosen as basic stripping reagents, but were less effective than any of the acidic reagents.

Table 2.15: Effect of different alkaline reagents on the stripping of yttrium

Stripping agents	% Stripping
0.1M Na_2CO_3	1.94
0.1M Na OH	2.13

2.20.1.4 Effect of different sulfuric acid concentrations.

A series of stripping experiments were carried out, using H_2SO_4 solution of concentration ranging from 2M to 14M. The obtained results are given in Table 2.16 and shown in Fig. 2.19. It is clear from the obtained results that stripping by 10M H_2SO_4 gives the best yttrium re-extraction percent, while the contact time was 10 minutes and phase ratio 1:1 organic/aqueous phase ratio, room temperature.

Table 2.16: Effect of sulfuric acid concentration on the stripping of yttrium.

$[H_2SO_4]$/M	% Stripping
2	11.13
6	18.61
10	37.22
14	33.60

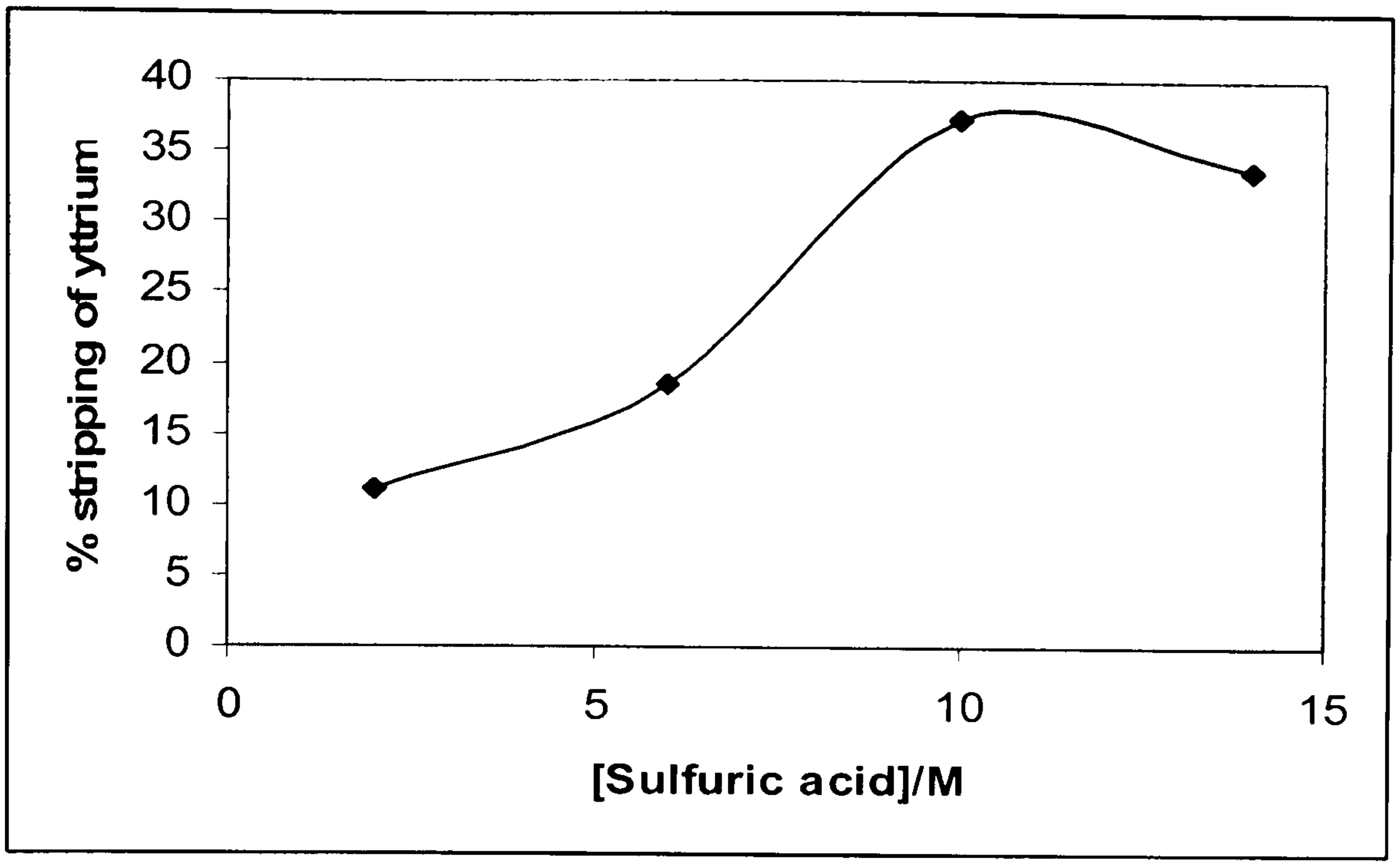


Figure 2.19: Effect of sulfuric acid concentration on the stripping of yttrium.

2.20.1.5 Effect of different nitric acid concentrations.

A series of stripping experiments were carried out, using HNO_3 solution of concentration ranging from 2M to 14M. The obtained results are given in Table 2.17 and shown in Fig. 2.20. It is clear from the obtained results that by increasing the concentration of nitric acid the stripping of yttrium increases to a maximum at 14M HNO_3, while the contact time was 10 minutes, phase ratio 1:1 organic/aqueous phase ratio at room temperature.

Table 2.17: Effect of nitric acid concentration on the stripping of yttrium.

$[HNO_3]$/M	% Stripping
2	8.40
6	16.30
10	22.90
14	23.80

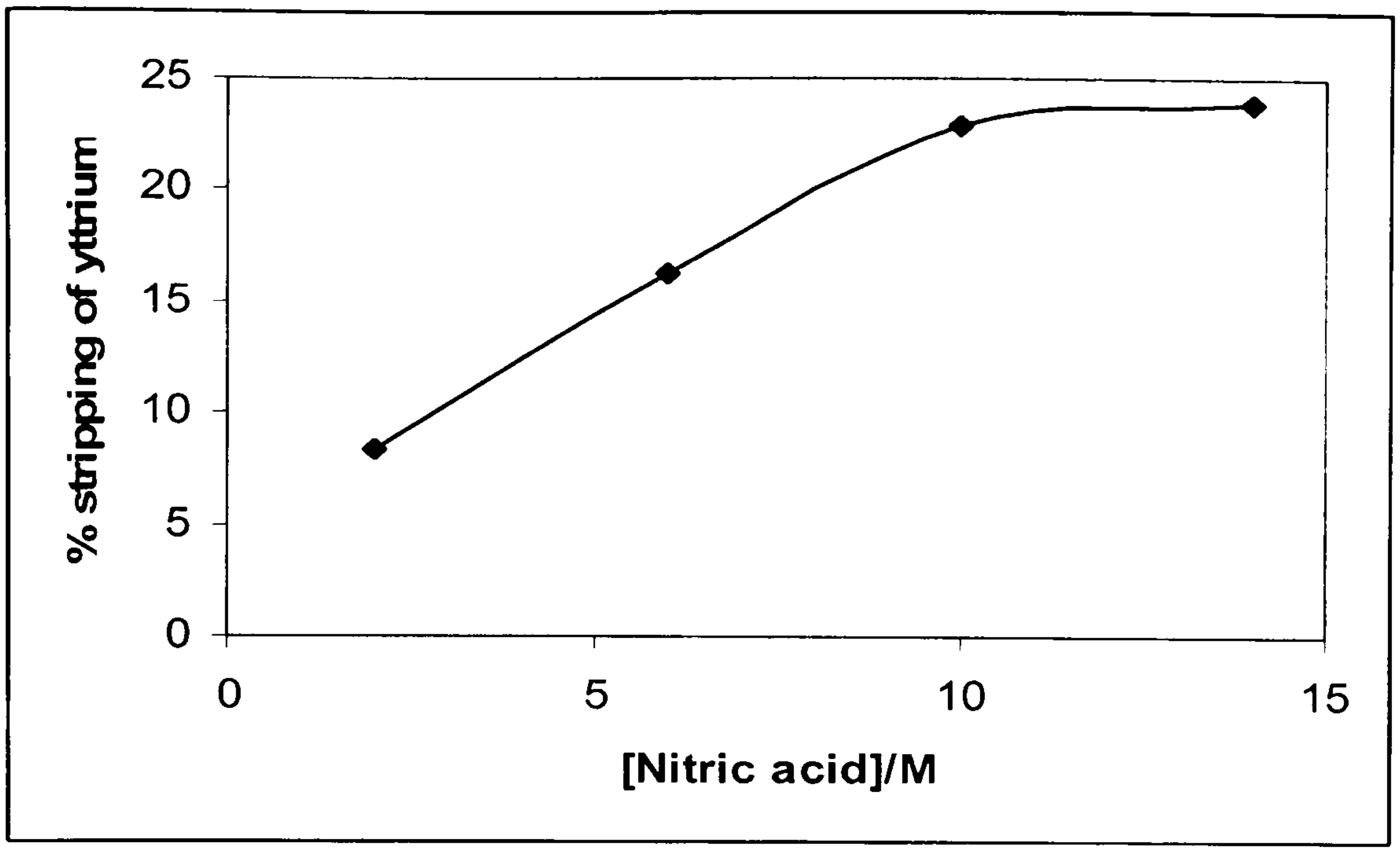


Figure 2.20: Effect of nitric acid concentration on the stripping of yttrium.

2.20.1.6 Effect of contact time on the stripping of yttrium.

The effect of contact time on the attainment of an equilibrium state has been studied at the time interval 1 to 20 minutes, while the other factors were kept at 10M H_2SO_4 and 1:1 (v/v) aqueous to organic phase ratio, the experiments were carried out at room temperature. The results obtained are given in Table 2.18 and shown in Fig. 2.21. It is obvious that contact time of 5 minutes is sufficient for yttrium stripping from the loaded solvent.

Table 2.18: Effect of mixing time on the stripping process of yttrium.

Time/minutes	% Stripping
1	20.02
5	60.00
10	60.10
15	60.12
20	60.14

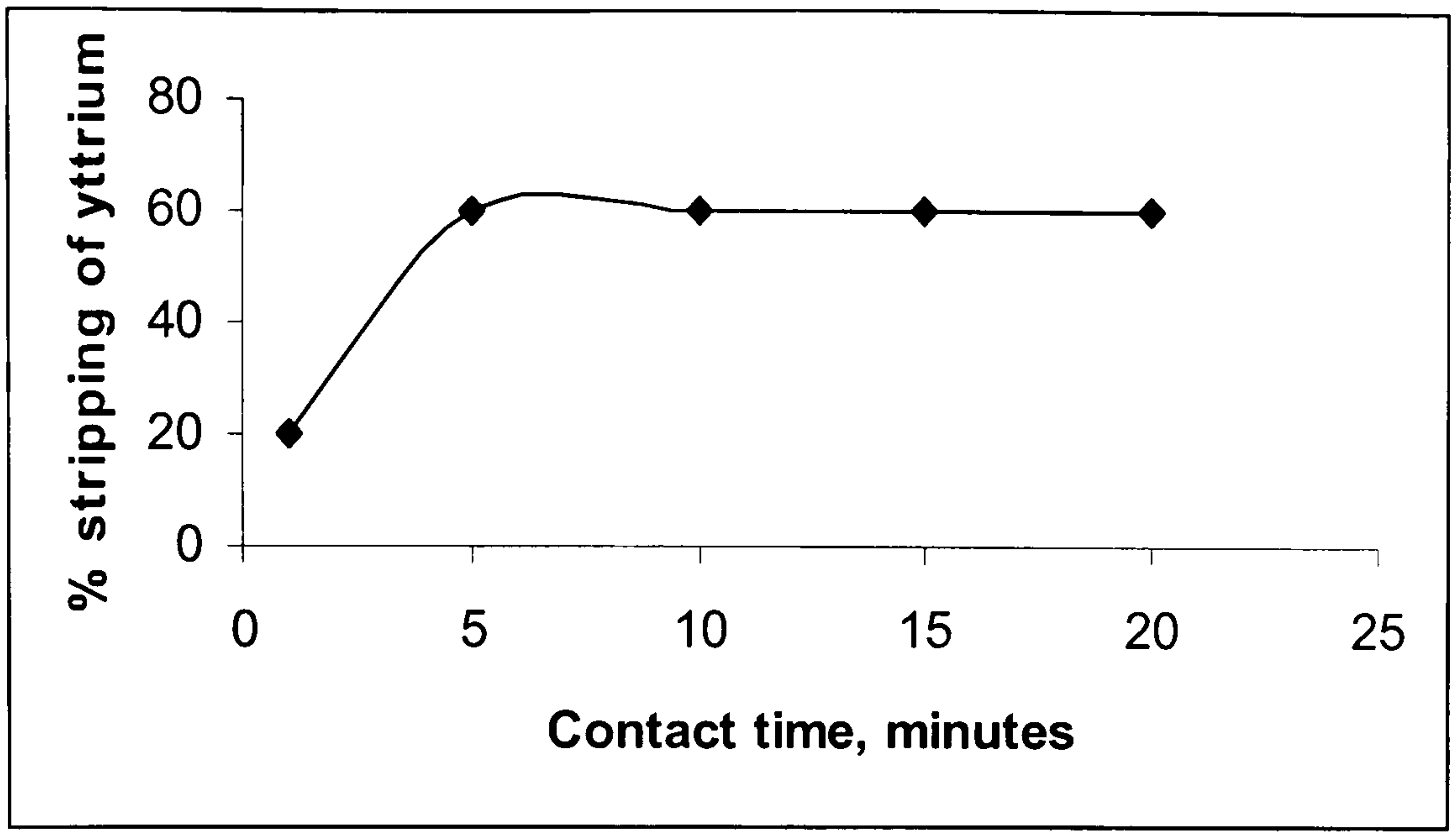


Figure 2.21: Effect of mixing time on the stripping process of yttrium.

2.21 Conclusions for liquid-liquid extraction of yttrium.

Liquid-liquid solvent extraction has the advantage of being easily engineered for continuous operation and has been proved remarkably robust since its introduction for uranium production. The optimum conditions for liquid-liquid extraction of yttrium from sulfate solution by tri-*iso*octylamine have been investigated: the concentration of TiOA is 0.08M, contact time 5 minutes which is quite adequate for high efficiency of extraction, pH 0.97 which is the same pH of stock solutions prepared, the best diluent is carbon tetrachloride, room temperature, 0.50M H_2SO_4 as aqueous composition, and by constructing the McCabe-Thiele diagram two stages are sufficient for almost complete yttrium extraction which approaches to the saturation of solvent.

Scrubbing the loaded solvent can be achieved with distilled water. Also, the suitable conditions for stripping of yttrium are: H_2SO_4 is the best stripping reagent, 10M H_2SO_4 concentration gives the highest stripping efficiency, mixing time for stripping 5 minutes.

2.22 References

1 E. Antico, A. Masana, M. Hidalgo, V. Salvado, M. Glesias, M. Valiente, *Anal. Chim. Acta*, (1996) **327**(3), 267.

2 T, Masahiro, S. Atsumi, K. Hiroki. Kiyo-Suzuka Kogyo Koto Senmon Gakko, (1999) **32**, 73.

3 M. Iglesais; E. Antico; V. Salvado; A. Masana; Valiente, *Solvent Extraction and Ion Exchange*, (1999) **17**(2), 277.

4 K. Yasuhiro, N. Yoshiyuki, A. Satoru. *Ind. Eng. Chem. Res.*, (1998) **37**(6), 2093.

5 E. Combes; C. Sella; D. Bauer; J. L sabot. *Hydrometallurgy*, (1999) **46**(1-2), 1.

6 Y. G. Wang, Y. Xiong, S. L. Meng and D. Q. Li, *Talanta*, (2004) **63**(2), 239.

7 A. W. Ashbrook, unpublished data found in reference 8.

8 G. M. Ritcey and A. W. Ashbrook, "*Solvent Extraction Principles and Applications to Process Metallurgy*" Part I, Elsevier Science Publishers B.V., (1984).

9 Z. Marczenco, "*Separation and Spectrophotometric Determination of Elements*", John Wily and Sons, Inc., New York, (1986), 580.

10 S. B. Savvin, Organic Reagents of the Arsenazo III Group, Atomizdat, Moscow, (1971).

11 W. Youshao, S. Chaohong, S. Guoxin, Z. Jiankang, and B. Borong; *Pro. of the Int. Conf. on uranium extraction*, China, (1996) 84.

12 A.W. Ashbrook, *J. Inorg. Nucl. Chem.*, (1972) **34**, 3243.

13 S. K. Patil, V. V. Ramakrishna, G. V. N. Avadhany and M. V. Ramaniah, *J. Inorg. Nucl. Chem.*, (1973) **35**, 2537.

14 C. F. Coleman, *Proc. Intern. Conf. Peaceful Uses Atomic Energy* (Geneva), (1958) **28**, 278.

15 Solvent Extraction Chemistry of Metals, Eds. H. A. C. McKay, T.V. Healy, I. L. Jenkins, and A. Naylor, Macmillan, London, (1967).

16 Y. Marcus and A. S. Kertes, *Ion Exchange and Solvent Extraction of Metal Complexes*, Willy-Interscience, New York, N. Y., (1969).

17 A. S. Kertes, in Recent Advances in Liquid-Liquid Extraction, Ed. C. Hanson, Pergamon, London, (1971).

18 R. Tremblay, and P. Bramwell, *Trans. Can. Inst. Min. Metal.*, (1959) **62**, 44.

19 D. J. Bauer, and R. E. Linstrom, U. S. Bur. Mines, RI-7524 (1971).

20 B. F. Myasoedov, M. K. Chmutova, and I. A. Lebedev, *Proceedings of the International Solvent Extraction Conf.*, The Hague, Pub. Society of Chemical Industry, London, (1971) 815.

21 W. Muller, and R. M. Diamond, *J. Phys. Chem.*, (1971) **70**, 3469.

22 J. F. Desreux, *Proceedings of the Int. Solvent Extraction Conf.*, The Hague, Pub.Society of Chemical Industry, London, (1971) 13228.

23 J. R. Ferraro, *Appl. Spectrosc.*, (1963) **17**, 12.

24 C. A. Blake, in Peaceful Uses of Atomic Energy, United Nations, Sen. Conf., 28/289, (1958)188.

25 Parameters of Solubility, ESSO Chemicals Publn.

26 G. M. Ritcey, and B. H. Lucas, *Proceedings of the International Solvent Extraction Conference*, Pub. Soc. Chem. Industry, London, (1974) 2437.

27 W. Manfroy, and T. Gunkler, *Proceedings of the International Solvent Extraction Conference*, Pub. Society of Chemical Industry, London, (1974) 725.

28 G. M. Ritcey, Unpublished data found in reference 8.

29 J. R. Ferraro, and D. F. Peppard, *Nucl. Sci. Eng.*, (1963) **16**, 389.

30 D. H. Liem, in Solvent Extraction Chemistry, Ed., D. Dynessen, J.–O. Liljenzin, and J. Rybderg, North-Holland, (1967) 264.

31 K. Bange, and J. W. Smith, *J. Chem. Soc.*, (1964) 4244.

32 G. Markovits, and A. S. Kertes, *J. Chem. Soc.*, (1964), 390.

33 A. S. Kertes, A. Beck, and V. Habousha, *J. Inorg. Nucl. Chem.*, (1961) **21**, 108.

34 A. W. Fletcher, and D. S. Flett, *J. Appl. Chem.*, (1964) **14**, 250.

35 C. J. Hardy, *Nucl. Sci. Eng.*, (1963) **16**, 401.

36 W. S. Singleton, in Fatty Acids, Ed. K. S. Markeley, Interscience, New York, N. Y., part I, (1960) 609.

37 T. G. Lenz, and M. Smutz, *J. Inorg. Nucl. Chem.*, (1966) **28**, 1119.

38 Y. Zhao, S. Si-Xui and F. Sheng-Yu, *J. Radioanal. Nucl. Chem.*, (2002) **251**, 503.

39 D. S. Flett, Natl. Inst. Metals, (Japan), (1967) **9**, 215.

40 C. R. Merigold, and R. B. Suddereth, Internat. Symp. on Hydrometallurgy, Ed. D. J. I. Evans, and R. S. Shoemaker, Pub. By AIME, New York, (1973), 552.

Chapter Three

Liquid-liquid extraction of cerium(III)

3.1 Introduction to cerium chemistry.

3.1.1 Natural occurrence of cerium.

Cerium is the most abundant element of the rare earth group. It ranks 28th in the abundances of the 83 naturally occurring elements of the Earth's lithosphere. The more important minerals containing cerium are allanite (also known as orthite), bastnaesite, cerite, and monazite. Allanite, which is a silicate containing rare earths, aluminium, calcium, and iron, is found widely in the United States, Germany, Madagascar, Russia, and Scandinavia.

Cerium is characterized chemically by having two stable valence states, Ce^{4+}, ceric, and Ce^{3+}, cerous and this property underlies several technological uses. The ceric ion is a powerful oxidizing agent but when associated with strongly coordinating ligands, especially oxygen-donors, is completely stabilized, and indeed cerium oxide CeO_2 (ceria) is the form of cerium most widely used. (1) First isolated as an impure oxide in 1803, the recognition that cerium was a unique element, and its relationship to other elements, were factors in the gradual development of the Periodic Table Concept. The separation and identification of all the individual 4f elements, cerium included, caused considerable confusion one hundred years ago but helped lead eventually to our understanding of atomic structure.

3.1.2 Mineral resources.

Although cerium has been found in many minerals (2) it is usually present as a trace element rather than as an essential component. Little of it occurs in economically significant deposits. The net result is that there are just two minerals that supply the bulk of the world's cerium. Bastnaesite and monazite are two minerals both containing predominantly light-lanthanides, and both have very similar cerium contents. Bastnaesite, which is essentially a rare earth fluorocarbonate, is the second most important commercial source for cerium and light rare earths. The major deposit of bastnaesite is found in Southern Calfornia. Cerite, which is a calcium-iron-rare earth silicate, is principally found in Sweden. Monazite, which is the principal source of cerium, is a phosphate containing thorium and the light rare earths. The most important deposits are located in the United States, Australia, India and South Africa.

Table 3.1: The rare earth content of various ores. (3)

Rare Earth Oxides			Ores							
			Monazite		**Bastnaest**		**Xenotime**		**Loparite**	
Ceric earths	**Lanthanum**	**La_2O_3**	32.90	92.40	32.00	98.90	0.50	8.40	28.00	97.9
	Cerium	**CeO_2**	46.00		49.00		5.00		57.40	
	Praseodymium	**Pr_6O_{11}**	5.10		4.40		0.70		3.70	
	Neodymium	**Nd_2O_3**	17.40		13.50		2.20		8.80	
Yttric earths	**Samarium**	**Sm_2O_3**	2.50	7.60	0.50	1.10	1.90	91.60	0.92	2.1
	Europium	**Eu_2O_3**	0.05		0.10		0.20		0.13	
	Gadolinium	**Gd_2O_3**	1.50		0.30		4.00		0.22	
	Terbium	**Tb_4O_7**	0.04		0.01		1.00		0.07	
	Dysprosium	**Dy_2O_3**	0.69		0.03		8.70		0.09	
	Holmium	**Ho_2O_3**	0.05		0.01		2.10		0.03	
	Erbium	**Er_2O_3**	0.20		0.01		5.40		0.07	
	Thulium	**Tm_2O_3**	0.01		0.02		0.90		0.07	
	Ytterbium	**Yb_2O_3**	0.12		0.01		6.20		0.30	
	Lutetium	**Lu_2O_3**	0.04		0.01		0.40		0.05	
	Yttrium	**Y_2O_3**	2.40		0.10		60.80		0.15	
	Thorium (2)	**ThO_2**	6.70		0.35		0.80		0.65	
	Uranium (2)	**U_3O_8**	0.28		0.05		1.20			

1- *Average value expressed in wt % of total rare earth oxides may vary from one deposit to another, and expressed in wt % of oxide to ore.*

3.1.3 Production and applications of cerium.

The production of cerium derivatives requires:

Production of a mineral concentrate by physical ore dressing techniques. Then attack by acid digestion on that concentrate to create a suitable mixed-lanthanide for later separation processes. Then either, direct production of cerium-rich materials, or separation of the mixed-lanthanide into individual pure lanthanide compounds of pure cerium.

Commercially, ceric oxide is the most important form of cerium. There are also many other applications in which mixtures of cerium, lanthanum, neodymium, and other rare earths are used. These mixtures may be of the form of metallic alloys, mixed oxides or mixed halides. Ceric oxide is used to polish glass, especially precision optical glasses. It is superior to rouge, in that it polishes glass much quicker. Because of its oxidizing power, cerium is used in glass, which is subjected to alpha, gamma, x-ray, light and electron radiation. The cerium decreases the rate of discoloration in glass, primarily by preventing divalent iron from forming, i.e. it oxidizes Fe(II) to Fe(III). This is especially useful in TV tubes, where electron radiation could cause the glass to discolour and destroy the colour quality of the TV picture. Ceric oxide is also used to opacify enamels, photo chromic glasses, ceramic coatings, refractory oxides, phosphorus, cathodes, capacitors and semiconductors, and as a catalyst. Because of cerium's low nuclear cross section, ceric oxide is also used as a diluent in uranium, plutonium or thorium oxide nuclear fuels.

The most common form of cerium-rare earth alloys is known as mischmetal, and it contains about 50% cerium, 25% lanthanum, 18% neodymium, 5% praseodymium and 2% other rare earths.

3.1.4 Recent developments in cerium extraction chemistry.

Liao Wuping ***et al*** (4) studied the solvent extraction of cerium(IV) and F from simulated sulfuric acid leaching of bastnaesite by Cyanex 923. This can extract not only Ce(IV) as $Ce(HSO_4)_2(SO_4).2(Cyanex\ 923)$ but also F^- as HF.(Cyanex 923). The extraction mechanism of Ce(IV) together with F can be related to the formation of $Ce(HF)(HSO_4)_2(SO_4).2(Cyanex\ 923)$. Boric acid in the leaching liquor, which was added to chelate F, was not extracted alone by Cyanex 923 and did not influence the cerium(IV) extraction. Boric acid can enhance the extraction of HF, forming $(HF)(H_3BO_3).(Cyanex\ 923)$ in the organic phase. HF was extracted from the bastnaesite leaches mainly together with Ce(IV). The temperature did not affect the extraction process.

Soldenhoff ***et al*** (5) have studied a new solvent extraction process for the purification of cerium from sulfate media. This process was developed specifically to recover cerium from a residue produced by the processing of concentrate from the Mt. Weld deposit in Western

Australia. The liquor treated by solvent extraction contained 62 g/l rare earths and the cerium to total rare earth ratio was 74%. Other impurities, including Fe and Th, totaled 2000 ppm. Di-2-ethylhexyl phosphoric acid in a low aromatic content diluent, was used to extract Ce^{4+} selectively over the trivalent rare earths. Partial co-extraction of Fe and Th occurred but it was found that these elements were not easily stripped and therefore selective back extraction of cerium was possible. The cerium was stripped from the organic phase by HCl and H_2O_2. In continuous counter-current trials two extraction stages and three stripping stages were used. A regeneration process was developed to prevent poisoning of the solvent by impurities. In the continuous counter-current trials, 97 % Ce(IV) extraction was achieved and the Ce to total rare earth ratio was upgraded to >99 %.

Takahashi, Toshio ***et al*** (6) studied solvent extraction of cerium(III) with phosphoric acid esters. Considerable attention was given to efficient separation of TRU (trans-uranium) actinides from nuclear wastes, and a new process, extraction chromatography, was developed. To develop the new process, the authors examined extractants, which were applied to an extraction chromatography separation system.

Bauer and Shaw (7) have studied metathesis of bastnaesite and solvent extraction of cerium. Bastnaesite concentrate was processed to recover total rare-earth content and obtain high-purity ceric nitrate. Reaction of the concentrate with 45% NaOH for 1 hour at 180 °C in stainless steel vessels effected 99% conversion to rare earth hydroxide. A drying step followed by solution in HNO_3 produced a quadrivalent Ce fraction amenable to extraction with $(BuO)_3PO$. Single-stage separation funnel experiments gave 90 % recovery of cerium(IV) nitrate at 99.9% purity. Fractional extraction in pressure-bubbler columns affected 98.5% recovery of 99.5% pure cerium(IV) nitrate.

Sato, Taichi and Keiichi (8) studied solvent extraction of cerium(III) from aqueous thiocyanate solutions by neutral organophosphorus compounds. The extraction of Ce(III) from aqueous solutions containing KSCN by TBP or TOPO in kerosene or benzene was studied under different conditions. IR spectral studies were carried out on the organic extractants. The distribution coefficient of Ce(III) for TBP increases linearly with increasing aqueous thiocyanate concentration. The equilibrium equation for the extraction by TBP can be expressed as follows:

$$Ce^{3+}(aq) + 3NCS^{-}(aq) \rightleftharpoons Ce(NCS)_3(aq) \quad (41)$$

$$Ce(NCS)_3(aq) + 4\,TBP(org) \rightleftharpoons Ce(NCS)_3.4TBP(org). \quad (42)$$

A similar result was also obtained for the extraction by TOPO, although the extraction efficiency of TOPO is higher than that of TBP. The IR results indicate that the thiocyanate ion coordinates to the Ce ion through the N atom and that the Ce ion combines with the phosphoryl O atom of the extractants.

Yu and Zheng (9) studied solvent extraction of cerium(III) with 1-(2-pyridylazo)-2-naphthol in $CHCl_3$ from perchloric acid media. The effect of equilibrium time, the pH of the aqueous phase and the concentration of extractant in organic phase on the extraction efficiency of Ce was studied, also an extraction mechanism is postulated.

Santhi *et al* (10) have studied synergism in the extraction of Ce(III) from thiocyanate solutions by using mixtures of 2-thenoyltrifluoroacetone (HTTA) (4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione) and bis-2-ethylhexyl sulfoxide (B2EHSO) or di-n-octyl sulfoxide (DOSO) in benzene. A very high synergistic enhancement of the order of 105 was observed. If a mixture of both dialkyl sulfoxides (B2EHSO + DOSO) is used, an additional synergistic effect is found due to the formation of a mixed, solvated complex when both reagents are added to the metal chelate. The extraction data were analyzed theoretically by taking into account complexation of the metal in the aqueous phase by inorganic ligands and plausible complexation in the organic phase.

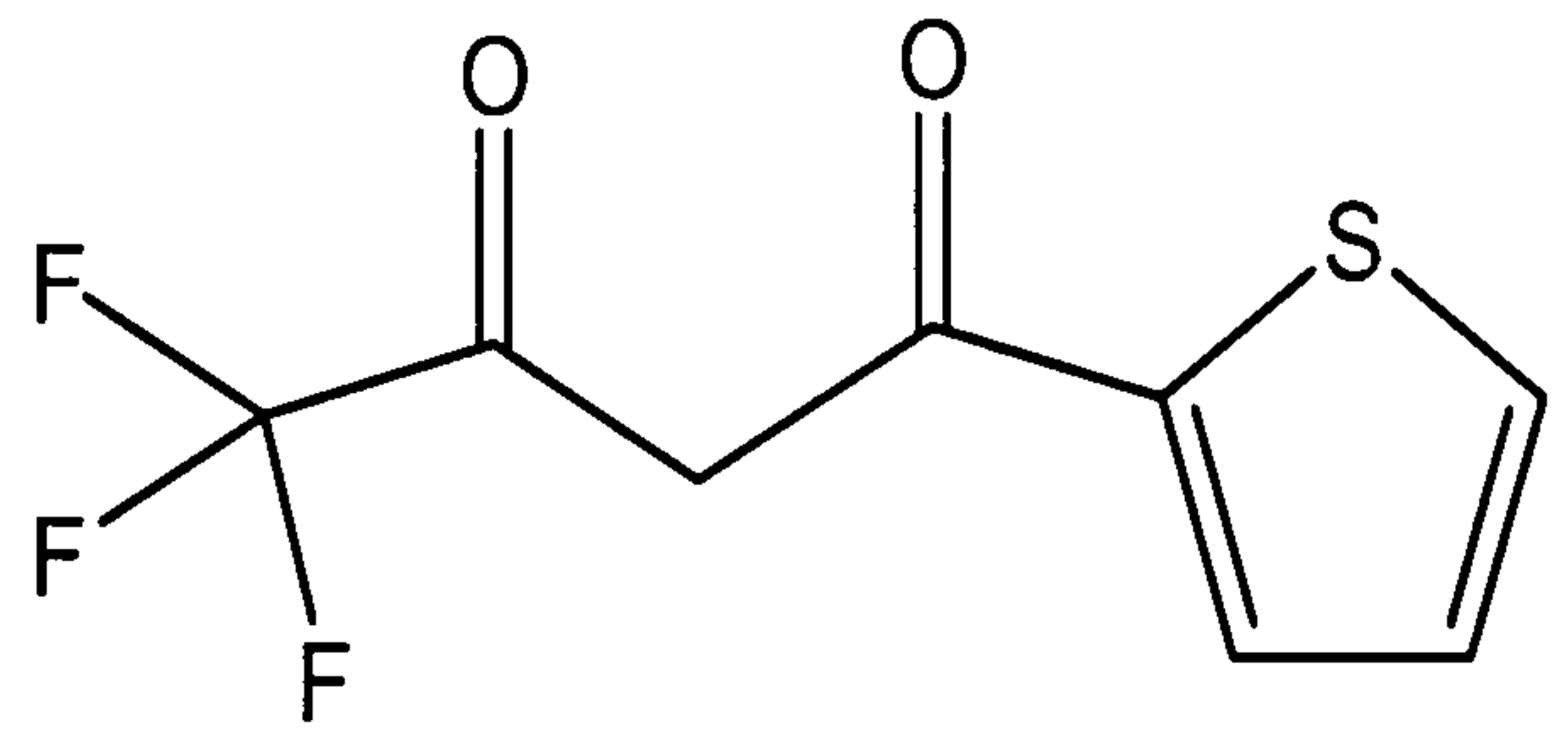


Figure 3.1: Chemical structure of 4,4,4-trifluoro-1-(2-thenoyl)-1,3- butanedione (HTTA).

Chatterjee and Basu (11) studied solvent extraction of cerium(III) with high molecular weight amines by using these amines in the extraction of cerium(III) as an EDTA complex from nearly neutral aqueous medium. The extraction conditions were optimized from the study of effects of several variables such as concentration of amine and EDTA, pH, nature of diluents *etc.* The method was applied for the determination of cerium in a few mineral samples.

Zhao ***et al*** (12) studied the coordination reaction during the solvent extraction of cerium(IV) and fluoride from mixed nitric acid and hydrofluoric acid solutions by di-(2-ethylhexyl)-2-ethylhexyl phosphonate, L (DEHEHP) in heptane. The extraction data have been analyzed by graphical methods taking into account all species extracted into the organic phase. Different variables influencing the extraction of Ce(IV), such as the concentrations of nitrate ions, hydrofluoric acid, and extractant have been studied. The results demonstrate that DEHEHP can extract not only $Ce(NO_3)_4$ as $Ce(NO_3)_4.2L$ and HF as $HF.H_2O.L$, but both together as $Ce(HF)(NO_3)_4.L$. The extraction equilibrium equations are determined according to slope analysis and IR spectra.

The equilibrium constants of the extracted complexes have been calculated, taking into account complexation between the metal ion and inorganic ligands in the aqueous phase and all complexes extracted into the organic phase. It is also shown that boric acid, which was added into the mixed solutions to complex with F^- is not extracted by DEHEHP, and neither does it affect the extraction of cerium(IV) and HF, nor change the extraction mechanism. Finally, this work points out the basis of separation of Ce(IV) and recovering F^- from nitric acid leach liquors of bastnaesite.

Further work (13) has studied the extraction of Ce(IV) from nitric acid solution using di-(-2-ethylhexyl) 2-ethylhexyl phosphate (DEHEHP, B) in heptane. Ce(IV) can be extracted effectively from nitric acid solution, whereas it is poorly extracted from sulfuric acid solution. Compared with some other organophosphorus esters, DEHEHP has moderate extractability for Ce(IV). The extraction efficiency varies with diluent in the order: aliphatic hydrocarbons > nitrobenzene > aromatic hydrocarbons > carbon tetrachloride > chloroform. Regeneration and loading capacities of DEHEHP have also been examined. Ce(IV) extraction increases with an increase of HNO_3 concentration, as well as extraction of HNO_3 and H_2O have been systematically studied. The Ce(IV) extraction increases with the increasing of HNO_3 concentration, and exhibit the maximum distribution ratio at 1-1.5 mol/L HNO_3. Nitric acid, as a source of nitrate ion, enhances the extraction of metal ion. But it also competes with the metal ions for extractant molecules under high acidity. The extraction equilibrium constants and IR spectroscopies of extracted complexes are determined. The extraction thermodynamic parameters are also calculated and the extraction reaction was found to be exothermic.

3.2 Results and discussion.

In order to obtain an efficient and economic separation of cerium(III), it has been necessary to study the relevant factors affecting the liquid-liquid extraction process to determine the optimum conditions for cerium(III) extraction from sulfate liquor. These factors include TiOA concentration, diluent, pH value, temperature, contact time, aqueous phase composition and construct McCabe-Thiele diagram for cerium(III) extraction. In addition, the synergistic effect of using TOPO and D2EHPA to enhance the extraction of cerium(III) has been investigated. The stripping process depends on a number of factors, which have to be studied to obtain the best stripping efficiency that matches at the same time economic considerations. The factors under consideration are effect of different reagents (strip solution) such as H_2SO_4, HNO_3 and HCl, effect of different reagent concentrations, effect of contact time, aqueous/organic phase ratio and construct McCabe-Thiele diagram for cerium(III) stripping. All of the following experiments followed the procedures described in detail in chapter 2.

3.2.1 Effect of different concentrations of tri-*iso*octylamine (TiOA) in carbon tetrachloride on the distribution coefficient of cerium(III).

Firstly the solvent must be equilibrated by contacting it with 0.5M sulfuric acid for 5 minutes. To 5 ml of the sulfate liquor, 5 ml of a solution of TiOA in CCl_4 was added with concentration ranging from 0.01 to 0.2M, and then the solution was shaken for 10 minutes at room temperature to attain equilibrium state. The optimum value of a 0.1M solution of TiOA in CCl_4 was chosen from the data reported in Table 3.2 and presented in Fig. 3.2, for economic reasons, by increasing the TiOA concentration the distribution coefficient of cerium(III) increases.

Table 3.2: Effect of different concentrations of solvent/carbon tetrachloride on the distribution coefficient of cerium(III).

[TiOA]/M	% Extraction	Distribution coefficient
0.01	90.87	9.95
0.04	91.05	10.60
0.06	91.10	10.90
0.08	92.95	11.18
0.1	93.20	11.31
0.2	93.22	13.76

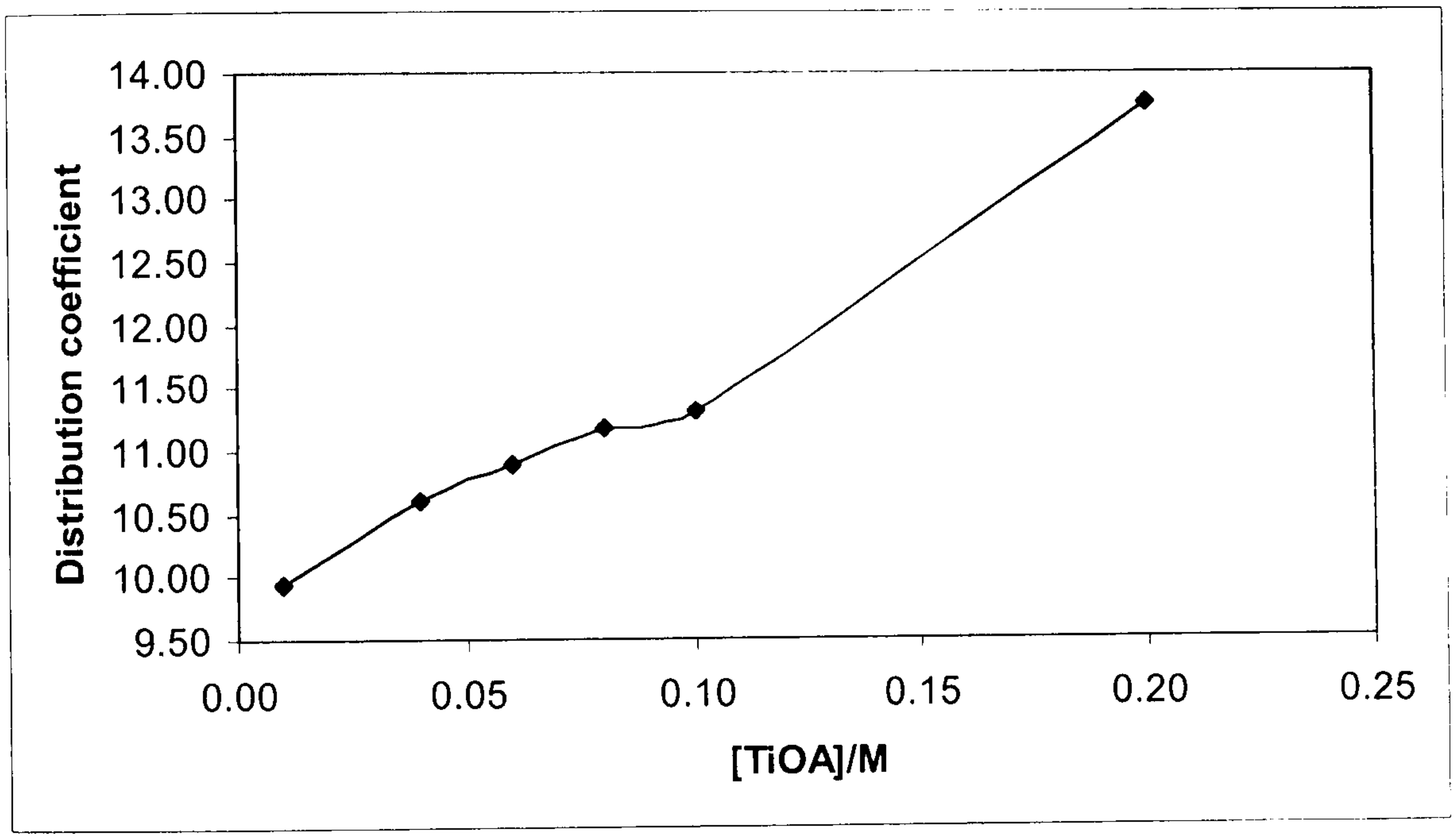


Figure 3.2: The effect of different concentrations of TiOA on the distribution coefficient of cerium(III).

3.2.2 Effect of contact time on the distribution coefficient of cerium(III).

The effect of contact time on the attainment of an equilibrium state was studied at intervals between 1–20 minutes, while the other factors were kept as mentioned before. The results obtained are given in Table 3.3 and shown in Fig. 3.3. It is obvious that a contact time of 5 minutes is quite adequate for efficient cerium(III) extraction and highest distribution coefficient. Also, increasing contact time above 5 minutes causes a slight change in distribution coefficient.

Table 3.3: Effect of contact time on the distribution coefficient of cerium(III) from 0.1M solvent/carbon tetrachloride.

Time/minutes	% Extraction	Distribution coefficient
1	88.40	7.62
5	93.20	13.71
10	93.15	13.59
15	93.10	13.49
20	93.10	13.49

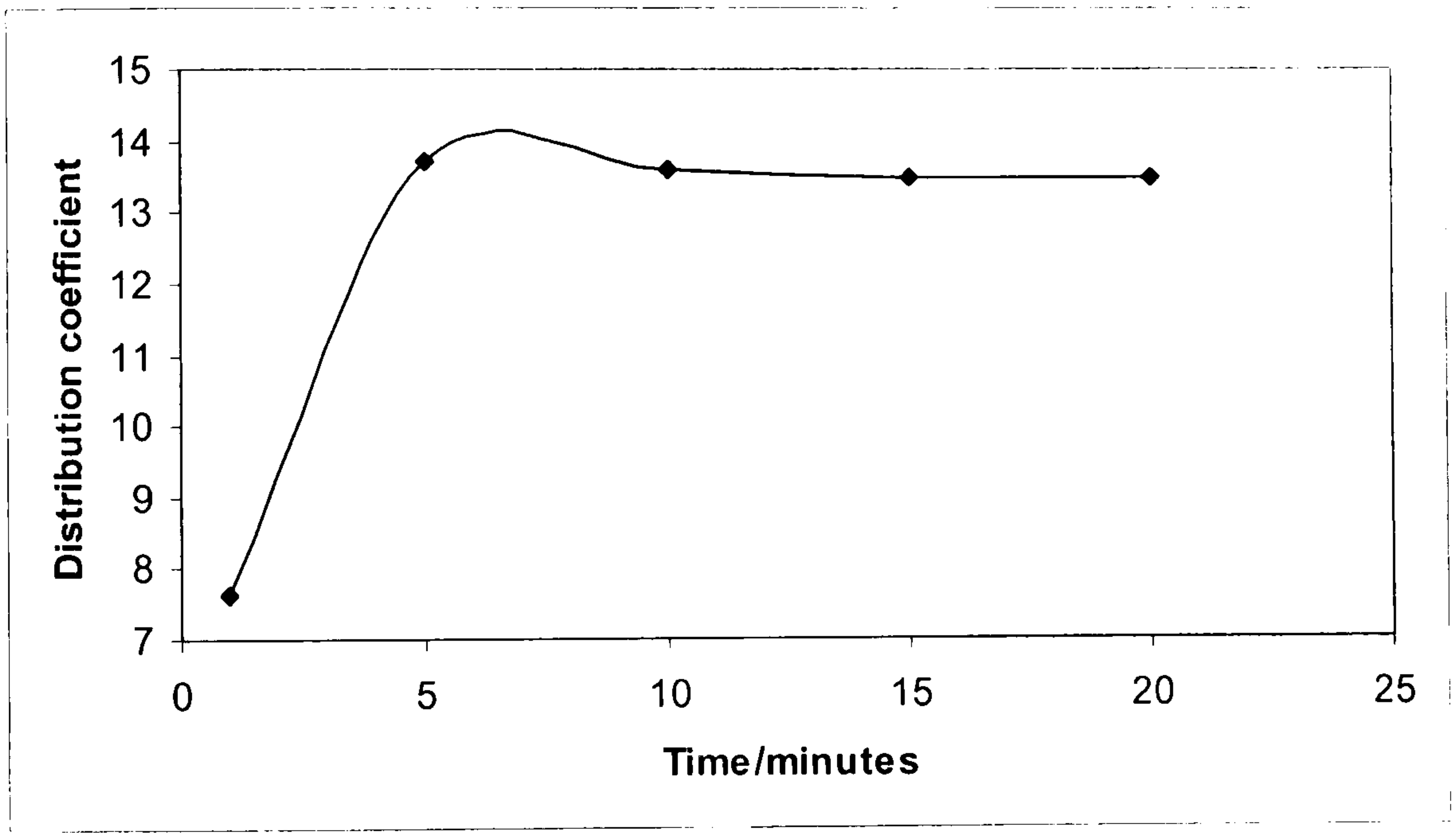


Figure 3.3: The effect of contact time on the distribution coefficient of cerium(III).

3.2.3 Effect of pH on the distribution coefficient of cerium(III).

The distribution coefficient has been studied by varying the pH values of the studied sulfate liquor from 0.5 to 1.55, using either sulfuric acid or sodium hydroxide. Other factors were fixed at 1:1 (v/v) organic to aqueous phase ratio, 0.1M TiOA in carbon tetrachloride, contact time 5 minutes and the experiments were carried out at room temperature. The results obtained are given in Table 3.4 and shown in Fig. 3.4. It is clear that a pH of the sulfate liquor of 0.9 can be taken as an optimum pH value. Fortunately, that is the same pH of the parent sulfate liquor under examination. However, by increasing pH above 0.9 there is a decrease in the distribution coefficient of Ce(III). The reason for that behavior is similar to that explained in section 2.11. (14)

Table 3.4: Variation of cerium(III) distribution coefficient with the pH of the sulfate solution.

pH	% Extraction	Distribution coefficient
0.50	76.90	3.32
0.70	78.40	3.63
0.90	93.20	13.71
1.25	81.98	4.55
1.55	80.90	4.24

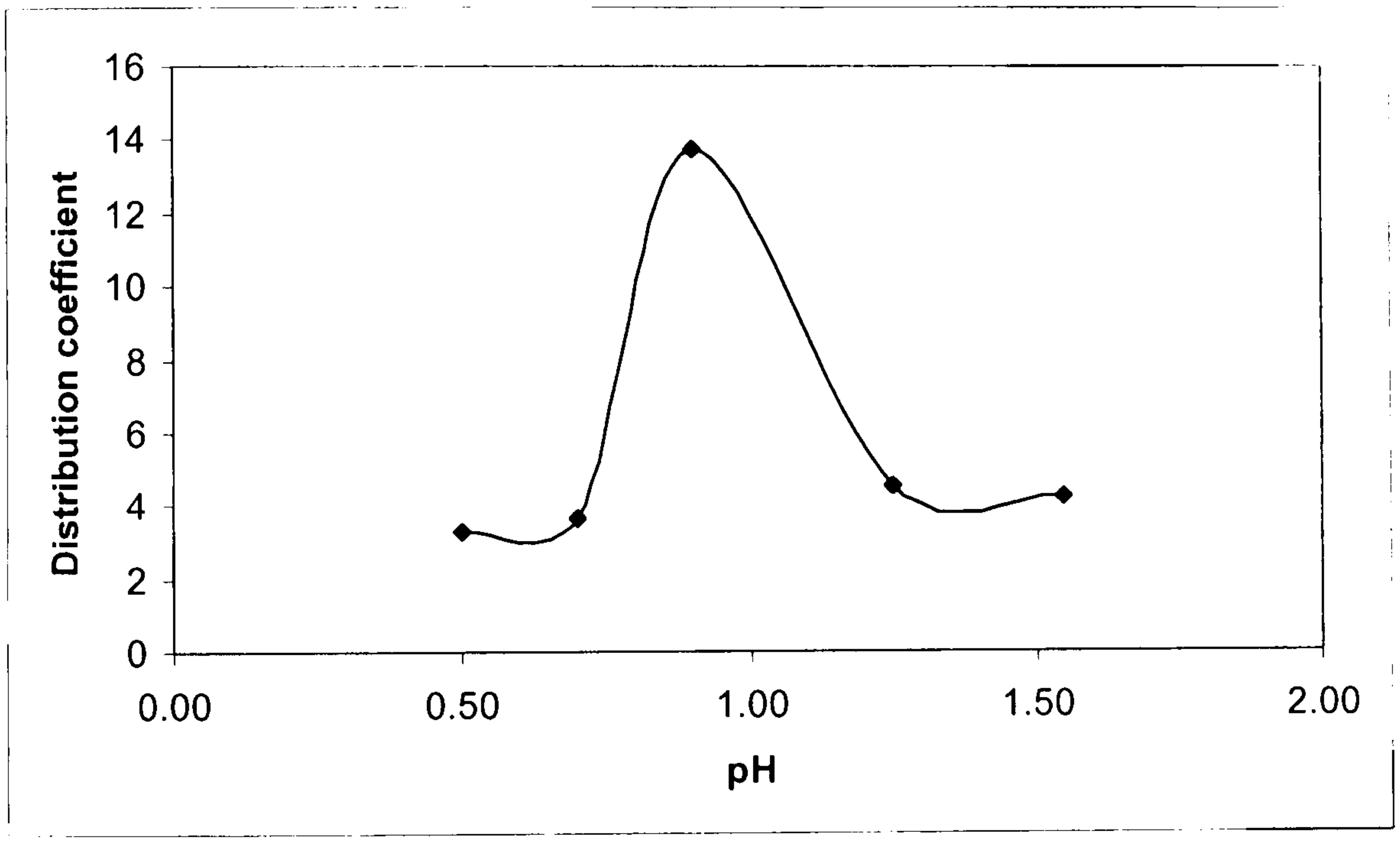


Figure 3.4: The effect of pH on the distribution coefficient of cerium(III).

3.2.4 Effect of different diluents on the distribution coefficient of cerium(III).

The distribution coefficient of cerium(III) has been studied using different organic diluents namely carbon tetrachloride, benzene, toluene, *o*-xylene, kerosene, and chloroform. The other studied factors were fixed at the values at which maximum distribution coefficient occurred i. e. 1:1 (v/v) organic to aqueous phase ratio, room temperature, 0.1M tri-*iso*octylamine in all diluents, contact time 5 minutes. Results are presents in Table 3.5. It is obvious that although benzene and toluene have dielectric constants in the same order of magnitude as that of CCl_4, they are both less efficient at extracting cerium(III). This is probably due to the lower solubility of the extracted species in these diluents as compared with CCl_4. This is probably a function of the different intermolecular diluent: diluent and solvent: diluent interactions that occur in aromatic and non-aromatic diluents. It is clear from Table 3.4 and Fig. 3.5 that chloroform is the best diluent.

Table 3.5: Effect of different diluents on the distribution coefficient of cerium(III).

Diluents		% Extraction	Distribution coefficient
Kerosene	**(1)**	**92.75**	**12.79**
Carbon tetrachloride	**(2)**	**93.25**	**13.80**
Chloroform	**(3)**	**93.50**	**14.38**
Benzene	**(4)**	**86.00**	**6.14**
Toluene	**(5)**	**85.75**	**6.02**
***O*-xylene**	**(6)**	**85.00**	**5.66**

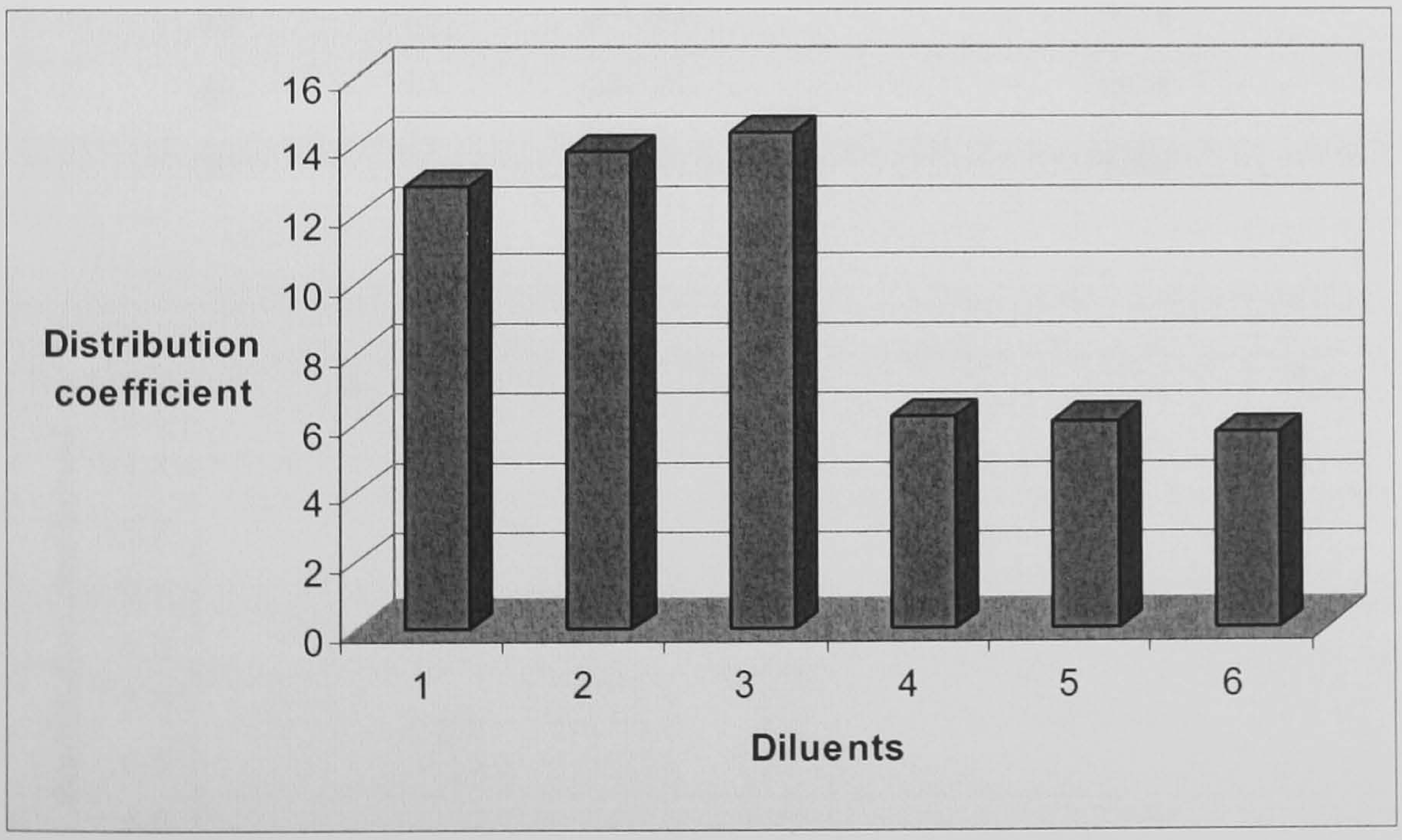


Figure 3.5: Effect of different diluents on the distribution coefficient of cerium(III).

3.2.5 Effect of temperature on the distribution coefficient of cerium(III).

For studying the effect of temperature on distribution coefficient and extraction percent, experiments were carried out in oil bath using an electric thermostat, the temperature of which was regulated from 25–50 °C. The following factors were kept constant at 1:1 (v/v) organic to aqueous phase ratio, pH 0.9, a contact time of 5 minutes, chloroform as diluent, and 0.1M TiOA. From the obtained results (Table 3.6 and Fig. 3.6) it is clear that room temperature can be considered as the best temperature. It is obvious from the data obtained, that distribution coefficient decreases with increasing temperature. This means that the extraction of cerium(III) is exothermic. This behaviour is similar to that reported by previous investigators. (15, 16)

Table 3.6: Effect of temperature on the distribution coefficient of cerium(III).

Temperature, °C	% Extraction	Distribution coefficient
25	93.75	13.00
30	91.25	10.43
35	90.00	9.00
40	88.75	6.51
50	84.75	5.56

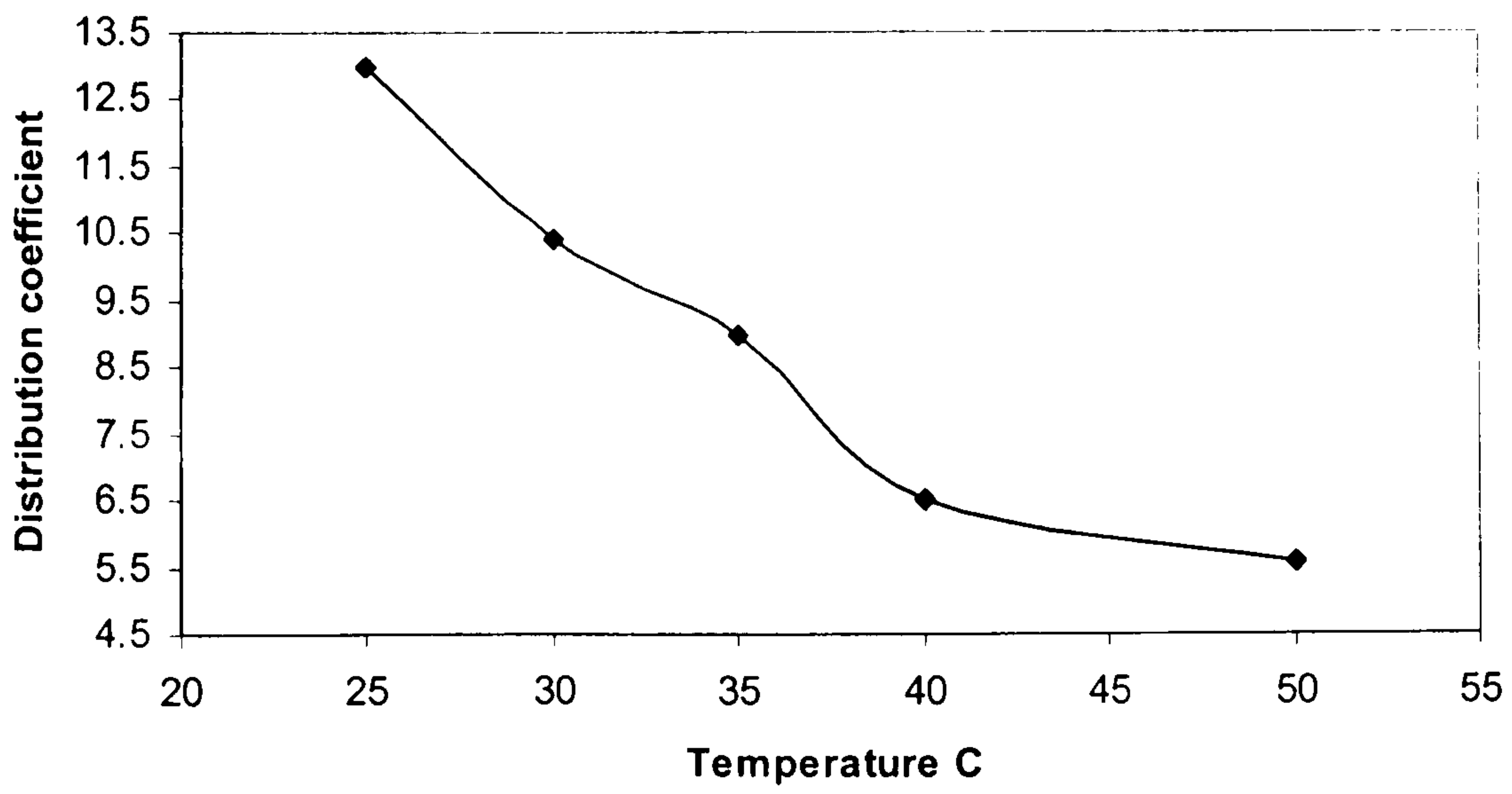


Figure 3.6: Effect of temperature on the distribution coefficient of cerium(III).

3.2.6 Distribution coefficients of cerium(III) as a function of aqueous H_2SO_4 concentration.

Fig. 3.7 shows the effect of different concentrations of H_2SO_4 on the distribution coefficients of cerium(III) in the two phases. The distribution coefficient of cerium(III) increases as the concentration of H_2SO_4 increases from 0.5-1.0M, but then decreases as the acid concentration is increased further. The reason for the initial increase in extraction may be caused by the salting-out effect of sulfuric acid. With further increase in H_2SO_4 concentration, the concentration of free extractant decreases, probably as a result of sulfuric acid co-extraction. However, the best concentration of H_2SO_4 to use for cerium(III) highest distribution coefficient is clearly 1M. Other factors in this experiment were fixed at 1:1 v/v organic to aqueous phase ratio, 0.1M TiOA in chloroform, mixing time 5 minutes and the experiments were carried out at room temperature. The results obtained are given in Table 3.7.

Table 3.7: Variation of cerium(III) distribution coefficient with concentration of H_2SO_4 solution.

$[H_2SO_4]$/M	% Extraction	Distribution coefficient
0.5	93.75	15.00
1	95.13	19.51
2	88.38	7.60
4	83.93	5.22
6	76.95	3.34

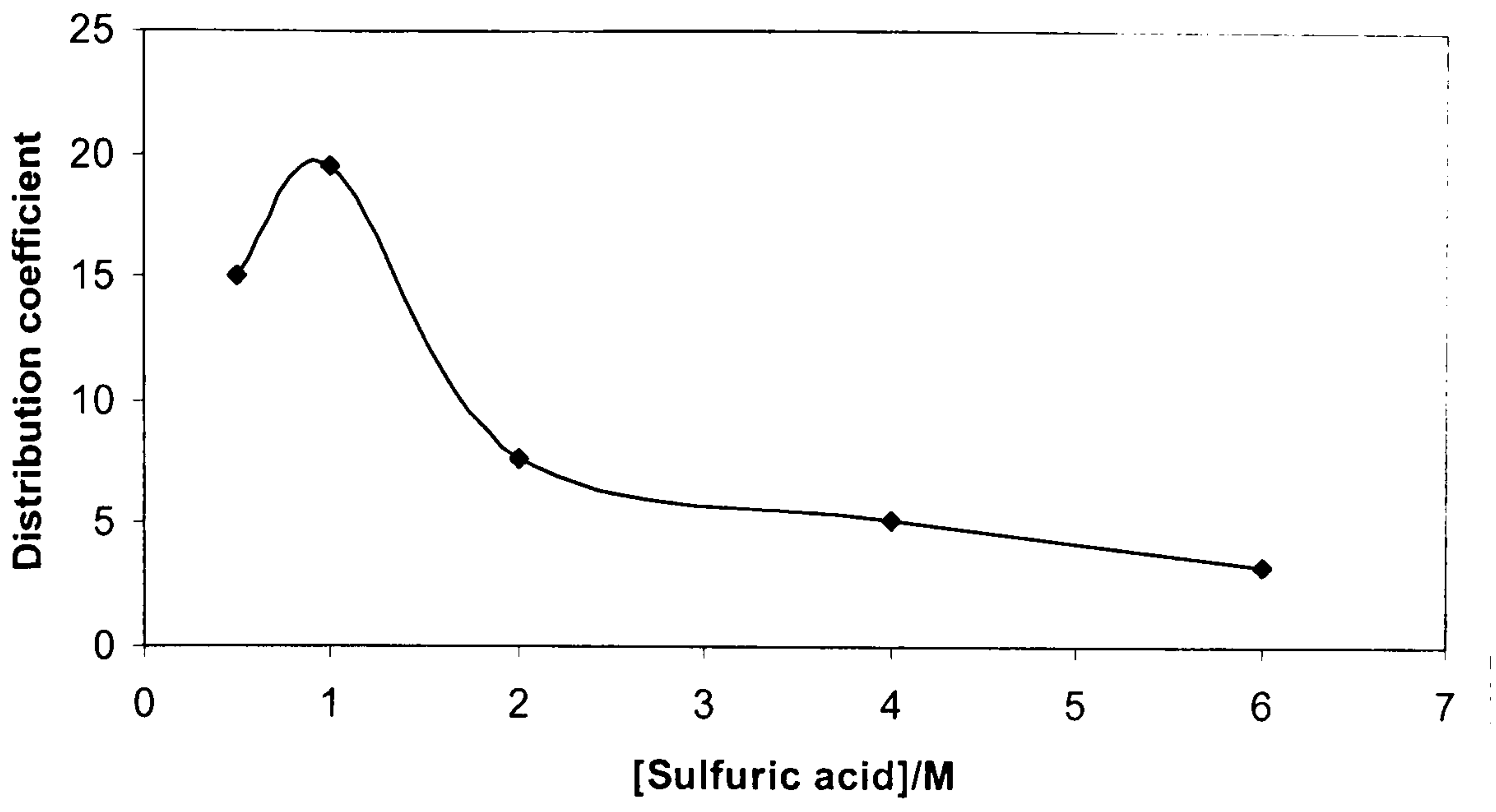


Figure 3.7: Effect of H_2SO_4 concentration on the distribution coefficient of cerium(III).

3.2.7 Equilibrium curve and construction of McCabe-Thiele diagram for cerium(III) extraction.

20 ml of each of the organic phase (0.1M TiOA in chloroform) and aqueous phase were contacted for 5 minutes until equilibrium is obtained. The phases were allowed to separate and the aqueous phase was removed and analysed. A measured portion of the organic phase was also taken for analysis. Fresh aqueous solution was then added to the organic phase to give the same phase ratio as that originally used. The phases were again contacted until equilibrium was obtained, and the procedure repeated. This process was carried out until saturation of the solvent with cerium(III) was obtained. Care must be taken to keep the same pH value of 0.9 throughout the series of shake-outs. The obtained data were used to obtain the equilibrium curve by plotting the cerium(III) concentration in the organic phase against its concentration in the aqueous phase. The next step was the construction of McCabe-Thiele diagram. From Fig. 3.8 we can see cerium(III) extraction under these conditions needs three extraction stages for nearly complete recovery.

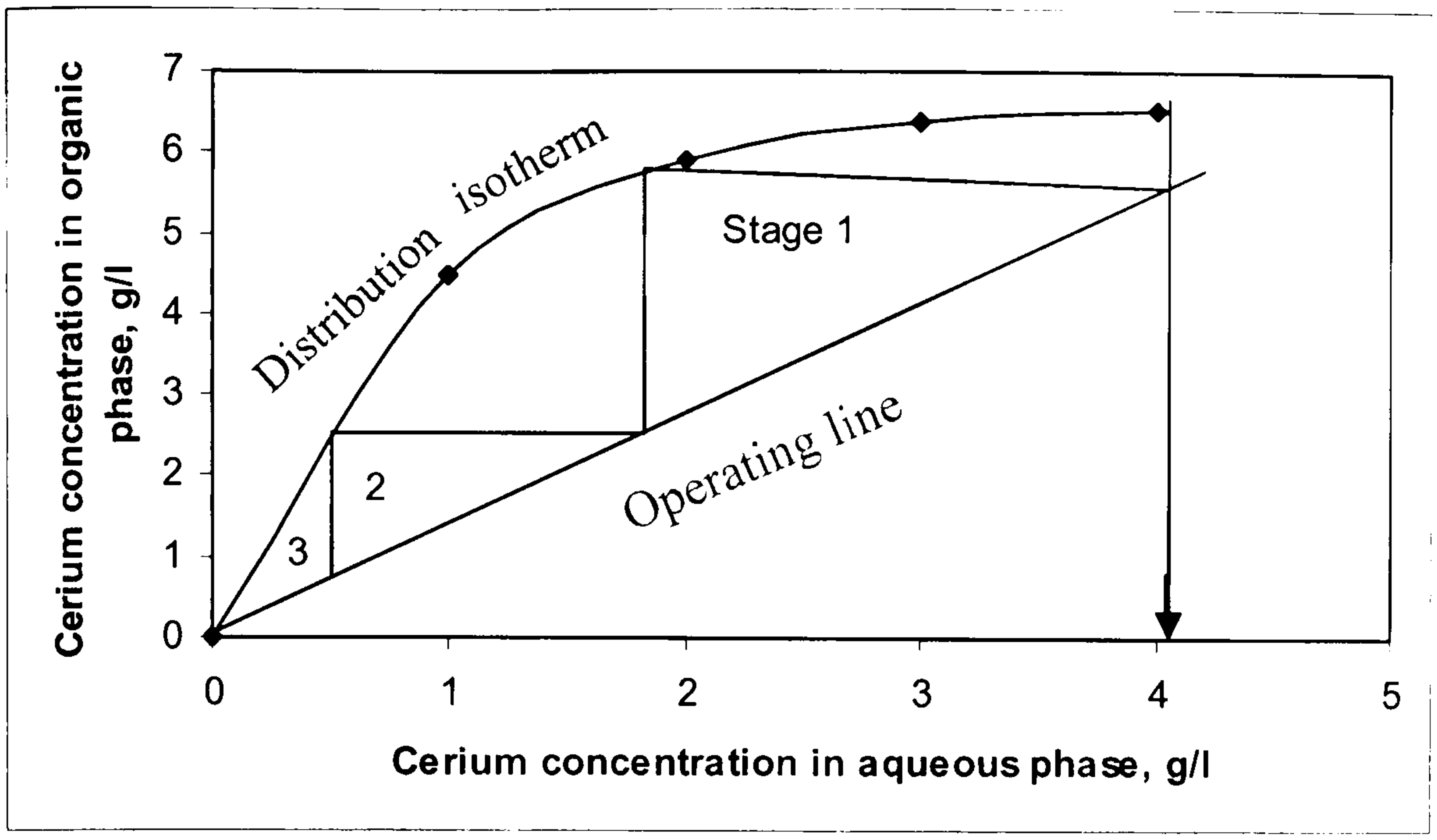


Figure 3.8: McCabe-Thiele diagram for cerium(III) extraction

3.3 Synergism and mixed extractants.

The major objective in using mixed extractants for the extraction of cerium(III) is to take advantage of any synergism that may result. It certainly appears that mixed extractant systems can offer much in the way of enhancing separation of cerium(III). (17, 18)

3.3.1 Effect of TOPO (trioctylphosphine oxide) on the extraction of cerium(III) (synergistic effect).

A stock solution of TOPO (0.1M in chloroform) was added to 0.1M TiOA/chloroform in different amounts. Table 3.8 and Fig. 3.9 show that by increasing the percentage of TOPO added there is a slight increase in the extraction of cerium(III). This means that TOPO is synergistic at lower concentrations. However, there is an enhancement in the extraction of cerium(III) when 40% volume of TOPO solution has been added, before another decrease at even higher added volume. This observation is reproducible but, as yet its origin is unknown.

Table 3.8: Effect of TOPO concentration on the extraction of cerium(III) (synergistic effect).

% TOPO by volume	% Cerium extraction
10	93.10
20	93.20
30	93.30
40	93.75
50	92.80

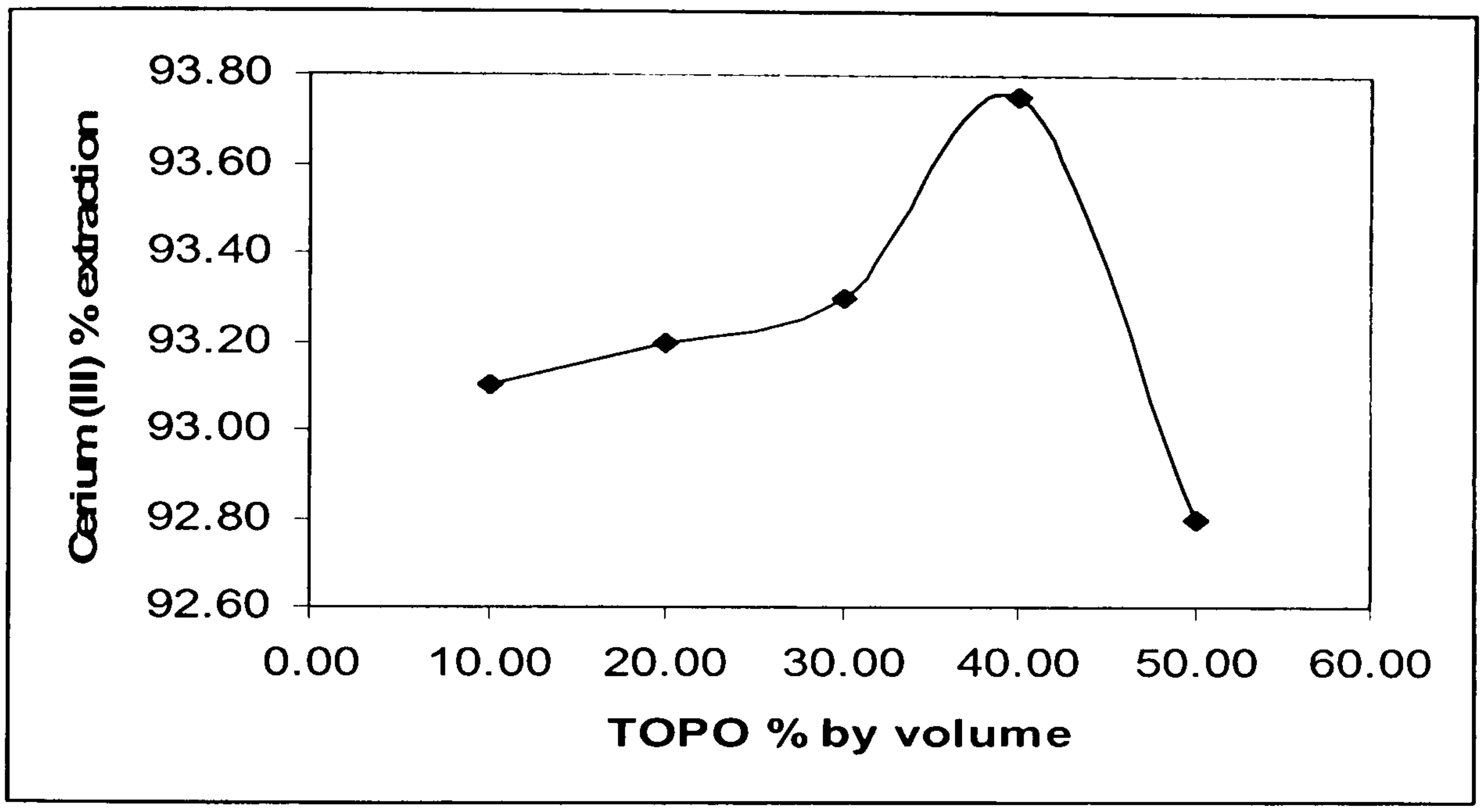


Figure 3.9: Effect of TOPO concentration on the extraction of cerium(III) (synergistic effect)

3.3.2 Effect of D2EHPA (di-2-ethylhexyl phosphoric acid) on the extraction of cerium(III) (synergistic effect).

Little is known of the formation of mixed complexes in amine extraction systems with D2EHPA. Some evidence is available that synergistic extraction of uranium (19) occurs with mixtures of tri-n-octyl amine and D2EHPA from high concentration of sulfate, in addition to forming the amine organophosphate salt, the phosphate species coordinates to the metal and enhances the extraction. A stock solution of D2EHPA 0.1M in chloroform was added to 0.1M TiOA/chloroform in different amounts. Table 3.9 and Fig. 3.10 show that by increasing the percentage of D2EHPA added there is an increase in the extraction of cerium(III). This means that D2EHPA is a good synergist and enhances the separation of cerium(III).

Table 3.9: Effect of D2EHPA concentration on the extraction of cerium(III) (synergistic effect).

% D2EHPA by volume	% Cerium extraction
10	93.30
20	93.90
30	94.20
40	94.70
50	95.00

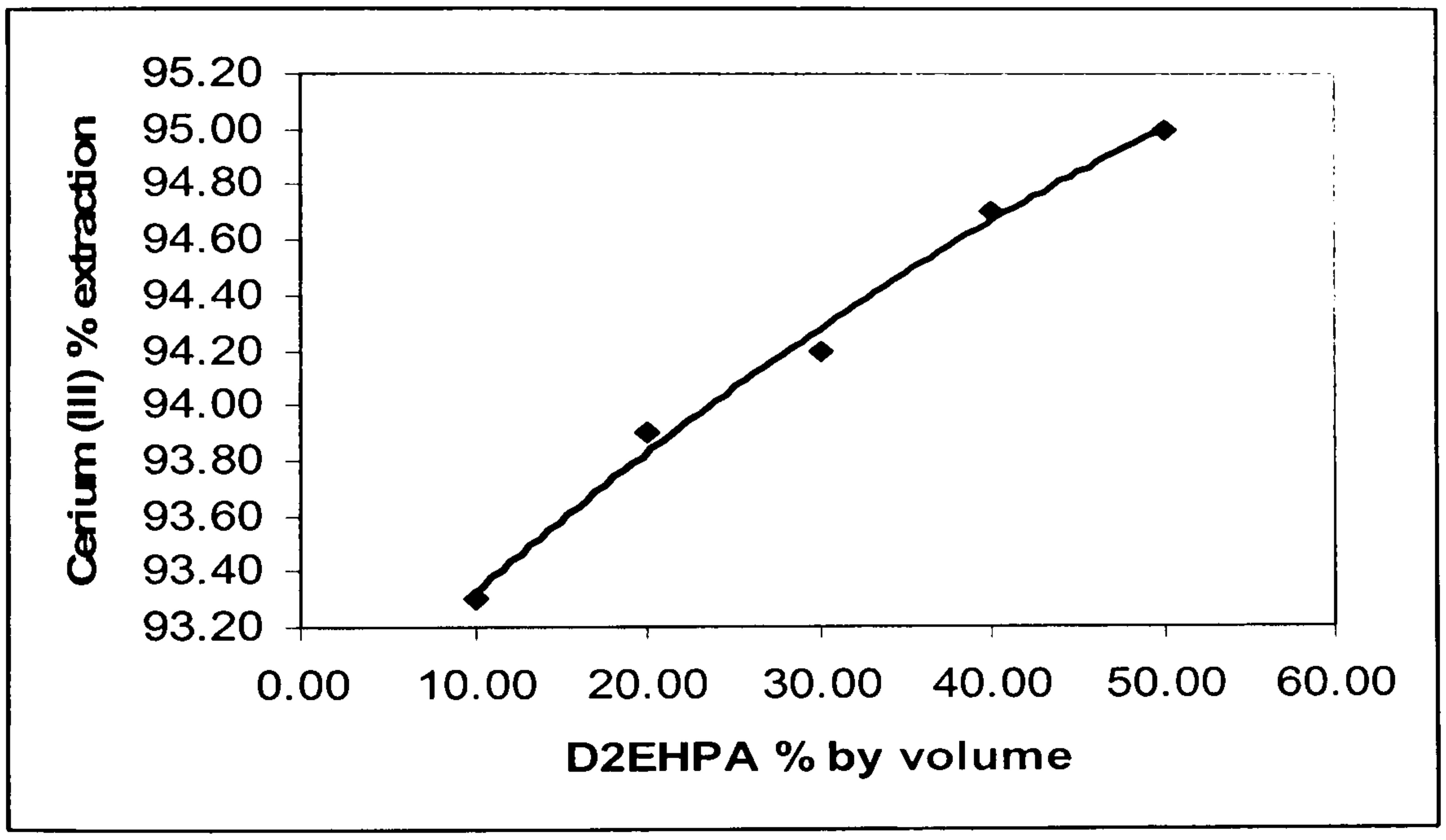


Figure 3.10: Effect of D2EHPA concentration on the extraction of cerium(III) (synergistic effect).

3.4 Scrubbing the loaded solvent cerium(III)

Washing of the organic phase (loaded solvent) containing cerium(III) after the extraction is carried out for several times with deionised water to remove any possible impurities. After this process the organic phase is transferred to a third stage, called a re-extraction step (stripping).

3.5 Stripping of cerium(III).

The general procedure for stripping cerium(III) in our experiments is as follows: the loaded solvent is contacted with a suitable acid or base strip solution, at an appropriate phase ratio, until equilibrium is attained. The aqueous phase is then removed and analysed for cerium(III). The stripping process depends on a number of factors, which have to be studied in order to obtain the best stripping efficiency that matches at the same time with economic considerations. The factors under consideration are: the effect of different reagents in the strip solution, the effect of different reagent concentrations, the contact time and the organic/aqueous phase ratio.

3.5.1 Effect of different sulfuric acid concentrations on the stripping of cerium(III).

A series of stripping experiments were carried out, using H_2SO_4 solutions of concentration ranging from 1M to 12M. The obtained results are given in Table 3.10 and shown in Fig. 3.11. It is clear from the obtained results that stripping by 6M H_2SO_4 gives the best cerium(III) re-extraction percent, while the contact time was 10 minutes and phase ratio 1:1 organic/aqueous and room temperature. However, by increasing H_2SO_4 concentration above 6M (pH decrease) there is a decrease in Ce(III) stripping, possibly owing to the protonation of the extractant which means that the stability of the extracted species is increased.

Table 3.10: Effect of sulfuric acid concentration on the stripping of cerium(III).

$[H_2SO_4]$/M	Cerium(III) % stripping
1	2.80
3	3.00
6	14.20
9	5.00
12	4.20

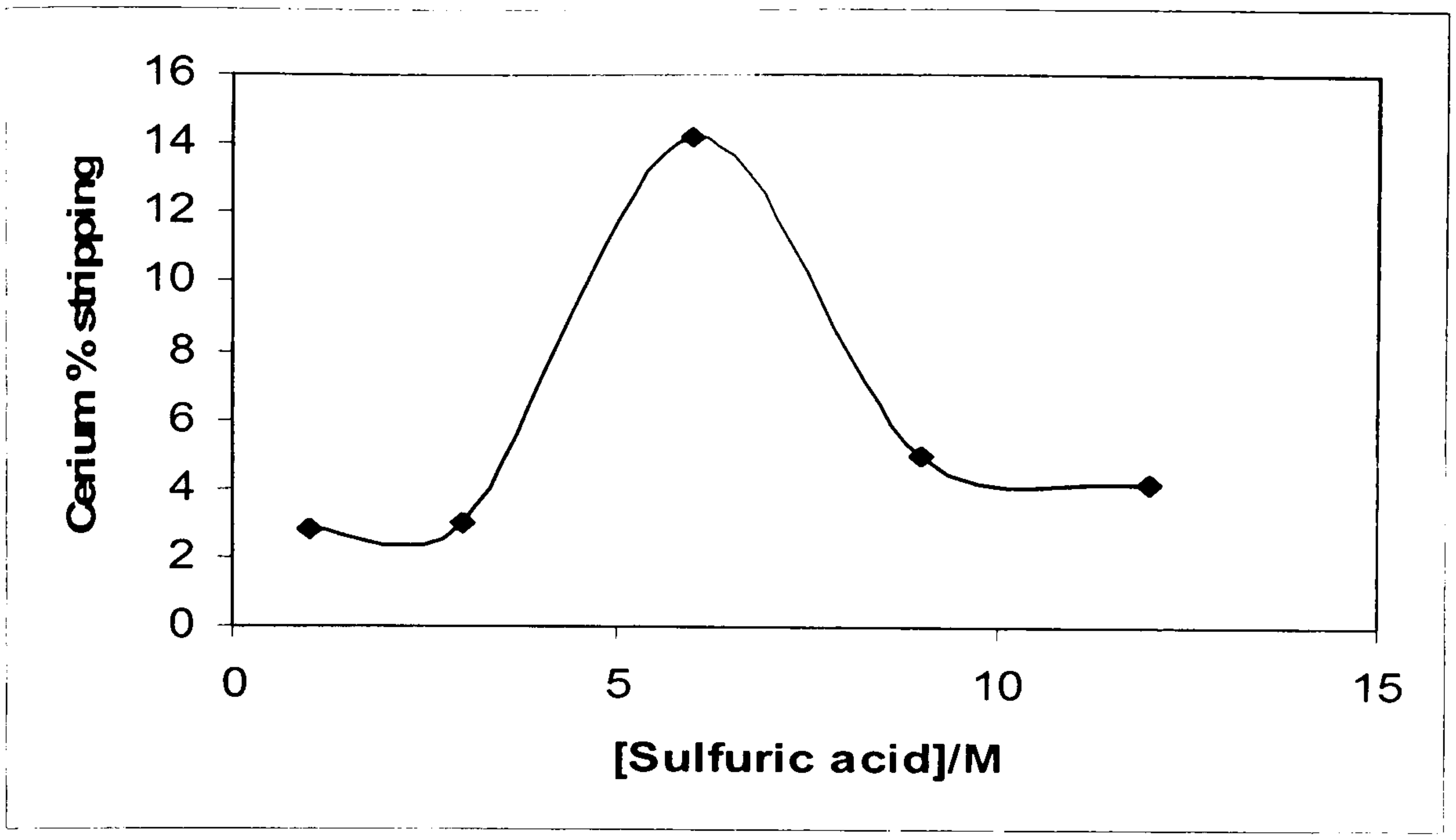


Figure 3.11: Effect of sulfuric acid concentration on the stripping of cerium(III).

3.5.2 Effect of different HCl concentrations on the stripping of cerium(III).

A series of stripping experiments were carried out, using HCl solutions of concentration ranging from 1M to 11.48M. The obtained results are given in Table 3.11 and shown in Fig. 3.12. It is clear from the obtained results that stripping by 6M HCl gives the best cerium(III) re-extraction percent, while the contact time was 10 minutes and phase ratio 1:1 organic/aqueous and room temperature.

Table 3.11: Effect of HCl concentration on the stripping of cerium(III).

[HCl]/M	Cerium(III) % stripping
1	10.50
3	34.60
6	37.55
9	35.55
11.48	25.15

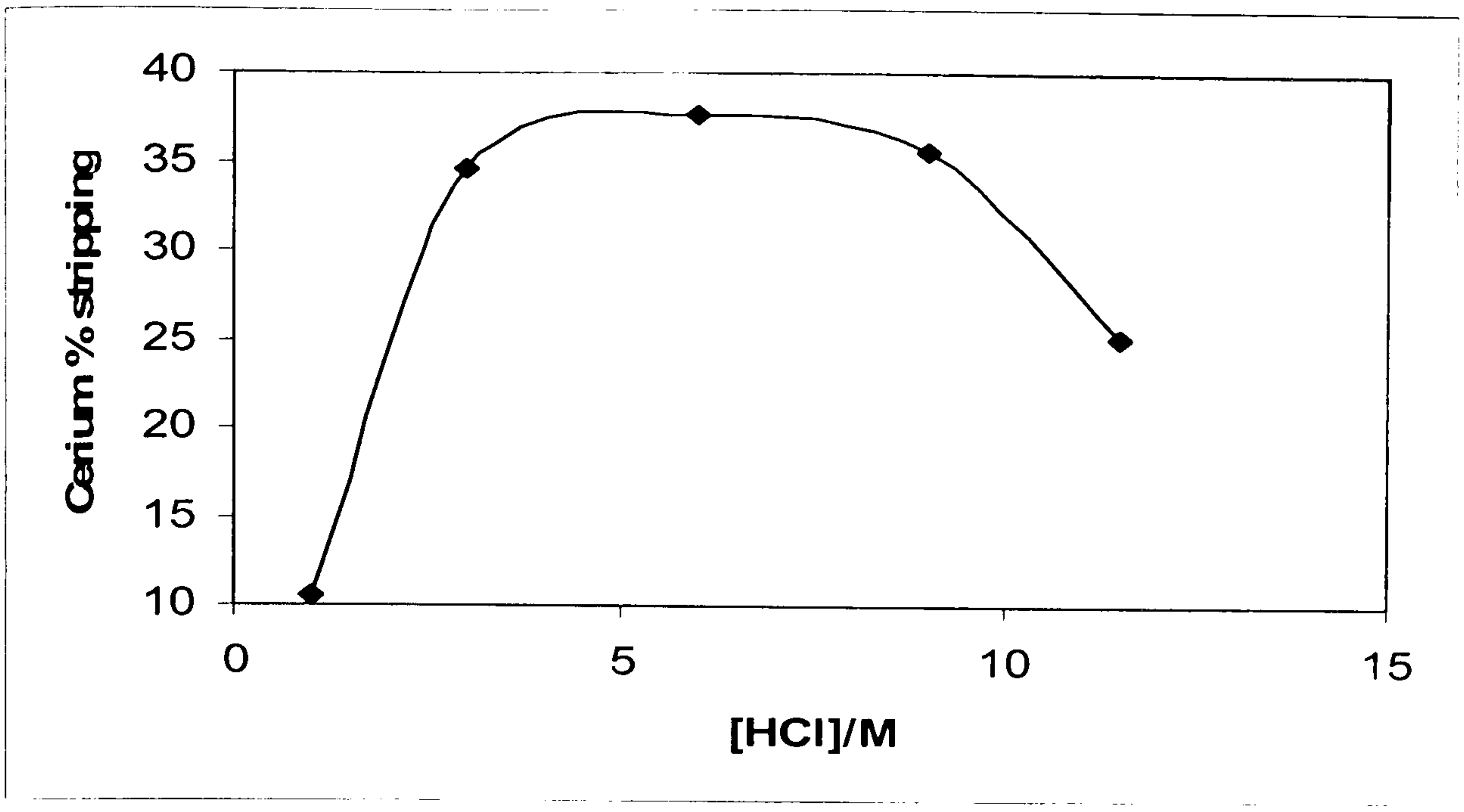


Figure 3.12: Effect of HCl concentration on the stripping of cerium(III).

3.5.3 Effect of different nitric acid concentrations on the stripping of cerium(III).

A series of stripping experiments were carried out, using HNO_3 solutions of concentration ranging from 1M to 12M. The obtained results are given in Table 3.12 and shown in Fig. 3.13. It is clear from the obtained results that stripping by 3M HNO_3 gives the best cerium(III) re-extraction percent, while the contact time was 10 minutes and phase ratio 1:1 organic/aqueous, room temperature.

Table 3.12: Effect of nitric acid concentration on the stripping of cerium(III).

$[HNO_3]$/M	Cerium(III) % stripping
1	42.25
3	60.17
6	27.63
9	21.10
12	19.40

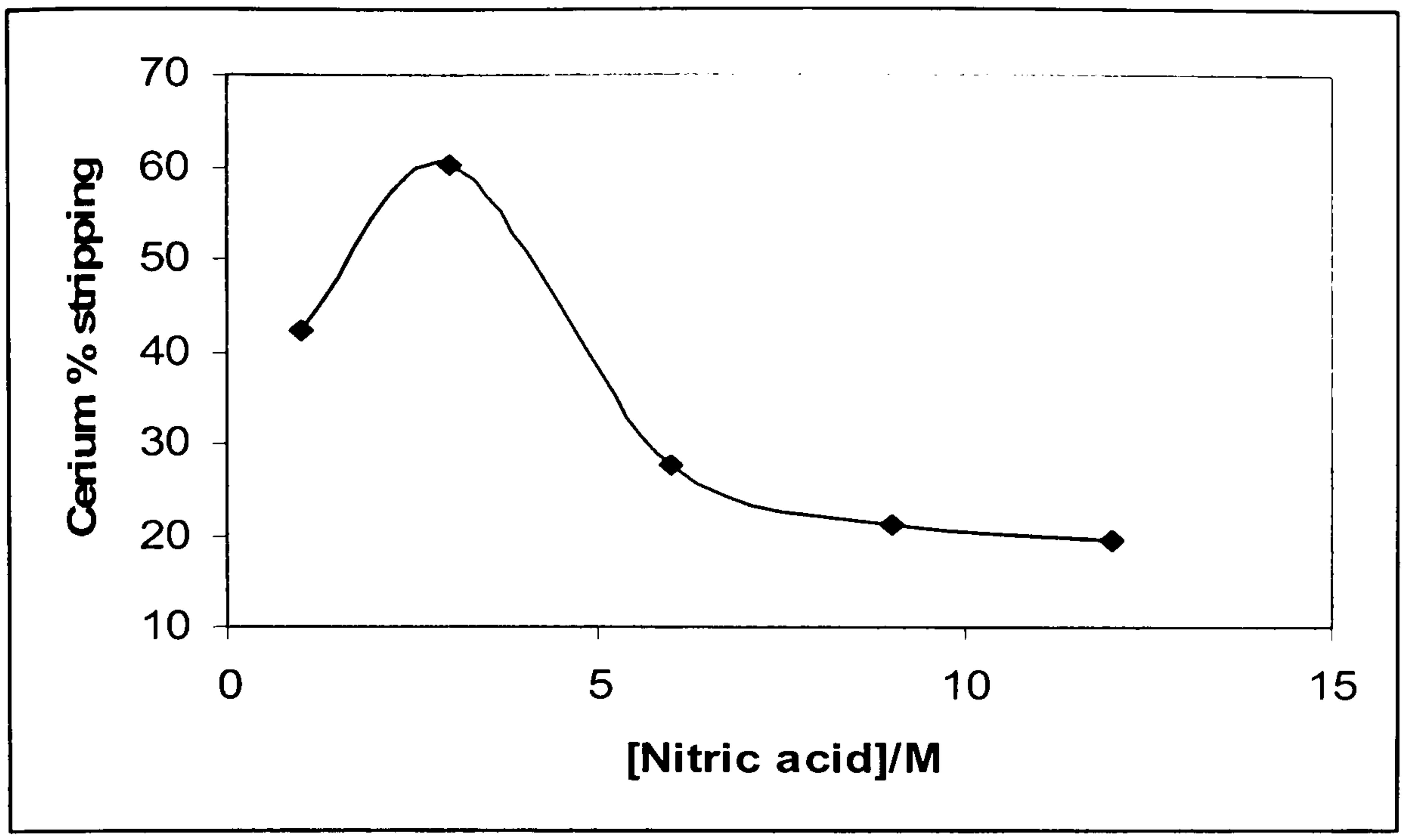


Figure 3.13: Effect of nitric acid concentration on the stripping of cerium(III).

By comparing the effect of the three different acids on the stripping of cerium(III), from Fig. 3.14 it is clear that 3M HNO_3 gave the highest recovery of cerium(III).

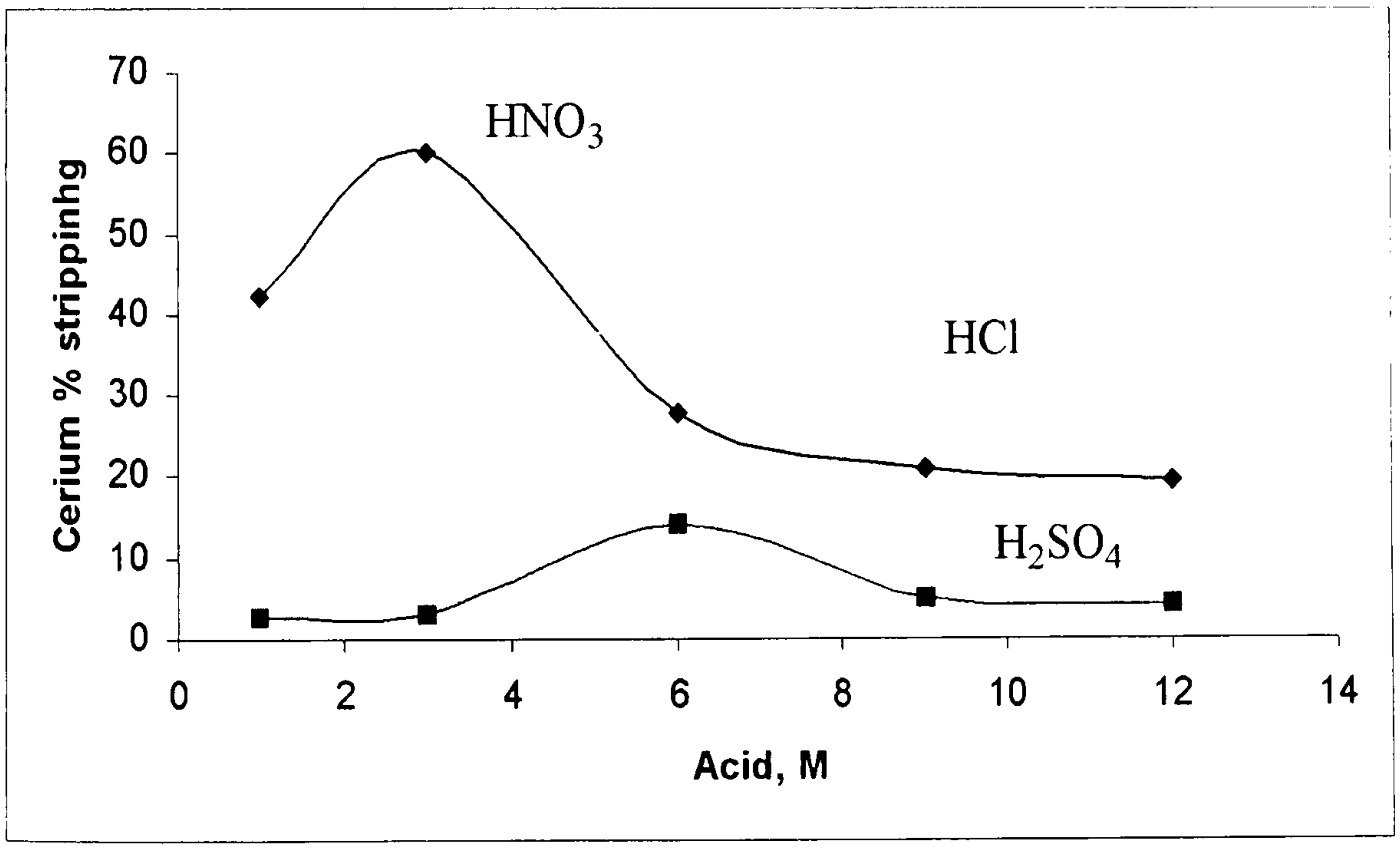


Figure 3.14: Effect of different acids on the stripping of cerium(III).

3.6 Effect of contact time on the stripping of cerium(III).

The effect of contact time on the attainment of an equilibrium state has been studied at the time interval 1 to 30 minutes, while the other factors were kept at 3M HNO_3 and 1:1 (v/v) aqueous to organic phase ratio, the experiments were carried out at room temperature. The results obtained are given in Table 3.13 and shown in Fig.3.15. It is obvious that contact time of 5 minutes is sufficient for cerium(III) stripping from the loaded solvent. But by increasing mixing time there a decrease in percent stripping of Ce(III) because some loaded organic droplets entrain to aqueous phase causing less amount of Ce(III) mass transfer from organic to aqueous phases.

Table 3.13: Effect of contact time on the stripping of cerium(III).

Time/minute	Cerium(III) % stripping
1	22.60
5	60.25
10	53.70
15	50.33
30	49.78

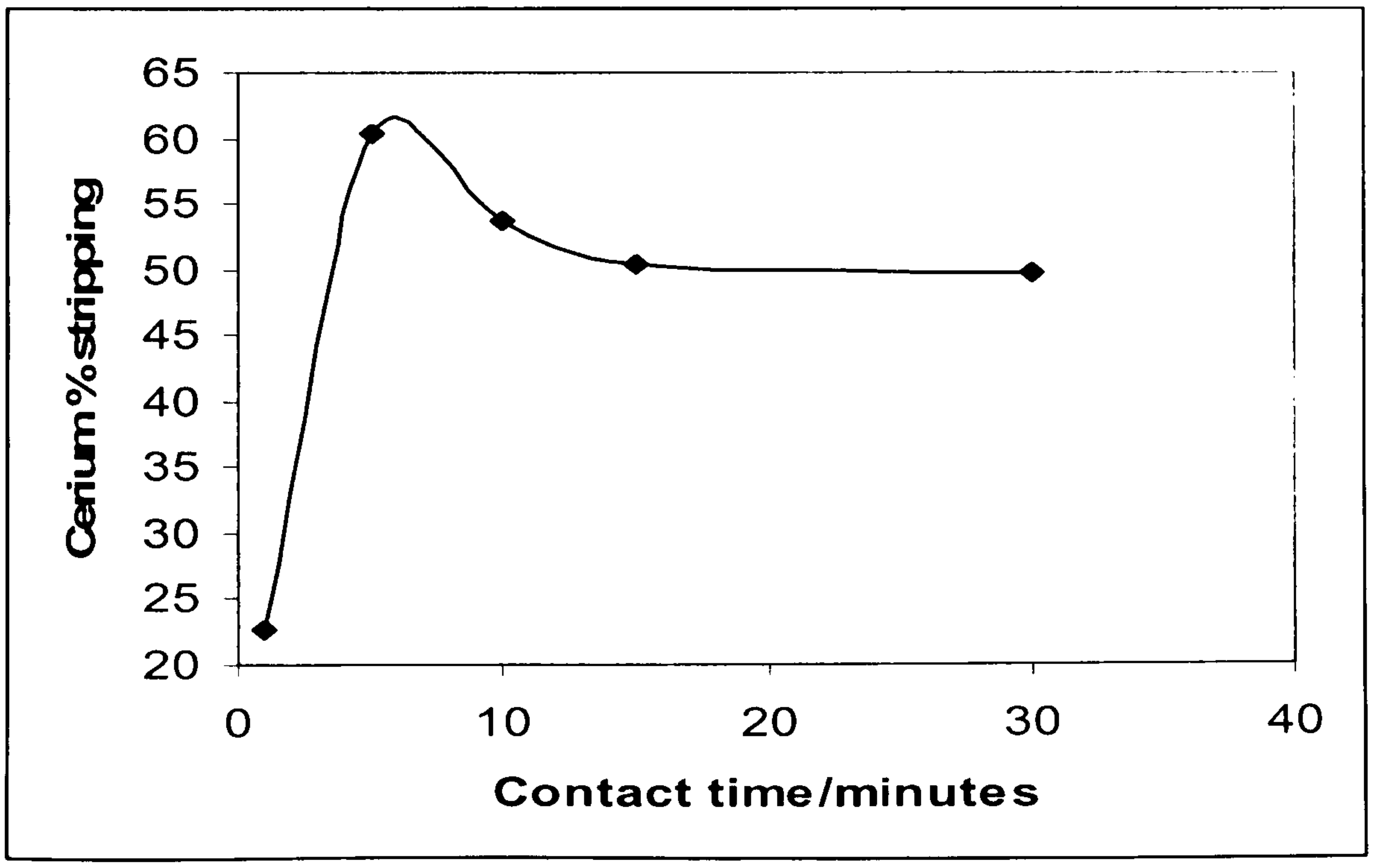


Figure 3.15: Effect of contact time on the stripping of cerium(III).

3.7 Effect of aqueous/organic phase ratio on the stripping of cerium(III).

This effect on the stripping process was studied by changing the aqueous/organic phase ratio (v/v) from 1:2 to 1:6. The results obtained are given in Table 3.14 and illustrated in Fig. 3.16. It is clear from the obtained results that aqueous/organic phase ratio 1:3 is the best ratio as it gives the best stripping efficiency of cerium(III).

Table 3.14: Effect of aqueous/organic ratio on the stripping process of cerium(III) using 3M HNO_3.

Aqueous/organic ratio	Cerium(III) distribution coefficient
1/2	4.33
1/3	5.21
1/4	3.98
1/5	3.80
1/6	3.80

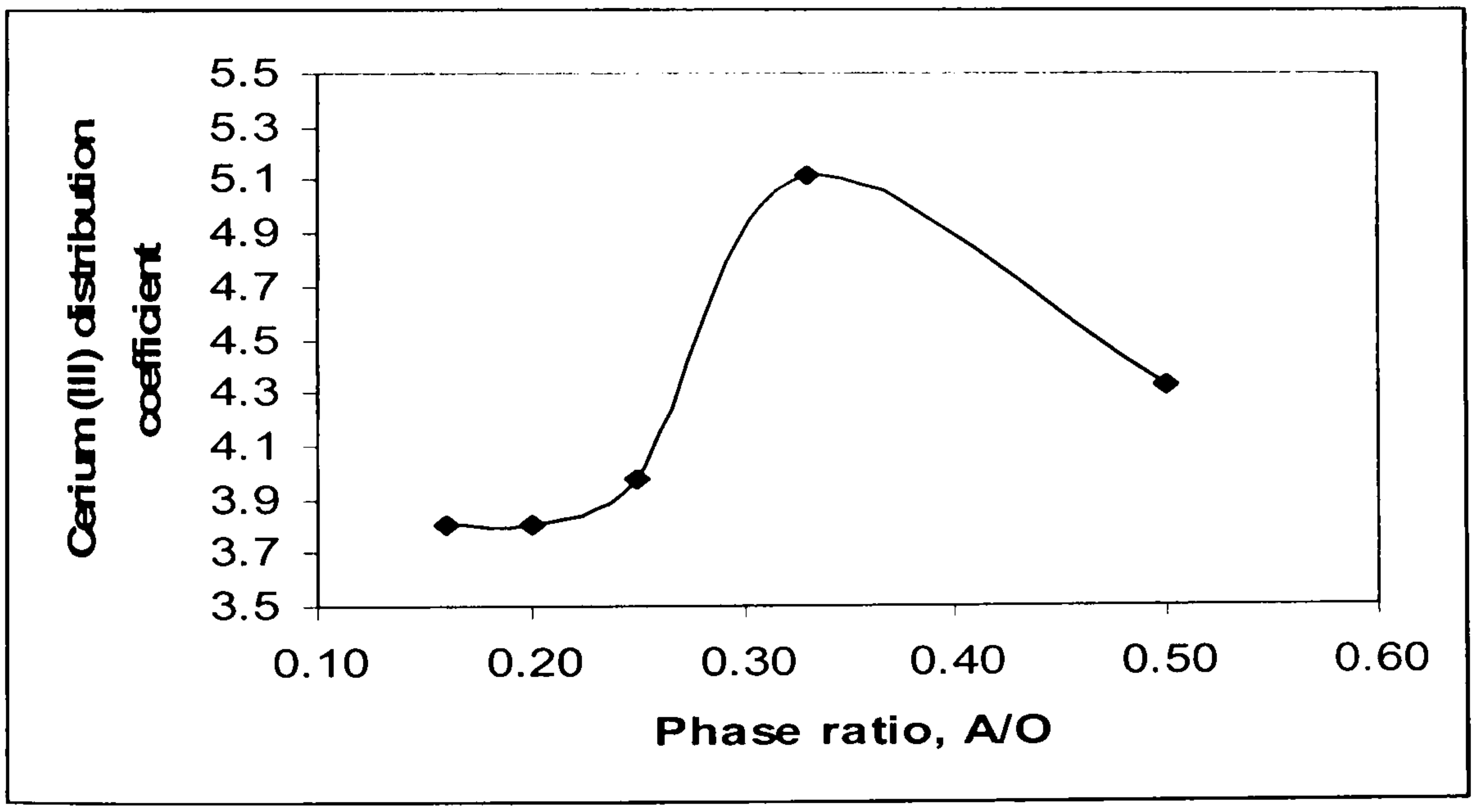


Figure 3.16: Effect of aqueous/organic ratio on the stripping process of cerium(III)

3.8 Equilibrium line and construction of McCabe-Thiele diagram for cerium(III) stripping.

15 ml of the aqueous phase (3M HNO_3) and loaded solvent were contacted for 5 minutes until equilibrium was obtained. The phases were allowed to separate. A measured portion of the aqueous phase was taken for analysis; fresh loaded solvent was added to the funnel containing the remainder of the aqueous phase, in an amount, to give the same phase ratio as that originally used. The phases were again contacted until equilibrium was obtained, and the same procedure repeated. This process was carried out until saturation of the aqueous phase with cerium. It is clear from Fig. 3.17 that three stages were found sufficient for complete recovery of cerium(III).

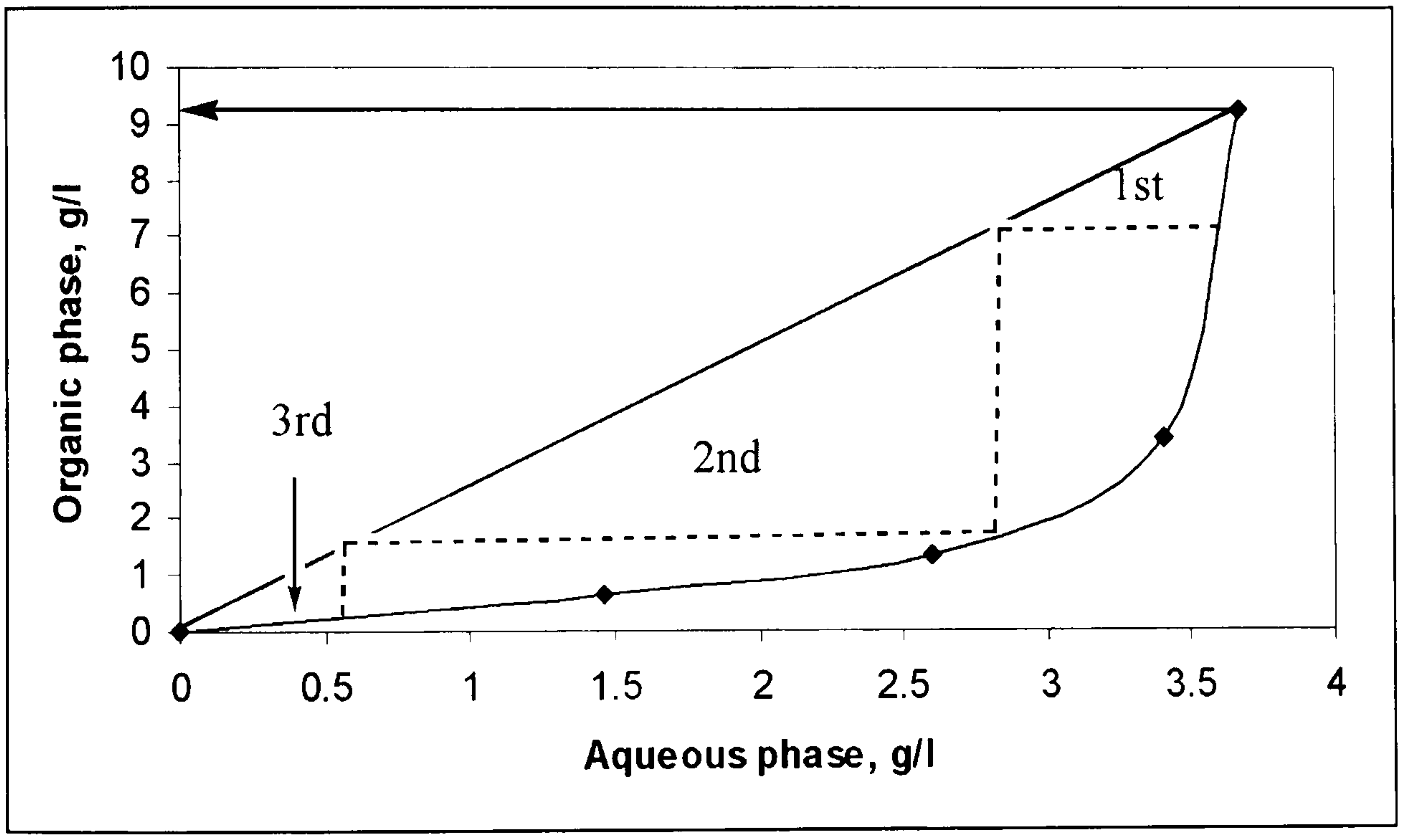


Figure 3.17: McCabe-Thiele diagram for cerium(III) stripping from loaded solvent.

3.9 Conclusions for liquid-liquid extraction of cerium(III).

Although the rare earth elements are in great demand as excellent functional materials, it is widely recognized that their mutual separation is very difficult because of their similar physical and chemical properties. A range of separation technologies (20) can be used to affect the transfer of cerium from the aqueous pregnant solution. The most commonly used are based on equilibria involving liquid-liquid (solvent extraction) and liquid-solid (ion-exchange and chelating resins) systems. The optimum conditions for liquid-liquid extraction of cerium(III) from sulfate solution by tri-*iso*octylamine have been investigated. The concentration of TiOA is 0.1M, contact time 5 minutes which is quite adequate for high efficiency of extraction, pH 0.90, the best diluent is chloroform, room temperature, 1M H_2SO_4 as aqueous phase composition, and by constructed the McCabe-Thiele diagram three stages are sufficient for almost complete cerium(III) extraction which approaches to the saturation of solvent.

Scrubbing the loaded solvent can be achieved with distilled water. Also, the suitable conditions for stripping of cerium(III) are: HNO_3 is the best stripping reagent, 3M HNO_3 concentration gives the highest stripping efficiency, mixing time for stripping 5 minutes, aqueous/organic phase ratio 1:3, by constructing McCabe-Thiele for stripping three stages are sufficient for complete recovery of cerium(III).

3.10 References.

1 "*Cerium: A Guide to its Role in Chemical Technology*", Molycorp, Inc., Mountain Pass, C A, U. S. A, (1995).

2 Mineralogy of the rare earth elements, A. M. Clark, in "*Rare Earth Element Geochemistry*" ed. P. Henderson, Publ. Elsevier, (1984), 33.

3 www.rhodia-ec.com/site_ec_us/our_expertise/page_production.htm.

4 L. Wuping, Y. Guihong and L. Deqian, *J. Solvent Extraction and Ion Exchange*, (2001) **19**(2), 243.

5 K. Soldenhoff, D. Wilkins and R. Ring, Materials Science Forum, (1999), 315.

6 T. Toshio, I. Kyoko, M. Kazuhiko, E. Yoshihiro, T. Senri, M. Shiro and S. Taichi, Proceeding of Symposium on Solvent Extraction, (1993), 41.

7 D. J. Bauer and V. E. Shaw, U.S., Bur. Mines, Rept. Invest. (1964).

8 S. Taichi and S. Keiichi, *J. of Alloys and Compounds*, (1993) **192**(1-2), 135.

9 Y. Yufu and Z. Zhijian, *J. Radioanal. Nucl. Chemistry*, (1985) **96**(3), 257.

10 P. B. Santhi, M. L. P. Reddy, T. R. Ramamohan and A. D. Damodaran, *J. Radioanal. Nucl. Chemistry*, (1993) **171**(2), 329.

11 A. Chatterjee and S. Basu, *J. of the Indian Chemical Society*, (1992) **69**(1), 29.

12 Z. Junmei, M. Shulan, L. Deqian, *J. Solvent Extraction and Ion Exchange*, (2004), **22**(5), 813.

13 Z. Junmei, M. Shulan, L. Deqian, *J. Solvent Extraction and Ion Exchange*, (2004), **22**(3), 429.

14 G. M. Ritcey and A. W. Ashbrook, "*Solvent Extraction Principles and Application to Process Metallurgy*" part 1, Elseiver Science Publishers B. V., (1984).

15 S. B. Savvin, Organic Reagents of the Arsenazo III Group, Atomizdat, Moscow, (1971).

16 W. Youshao, S. Chaohong, S. Guoxin, Z. Jiankang, and B. Borong; Pro. of the Int. Conf. on uranium extraction, China, (1996) 84.

17 J. D. Thornton, "*Science and Practice of Liquid-Liquid Extraction*", Clarendon Press, Oxford (1992) **2**.

18 B. Gupta, P. Malik, and A. Deep, *J. Solvent Extraction and Ion Exchange*, (2003) **21**, 239

19 C. Deptula and S. Minc, *J. Inorg. Nucl. Chem.* (1967) **29**, 159.

20 S. G. Galbraith, P. A. Tasker, *Supramolecular Chemistry* (2005) **17**, 191.

Chapter Four

Liquid–liquid extraction of lanthanum

4.1 Brief introduction to lanthanum.

Lanthanum is a silvery white, metallic element belonging to Group 3 of the periodic table and is often considered to be one of the lanthanides. Found in some rare-earth minerals usually in combination with cerium and other rare-earth elements, lanthanum is malleable, ductile, and soft enough to be cut with a knife. It is one of the most reactive of the rare-earth elements. It oxidises rapidly when exposed to air. Cold water attacks lanthanum slowly, and hot water attacks it much more rapidly. The metal reacts directly with elemental carbon, nitrogen, boron, selenium, silicon, phosphorus, sulphur, and with halogens. Lanthanum, one of the most abundant of the lanthanides, it is also an important element of mischmetal hydrogen-absorbing alloy. (1)

4.1.1 Applications

Uses of lanthanum include the following:
Lanthanum is used in carbon lighting applications, especially by the motion picture industry for studio lighting and projection. (2) Lanthanum oxide improves the alkali resistance of glass, and is used in making special optical glasses, such as infrared absorbing glass and camera and telescope lenses, because of the high refractive index and low dispersion of rare-earth glasses. (3) Small amounts of lanthanum are added to steel to improve its malleability, resistance to impact and ductility. Small amounts of lanthanum are added to iron, which helps to produce nodular cast iron. Small amounts of lanthanum can be added to molybdenum to decrease the hardness of this metal and its sensitivity to temperature variations. Mischmetal, a pyrophoric alloy used e.g. in lighter flints, and contains 25% to 45% lanthanum. The oxide and the boride are used in electronic vacuum tubes. Hydrogen sponge alloys can contain lanthanum. These alloys are capable of storing up to 400 times their own volume of hydrogen gas in a reversible adsorption process. Also, lanthanum used as petroleum cracking catalysts, and gas lantern mantles. Finally lanthanum is used in glass and lapidary polishing compound, beside La-Ba used in age dating of rocks and ores.

4.1.2 History and occurence.

Lanthanum was discovered in 1839 by C. G. Mosander, when he partially decomposed a sample of cerium nitrate by heating and treating the resulting salt with dilute nitric acid. From the resulting solution, he isolated a new rare earth element he called *lantana*. Lanthanum was isolated in relatively pure form in 1923. The word lanthanum comes from the Greek *lanthanien,* to lie hidden. Monazite (Ce, La, Th, Nd, Y)PO_4, and bastnaesite (Ce, La, Y)CO_3F, are the principal ores in which lanthanum occurs, in to 25 % and 38 % by weight respectively. (4, 5) Lanthanum has no known biological role. The element is not absorbed orally, and when injected its elimination is very slow. Lanthanum carbonate is being studied as a compound to absorb excess phosphate in cases of end-stage renal failure. Lanthanum chloride ($LaCl_3$) is known to have anticoagulant properties. Naturally occurring lanthanum is composed of one stable and one radioactive isotope, ^{139}La, and ^{138}La respectively with, ^{139}La, being the most abundant (99.91% natural abundance). 31 radioisotopes have been characterized with the most stable being ^{138}La with a half-life 1.05 x 10^{11} years, and ^{137}La with a half-life of 60,000 years. All of the remaining radioactive isotopes have half-lives that are less than 24 hours and the majority of these have half lives that are less than 1 minute.

Lanthanum has a low to moderate level of toxicity, and should be handled with care. In animals, the injection of lanthanum solutions produces glycohemia, low blood pressure, and degeneration of the spleen and hepatic alterations.

4.1.3 Recent developments in lanthanum extraction chemistry.

Ramakul and Panchareon (6) studied the synergistic extraction and separation of mixtures of lanthanum and neodymium by using a mixture of thenoyltrifluoroacetone (HTTA) and trioctylamine (TOA) which are extractants dissolved in benzene as a membrane solution. The membrane solution was supported by a microporous hydrophobic hollow fibre membrane extractor. The effects of changing the pH of the feed solutions, and concentration of HTTA and TOA in the membrane were studied. The results reveal that a slight change in the pH of the feed solution has a big effect on the percentage of extraction, with the maximum value at pH 2.5. Percentage of extraction is increased considerably when TOA is added to HTTA and lanthanum can be extracted and recovered more than neodymium. When the concentration of TOA is constant, the percentage of extraction is increased in accordance with an increased concentration of HTTA. When the concentration of HTTA is constant, the percentage of extraction increases with an increase in TOA concentration, more noticeably than when increases the concentration of HTTA. However, the increase in extraction may be due to the increase in viscosity of the membrane.

Agrawal ***et al*** (7) investigated the use of N-phenylbenzo-18-crown-6-hydroxamic acids for the separation of lanthanum(III) and cerium(IV) from monazite. Lanthanum(III) and cerium(IV) are extracted and separated in the presence of thorium, uranium and other associated cations at pH 8.8 and 9.5 respectively in dichloromethane. Lanthanum(III) gives a colourless complex with the reagent which is extracted into dichloromethane and has molar absorptivity 6.5 x 10^3 L mol^{-1} cm^{-1} at 385 nm. Cerium(IV) forms a red complex with the reagent extracted in dichloromethane with λ_{max} 450nm and molar absorptivity of 6.5 x 10^3 L mol^{-1} cm^{-1}. For trace determination the liquors are inserted directly into plasma for ICP AES measurements of La(III) and Ce(IV). The complexes of lanthanum(III) and cerium(IV) are very stable.

Saleh ***et al*** (8) have studied the extraction behaviour of La(III) from acidic nitrate-acetato medium by bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272, H_2A_2) in toluene either alone or in combination with trioctylphosphine oxide (TOPO, B) as a function of contact time, aqueous phase concentration of La^{3+}, H^+, NO_3^-, and AC (acetate), Cyanex 272 and TOPO concentration in the organic phase and temperature. The distribution coefficient is found to decrease with increasing La^{3+} concentration up to 7.34 mM La^{3+}in the aqueous phase, after which it increases up to 9.79 mM La^{3+} concentration and again decreases. The distribution coefficient decreases with increasing acetate ion concentration at higher acetate ion concentration with and without TOPO but is less dependant at low acetate concentrations. The synergistic effect of TOPO is found only at higher concentrations. These results suggest that the $[La(Ac)_2A.3HA]_{(o)}$ and $[La(Ac)A_2.B]_{(o)}$ species are extracted in the system without and with TOPO respectively.

Morais and Ciminelli (9) have described the development of a solvent extraction process for the recovery of high-grade lanthanum oxide from light rare earth elements (La, Pr, Nd) from chloride solution. In a preliminary stage, process parameters and experimental conditions were explored in bench-scale experiments. The effect of variables such as nature and concentration of extractants (di-2-ethylhexylphosphoric acid [D2EHPA] and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester [HEH(EHP)]), contact time, acidity and rare earth concentration in the extraction stage as well as the effect of the hydrochloric acid concentration in the stripping stage was investigated. The continuous counter-current experiments were carried out in a mini-battery unit of mixer-settlers. The final set-up was comprised of 22 stages: 8 for extraction, 8 for scrubbing and 6 for stripping.

Curtui and Haiduc (10) investigated the extraction of lanthanum(III) and cerium(III) with dialkyldithiophosphoric acids, into different polar and nonpolar solvents (cyclohexane, benzene, CCl_4, chloroform, diethylether, dibutylether, n-butanol, and cyclohexanone) from aqueous solution containing perchlorate, nitrate, and chloride anions. The effect of various factors such as nature of solvent, pH, metal concentration, and foreign anions presenting the aqueous phase was investigated in order to establish the mechanism of extraction process. The data obtained suggest an ion-exchange mechanism. The anions present in the aqueous phase do not participate in the extraction process and do not influence significantly the magnitude of the extraction ratio either. The extracted species in the organic phase is a 1:2 complex of lanthanide with dialkyldithiophosphoric acid. The extraction efficiency is calculated and the possibility of Th-rare earths separation is discussed.

Noro and Sekine (11) studied the solvent extraction of lanthanum(III), europium(III), and lutetium(III) in 0.1 mol/dm^3 sodium nitrate solutions with 5,7-dichloro-8-quinolinol (HA) into chloroform in the absence and presence of tetrabutylammonium ions (tba+) or trioctylphosphine oxide (TOPO). In the absence of tba+ or TOPO, the extracted species were the MA_3 and MA_3HA (self-adduct), though MA_4-tba+ was found when tba+ was added. MA_3TOPO and $MA_3 (TOPO)_2$ were found when TOPO was added in addition to the above mentioned two species. The anionic complex or TOPO greatly enhance the extraction. The data were statistically analyzed and the equilibrium constants for the extraction of these species were determined. The extraction of the MA_3 is the order $LaA_3 < EuA_3 < LuA_3$. Although, the separation of these three metal ions by solvent extraction with this chelating extractant is not much affected by the addition of TOPO, it is greatly improved by the addition of TBA^+.

4.2 Results and discussion.

In order to obtain an efficient and economic separation of lanthanum, it has been necessary to study the relevant factors affecting the liquid-liquid extraction process to determine the optimum conditions for lanthanum extraction from sulfate liquor. These factors include different amine extractants, TiOA concentration, diluent, pH value, temperature, contact time and aqueous phase composition. In addition, the synergistic effect of using TOPO, D2EHPA and TBP to enhance the extraction of lanthanum has been investigated. The stripping process depends on a number of factors, which have to be studied to obtain the best stripping efficiency that matches at the same time economic considerations. The factors under consideration are effect of different reagents (strip solution) such as H_2SO_4, HNO_3, and HCl, effect of different reagent concentrations and effect of contact time. All these experiments were performed using the procedures described in detail in chapter 2.

4.2.1 Effect of different amine extractants on the distribution coefficient of lanthanum.

Firstly the solvents (extractants) were equilibrated by contacting with 0.5M sulfuric acid for 5 minutes. To 5 ml of the sulfate liquor (lanthanum initial concentration 5.22×10^{-3} $Mol.dm^{-3}$), 5 ml of solutions of different extractants (amines) in CCl_4 were added in the same concentration (0.1M), and the solutions were shaken for 10 minutes at room temperature to attain equilibrium state. The optimum extractant is TiOA in CCl_4 as can be seen from the data reported in Table 4.1 and presented in Fig. 4.1, which gives the highest distribution coefficient.

Table 4.1: Effect of different amine extractants on the distribution coefficient of lanthanum.

Amine	Lanthanum % extraction	Distribution coefficient
Tri-*iso*octyl amine (1)	**92.80**	**12.89**
Tri-n-octylamine (2)	**90.00**	**9.00**
Tris(2-aminoethyl)amine (3)	**88.00**	**8.00**
Triethylamine (4)	**85.60**	**5.94**

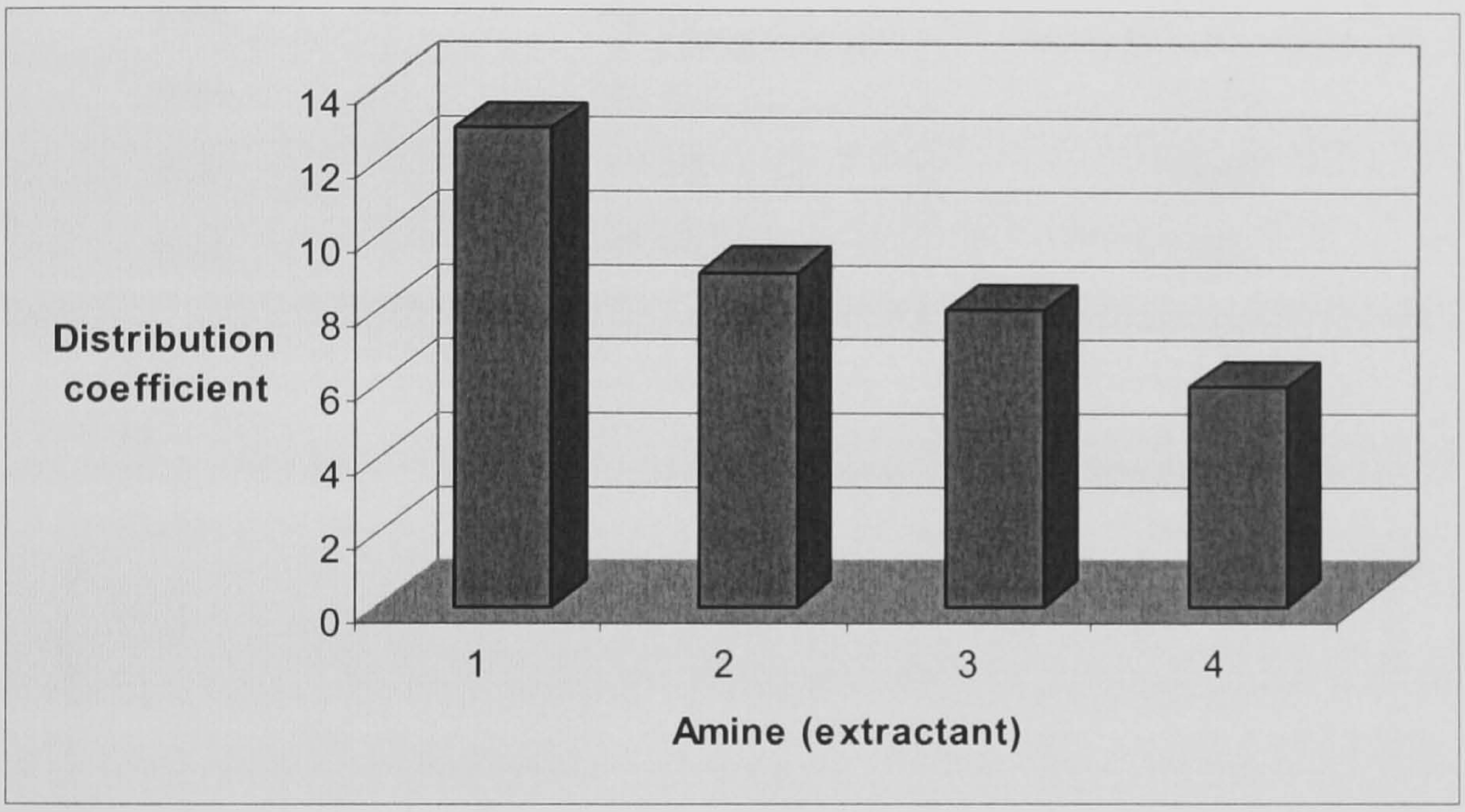


Figure 4.1: Effect of different amine extractants on the distribution coefficient of lanthanum.

4.2.1.2 Effect of different concentrations of tri-*iso*octyl amine in carbon tetrachloride on the distribution coefficient of lanthanum.

Firstly the solvent was equilibrated by contacting it with sulfuric acid solution (pH 2.5) for 10 minutes. To 10 ml of the sulfate liquor at pH 2.5, 10 ml of a solution of TiOA in CCl_4 was added with concentrations ranging from 0.02 to 0.15M. The solution was then shaken for 10 minutes at room temperature to attain equilibrium state. The optimum value of a 0.1M solution of TiOA in CCl_4 was seen from the data reported in Table 4.2 and represented in Fig. 4.2, by increasing TiOA concentration the distribution coefficient is increased further increase above 0.1M TiOA there is a plateau.

Table 4.2: Effect of concentration of TiOA on the distribution coefficient of lanthanum from sulfuric acid medium.

[TiOA]/M	Lanthanum % extraction	Distribution coefficient
0.02	88.60	7.77
0.04	90.40	9.42
0.06	91.80	11.19
0.08	92.40	12.16
0.1	92.80	12.89
0.15	92.90	13.08

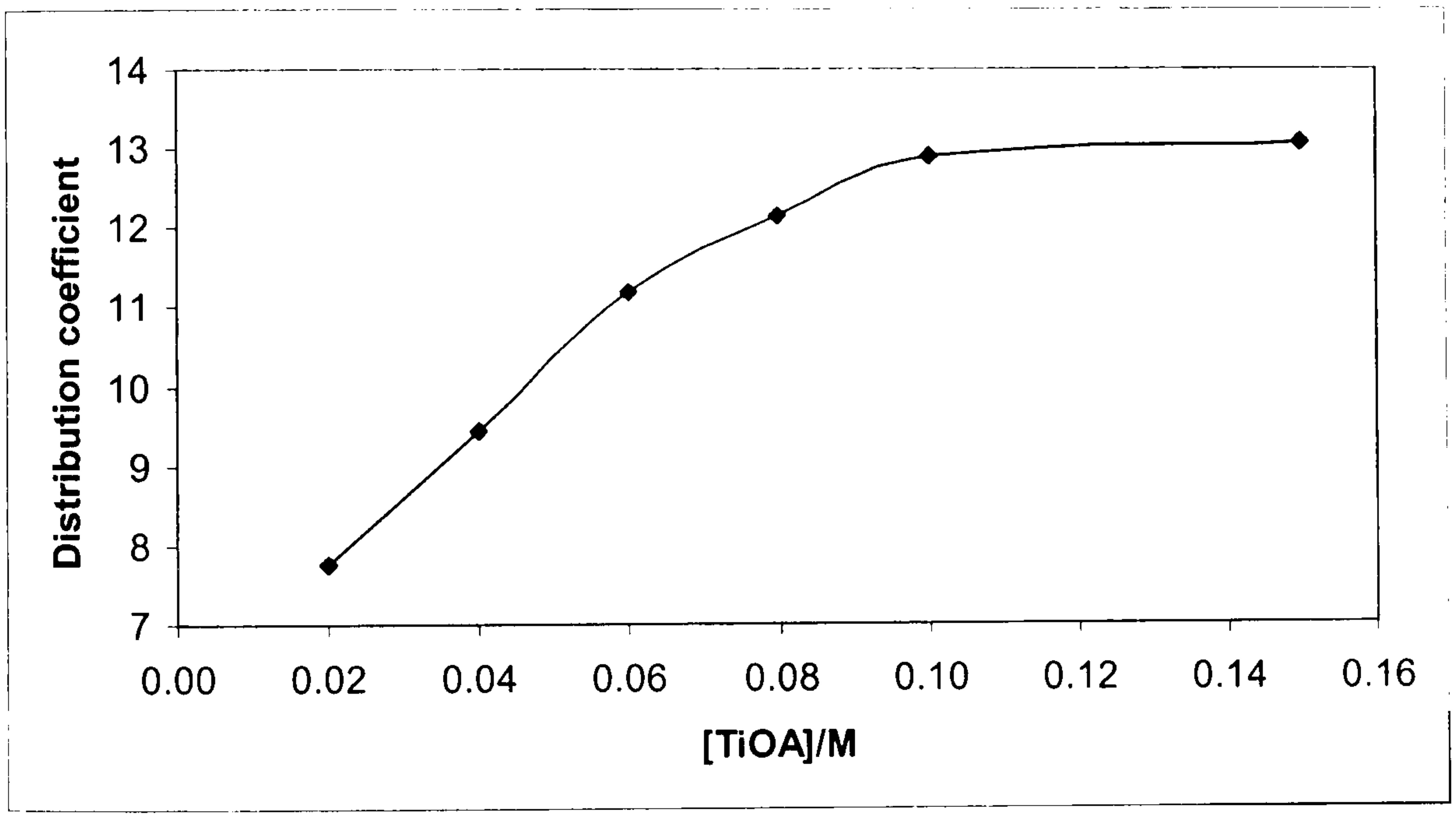


Figure 4.2: The effect of concentration of TiOA on the distribution coefficient of lanthanum from sulfuric acid medium.

4.2.1.3 Effect of equilibration time on the distribution coefficient of lanthanum.

The effect of contact time on the attainment of an equilibrium state was studied at intervals between 1–30 minutes, while the other factors were kept as previously mentioned. The results obtained are given in Table 4.3 and shown in Fig. 4.3. It is obvious that contact time of 5 minutes is quite adequate for efficient lanthanum distribution coefficient and by increasing the shaking time the distribution coefficient is decreased, and this behaviour was similar to that explained in section 2.9.

Table 4.3: Effect of contact time on the distribution coefficient of lanthanum.

Time/minutes	Lanthanum % extraction	Distribution coefficient
1	88.80	7.93
5	93.00	13.29
10	92.80	12.89
15	91.60	10.90
20	90.20	9.20
30	89.00	8.09

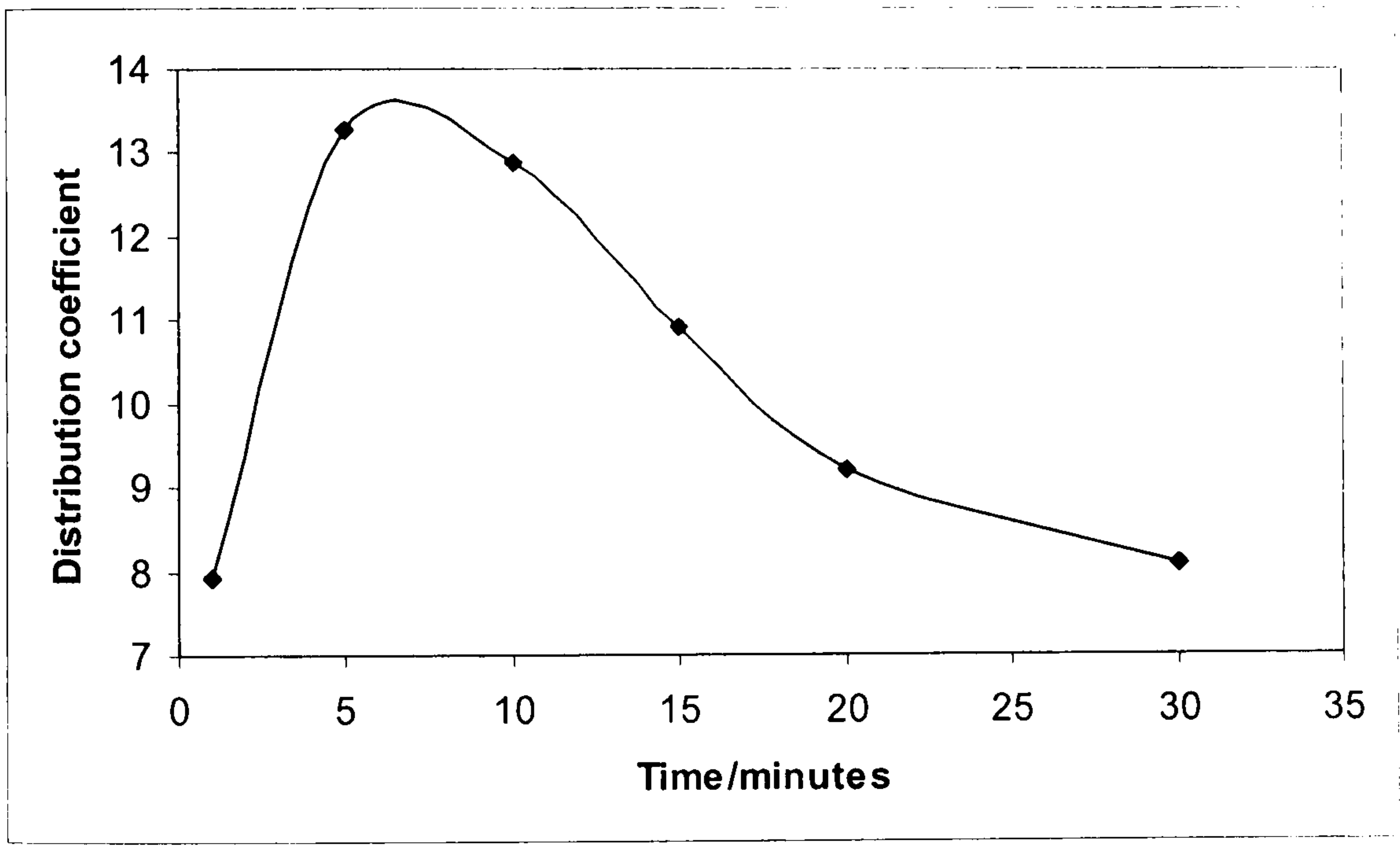


Figure 4.3: The effect of contact time on the distribution coefficient of lanthanum.

4.2.1.4 Effect of pH on the distribution coefficient of lanthanum.

The distribution coefficient has been studied by varying the pH values of the sulfate liquor from 0.7 to 5.9, using either sulfuric acid or sodium hydroxide. Other factors were fixed at 1:1 (v/v) organic to aqueous phase ratio, 0.1M TiOA in carbon tetrachloride, contact time 5 minutes and the experiments were carried out at room temperature. The results obtained are given in Table 4.4 and shown in Fig. 4.4. It is clear that the pH 1.1 of the sulfate liquor can be taken as an optimum pH value. Fortunately, that is the same pH of the parent sulfate liquor under examination. The reason for the decrease in lanthanum distribution coefficient was illustrated in section 2.10.

Table 4.4: Effect of pH on the distribution coefficient of lanthanum.

pH	Lanthanum % extraction	Distribution coefficient
0.70	90.00	9.00
0.80	91.60	10.90
1.10	93.20	13.71
1.82	92.60	12.51
2.00	92.20	11.82
2.50	91.00	10.11
3.10	90.80	9.87
3.90	90.60	9.64
5.90	90.60	9.64

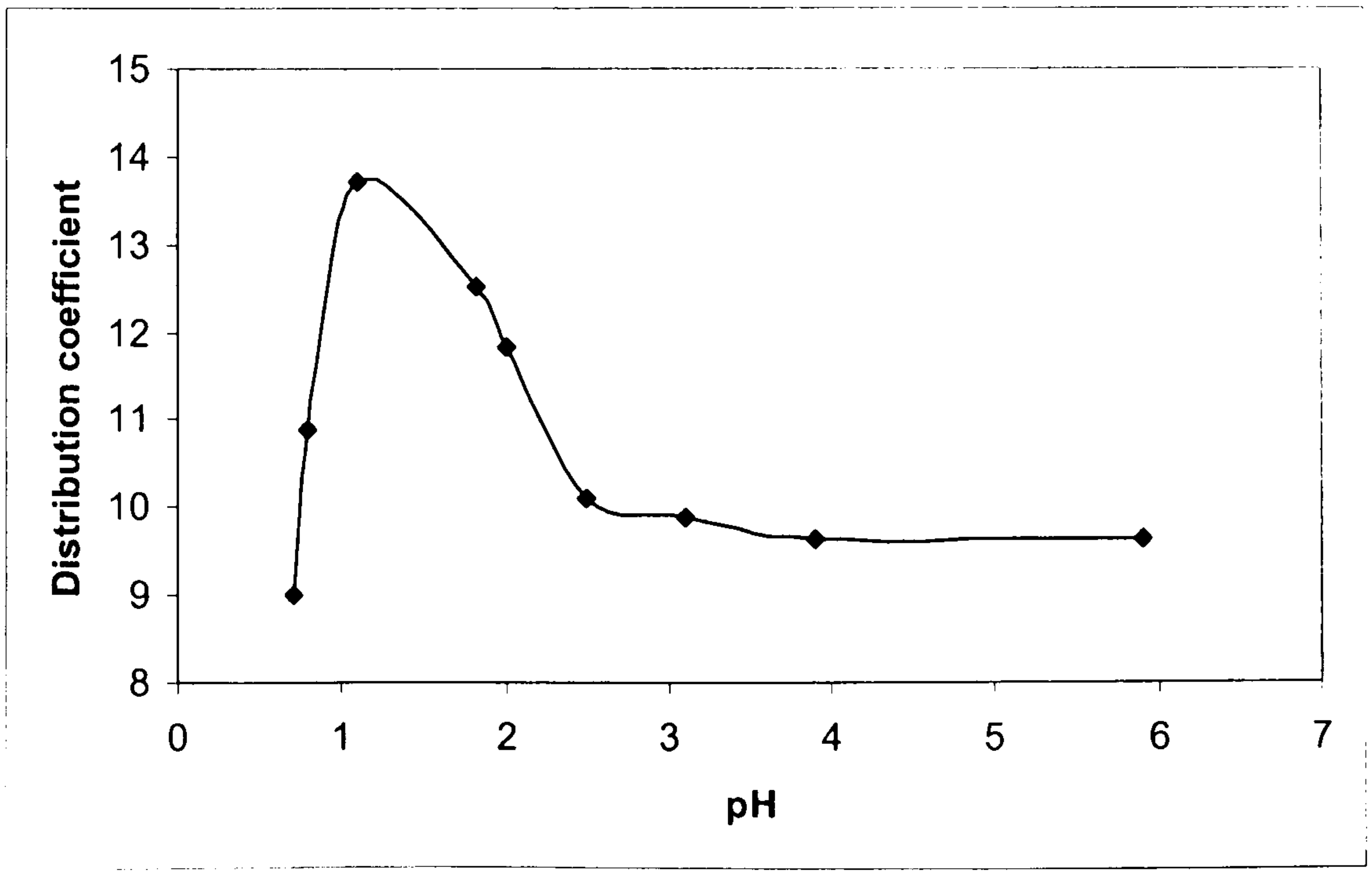


Figure 4.4: Effect of pH on the distribution coefficient of lanthanum.

4.2.1.5 Effect of temperature on the distribution coefficient of lanthanum.

For studying the effect of temperature on the distribution coefficient and extraction percent, experiments were carried out in oil bath using an electric thermostat, the temperature of which was regulated from 20–60°C. The following factors were kept constant at 1:1 (v/v) organic to aqueous phase ratio, pH 1.1, a contact time of 5 minutes, carbon tetrachloride as diluent and 0.1M TiOA. From the obtained results (Table 4.5 and Fig. 4.5) it is clear that room temperature can be considered as the best temperature for lanthanum distribution coefficient. It is obvious from the data obtained, that distribution coefficient decreases with increasing temperature. This means that the extraction of lanthanum is exothermic. This behaviour is similar to that reported by previous investigators. (12, 13)

Table 4.5: Effect of temperature on the distribution coefficient of lanthanum.

Temperature, °C	Lanthanum % extraction	Distribution coefficient
20	93.20	13.71
25	92.80	12.89
32	92.00	11.50
38	91.00	10.11
45	90.00	9.00
52	89.00	8.09
60	88.00	7.30

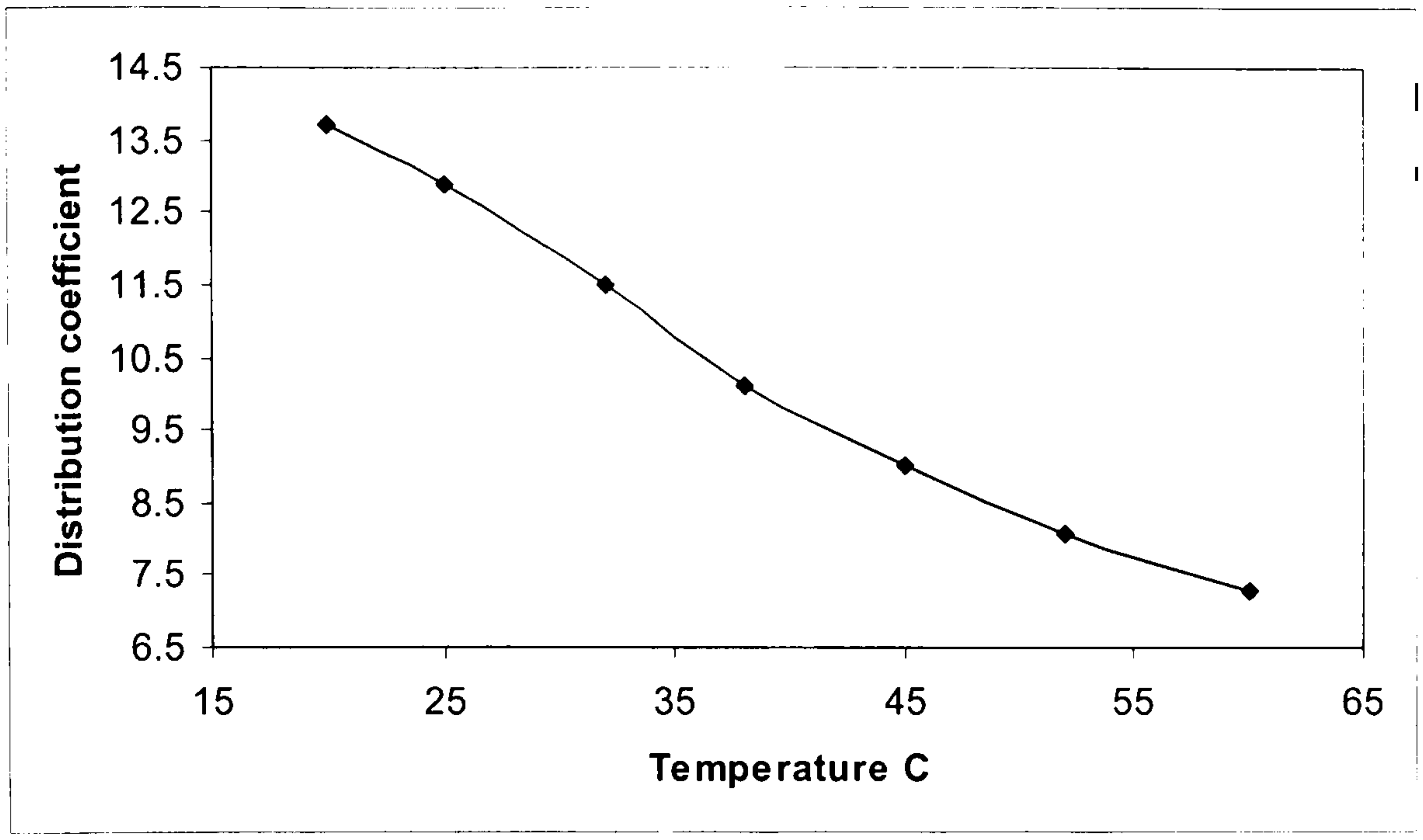


Figure 4.5: Effect of temperature on the distribution coefficient of lanthanum.

4.2.1.6 Effect of diluent on the distribution coefficient of lanthanum.

The distribution coefficient of lanthanum has been studied using different organic diluents, namely chloroform, carbon tetrachloride, toluene, benzene, *o*-xylene, dichloromethane, and kerosene. The other factors were fixed at the values at which maximum distribution coefficient occurred i.e. 1:1 (v/v) organic to aqueous phase ratio, room temperature, 0.1M tri–*iso*octylamine in all diluents, and a contact time of 5 minutes. Results are presented in Table 4.6. It is obvious that although benzene and toluene have dielectric constant of the same order of magnitude as that of carbon tetrachloride, both are less efficient at extraction of lanthanum. This is probably due to the lower solubility of the extracted species in these diluents as compared with carbon tetrachloride. This is probably a function of the different intermolecular diluent:diluent and solvent:diluent interactions that occur in aromatic and non-aromatic diluents. It is clear from Table 4.6 and Fig.4.6 that carbon tetrachloride is the best diluent.

Table 4.6: Effect of diluent on the distribution coefficient of lanthanum.

Diluents		Lanthanum % extraction	Distribution coefficient
Chloroform	(1)	92.80	12.89
Carbon tetrachloride	(2)	93.00	13.29
Toluene	(3)	92.00	11.50
Benzene	(4)	91.00	10.11
O-xylene	(5)	91.40	10.63
Dichloromethane	(6)	90.80	9.87
Kerosene	(7)	90.00	9.00

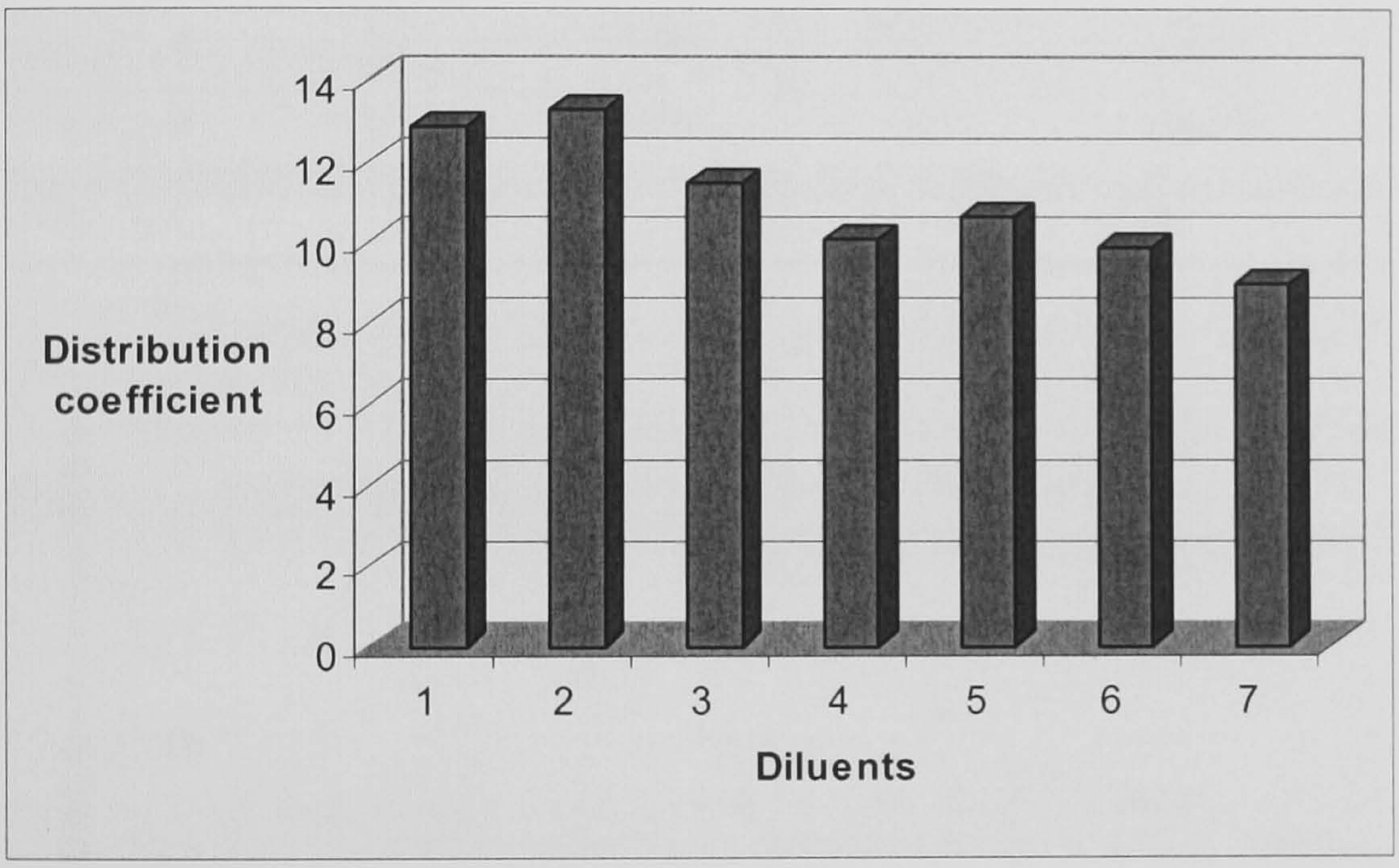


Figure 4.6: Effect of diluent on the distribution coefficient of lanthanum.

4.2.1.7 Distribution coefficients of lanthanum as a function of aqueous H_2SO_4 concentration.

Fig. 4.7 shows the effect of concentration of H_2SO_4 on the distribution coefficients of lanthanum in the two phases. The distribution coefficient of lanthanum increases as the concentration of H_2SO_4 increases from 0.5-2.0M, but then decreases as the acid concentration is increased further. The reason for this high-concentration decrease is unknown. However, the best concentration of H_2SO_4 to use for lanthanum highest distribution coefficient is clearly 2M. Other factors in this experiment were fixed at

1:1 v/v organic to aqueous phase ratio, 0.1M TiOA in carbon tetrachloride, mixing time 5 minutes and the experiments were carried out at room temperature. The results obtained are given in Table 4.7 and Fig. 4.7.

Table 4.7: Effect of sulfuric acid concentration on the distribution coefficient of lanthanum.

$[H_2SO_4]$/M	Lanthanum % extraction	Distribution coefficient
0.5	92.60	12.51
1	93.00	13.29
2	93.20	13.71
4	92.40	12.16
6	92.00	11.50

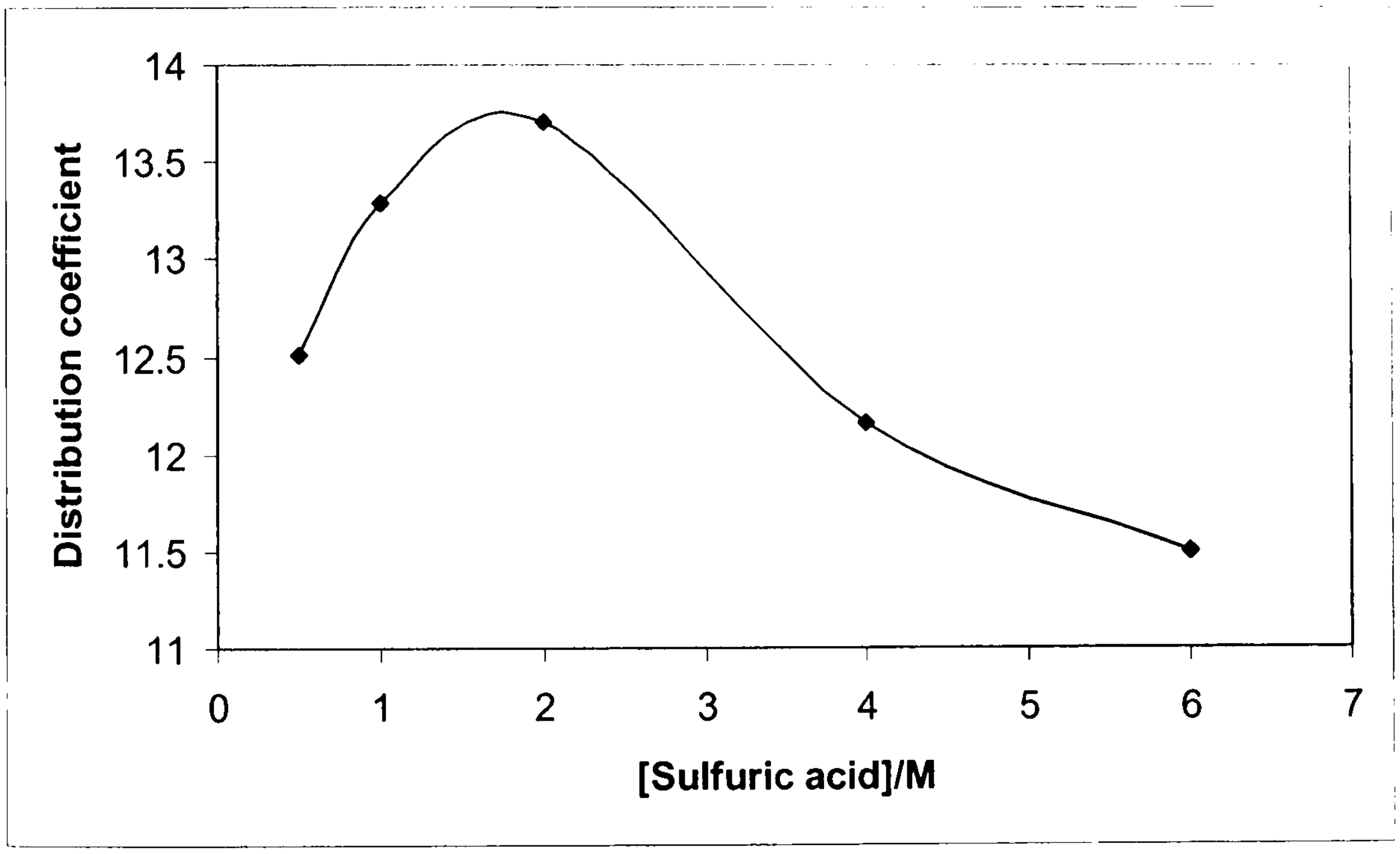


Figure 4.7: Effect of sulfuric acid concentration on the distribution coefficient of lanthanum.

4.2.1.8 Effect of TOPO (trioctyl phosphine oxide) on the distribution coefficient of lanthanum (synergistic effect).

A stock solution of TOPO (0.1M in carbon tetrachloride) was added to 0.1M TiOA/carbon tetrachloride in differing amounts. Table 4.8 and Fig. 4.8 show that by increasing the percentage of TOPO, there is an increase in the distribution coefficient of lanthanum, indicating that TOPO is a synergistic enhancer in the extraction of lanthanum, until 40 % volume of TOPO solution has been added. After this the distribution coefficient of lanthanum decreases, probably due to complex formation between TiOA and TOPO being more favourable than complexation with lanthanum. (14)

Table 4.8: Effect of TOPO concentration on the distribution coefficient of lanthanum (synergistic effect).

% TOPO by volume	% Extraction	Distribution coefficient
10	92.60	12.56
20	93.00	13.28
30	93.40	14.15
40	93.60	14.63
50	91.40	10.63

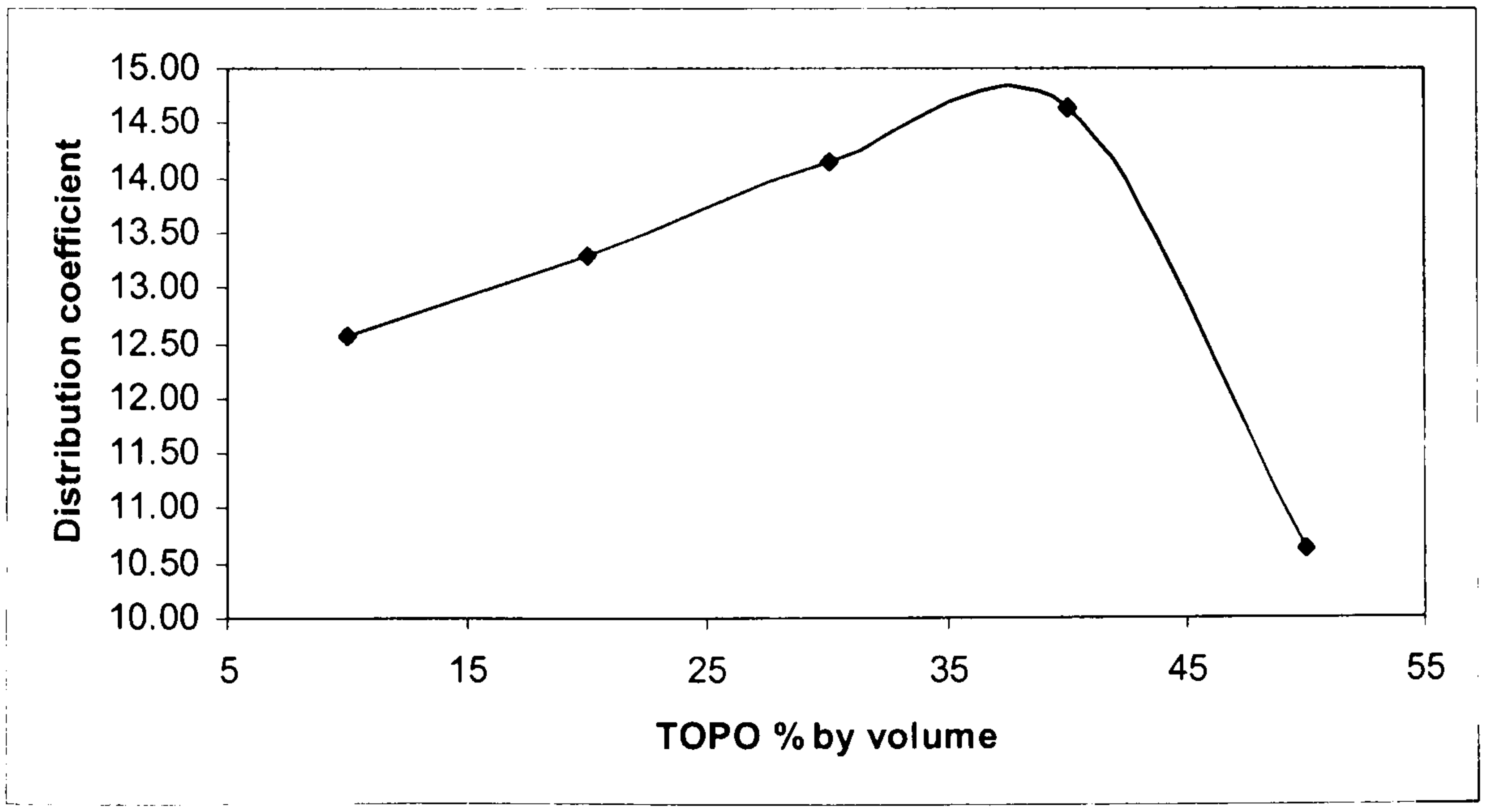


Figure 4.8: Effect of TOPO concentration on the distribution coefficient of lanthanum (synergistic effect).

4.2.1.9 Effect of D2EHPA (di-2-ethylhexyl phosphoric acid) on the distribution coefficient of lanthanum (synergistic effect).

A stock solution of D2EHPA (0.1M in carbon tetrachloride) was added to 0.1M TiOA/carbon tetrachloride in different amounts. Table 4.9 and Fig. 4.9 show that by increasing the amount of D2EHPA added there is an increase in the distribution coefficient of lanthanum. This means that D2EHPA is a synergistic enhancer in the extraction of lanthanum. Little is known of the formation of mixed complexes in amine extraction systems. Some evidence suggests that the synergistic extraction of uranium (15, 16) occurs with mixtures of tri-n-octylamine and D2EHPA from high concentrations of sulfate. In addition to forming the amine organophosphate salt, the phosphate species also coordinates to the metal and enhances the distribution coefficient.

Table 4.9: Effect of D2EHPA concentration on the distribution coefficient of lanthanum (synergistic effect).

% D2EHPA by volume	% Extraction	Distribution coefficient
10	93.00	13.28
20	93.60	14.63
30	94.00	15.66
40	94.40	16.85
50	94.6	17.52

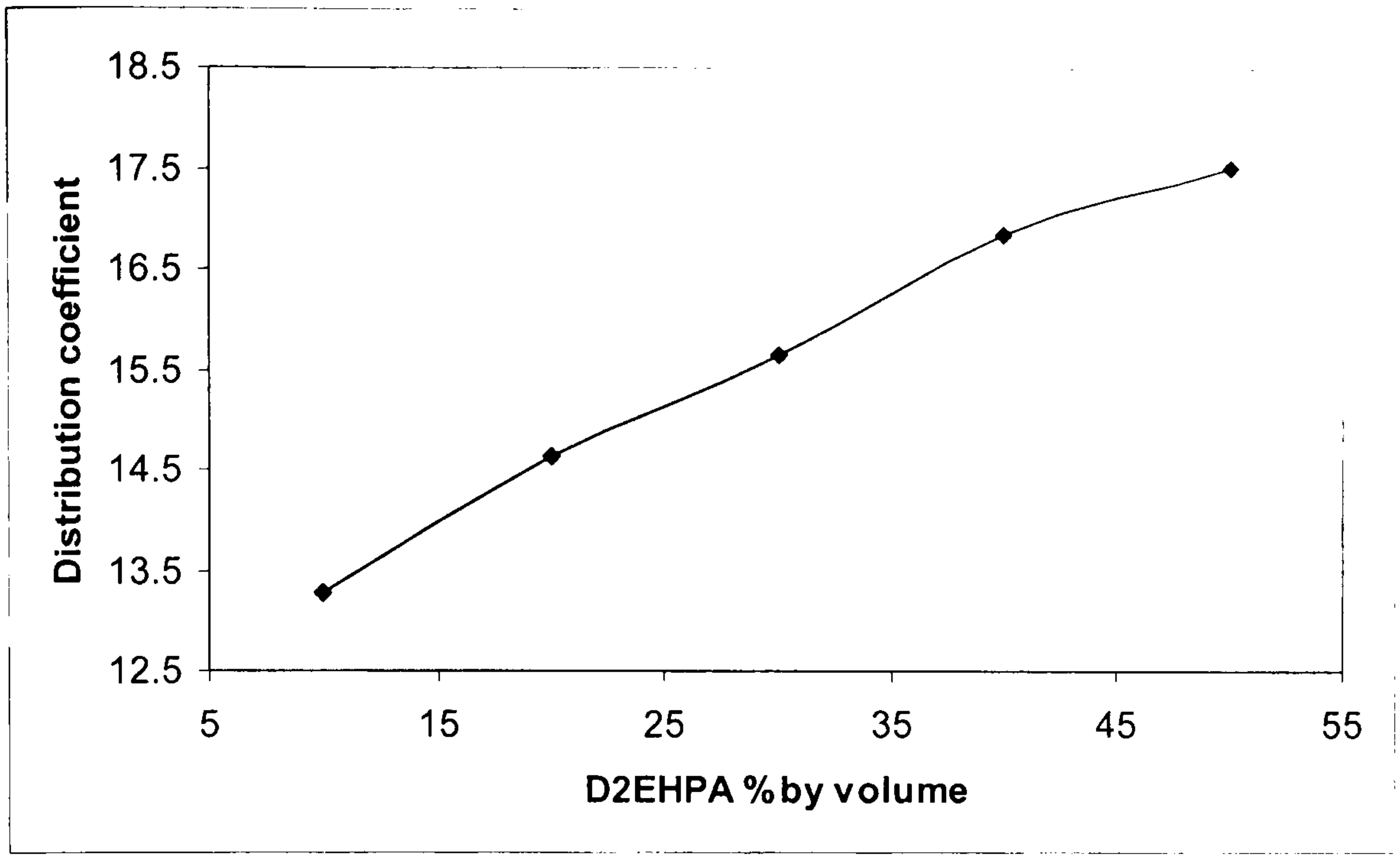


Figure 4.9: Effect of D2EHPA concentration on the distribution coefficient of lanthanum (synergistic effect).

4.2.1.10 Effect of TBP (tributyl phosphate) on the distribution coefficient of lanthanum (synergistic effect).

A stock solution of TBP (0.1M in carbon tetrachloride) was added to 0.1M TiOA/carbon tetrachloride in differing amounts. Table 4.10 and Fig. 4.10 show that upon increasing the percentage of TBP up to 20 % there is an increase in the distribution coefficient of lanthanum, followed by a decrease at higher concentration. This may be because the reaction between extractants might be more favourable than complexation with the lanthanum. (17, 18)

Table 4.10: Effect of TBP concentration on the distribution coefficient of lanthanum (synergistic effect).

TBP % by volume	Lanthanum % extraction	Distribution coefficient
10	94.20	16.24
20	95.00	19.00
30	94.40	16.86
40	93.80	15.13
50	93.70	14.87

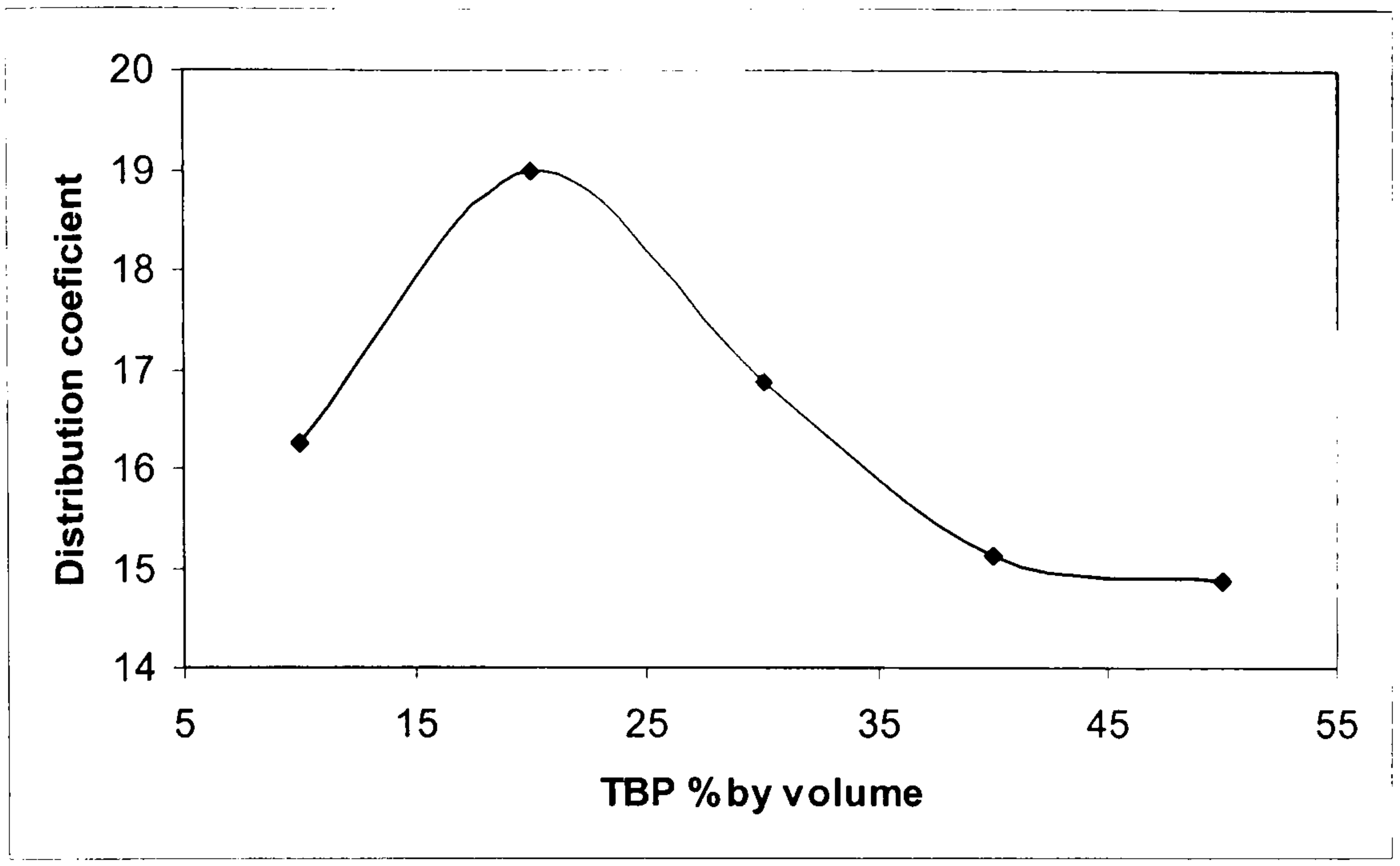


Figure 4.10: Effect of TBP concentration on the distribution coefficient of lanthanum (synergistic effect).

4.2.2 Scrubbing the loaded solvent (lanthanum).

Washing of the organic phase (loaded solvent) containing lanthanum is carried out several times with deionised water to remove any possible impurities. After this process the organic phase is transferred into a third stage, called the re-extraction step or stripping.

4.2.3 Stripping of lanthanum.

The general procedure for stripping lanthanum in our experiments was as follows: the loaded solvent was contacted with a suitable acid or base strip solution, at an appropriate phase ratio, until equilibrium was attained. The aqueous phase was then removed and analysed for lanthanum. The stripping process depends on a number of factors, which have to be studied in order to obtain the best stripping efficiency that matches at the same time with economic considerations. The factors under consideration were: the effect of different reagents in the strip solution, the effect of reagent concentration, the contact time and the organic/aqueous phase ratio.

4.2.3.1 Effect of sulfuric acid concentrations on the stripping of lanthanum.

A series of stripping experiments were carried out using H_2SO_4 solutions with concentration ranging from 0.5M to 9M. The obtained results are given in Table 4.11 and shown in Fig. 4.11. It is clear from the results that stripping by 6M H_2SO_4 gives the best lanthanum re-extraction percent, while the contact time of 10 minutes, phase ratio 1:1 organic/aqueous, and room temperature were kept constant.

Table 4.11: Effect of sulfuric acid concentration on the stripping efficiency of lanthanum.

[H_2SO_4]/M	**Lanthanum % stripping**
0.5	**12.56**
1	**21.80**
3	**43.22**
6	**75.61**
9	**66.32**

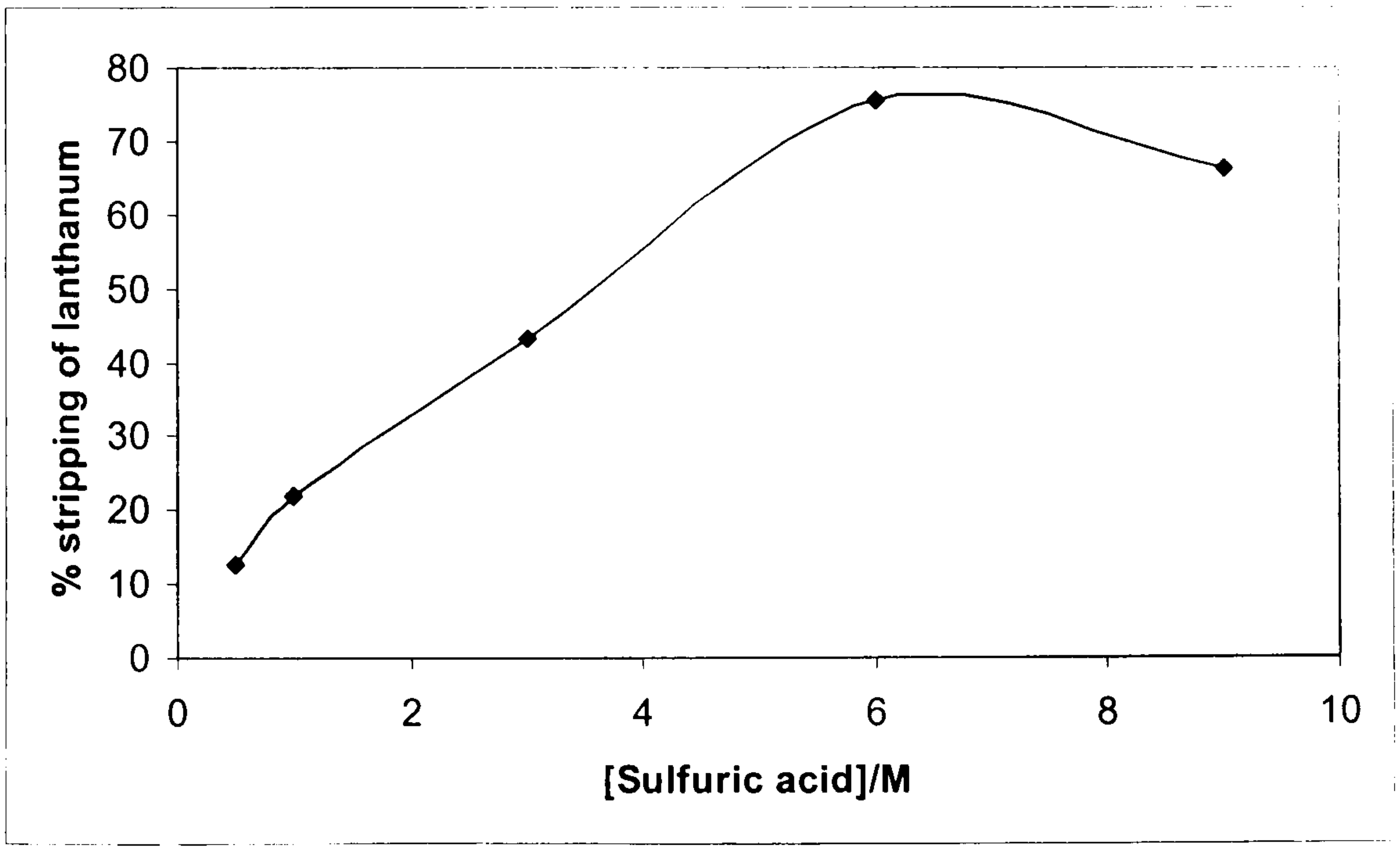


Figure 4.11: Effect of sulfuric acid concentration on the stripping of lanthanum.

4.2.3.2 Effect of different nitric acid concentrations on the stripping of lanthanum.

A series of stripping experiments were carried out using HNO_3 solutions with concentration ranging from 0.5M to 9M. The obtained results are given in Table 4.12 and shown in Fig. 4.12. It is clear from the results that the stripping of lanthanum by HNO_3 increased with increasing the concentration of HNO_3, while the contact time of 10 minutes, with phase ratio 1:1 organic/aqueous, and room temperature were kept constant.

Table 4.12: Effect of nitric acid concentration on the stripping efficiency of lanthanum.

$[HNO_3]$/M	Lanthanum % stripping
0.5	3.08
1	6.05
3	11.52
6	13.63
9	15.27

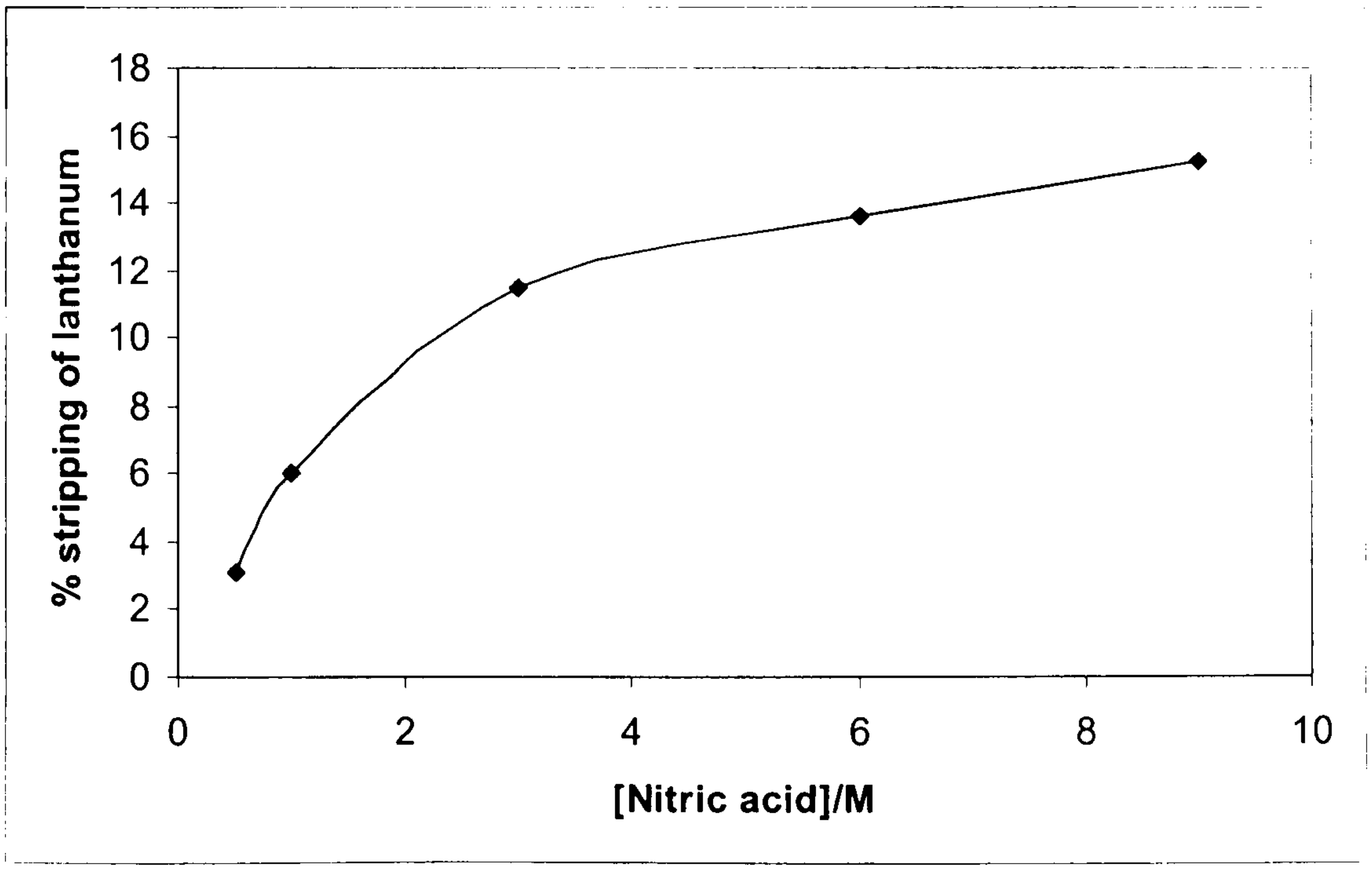


Figure 4.12: Effect of nitric acid concentration on the stripping of lanthanum.

4.2.3.3 Effect of different HCl concentrations on the stripping of lanthanum.

A series of stripping experiments were carried out using HCl solution of concentration ranging from 0.5M to 9M. The obtained results are given in Table 4.13 and shown in Fig. 4.13. It is clear from the results that stripping by 1M HCl gives the best lanthanum re-extraction percent, while the contact time of 10 minutes, phase ratio 1:1 organic/aqueous, and room temperature were kept constant.

Table 4.13: Effect of HCl concentration on the stripping efficiency of lanthanum.

[HCl]/M	Lanthanum % stripping
0.5	4.22
1	17.43
3	15.49
6	12.35
9	9.66

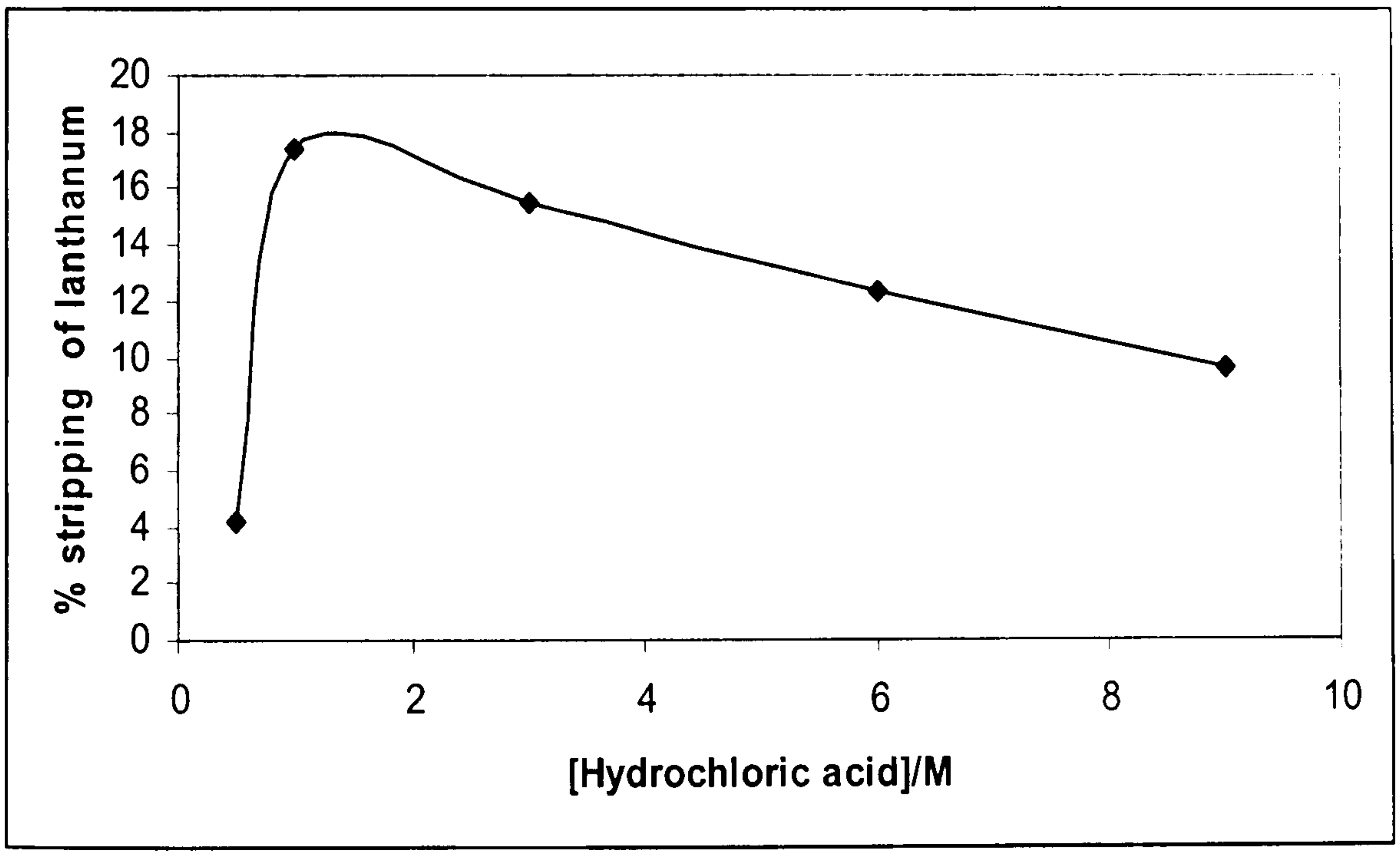


Figure 4.13: Effect of HCl concentration on the stripping of lanthanum.

By comparing the effect of the three different acids on the stripping of lanthanum, (Fig. 4.14) it is clear that 6M H_2SO_4 gives the highest recovery of lanthanum and this will be used in further experiments.

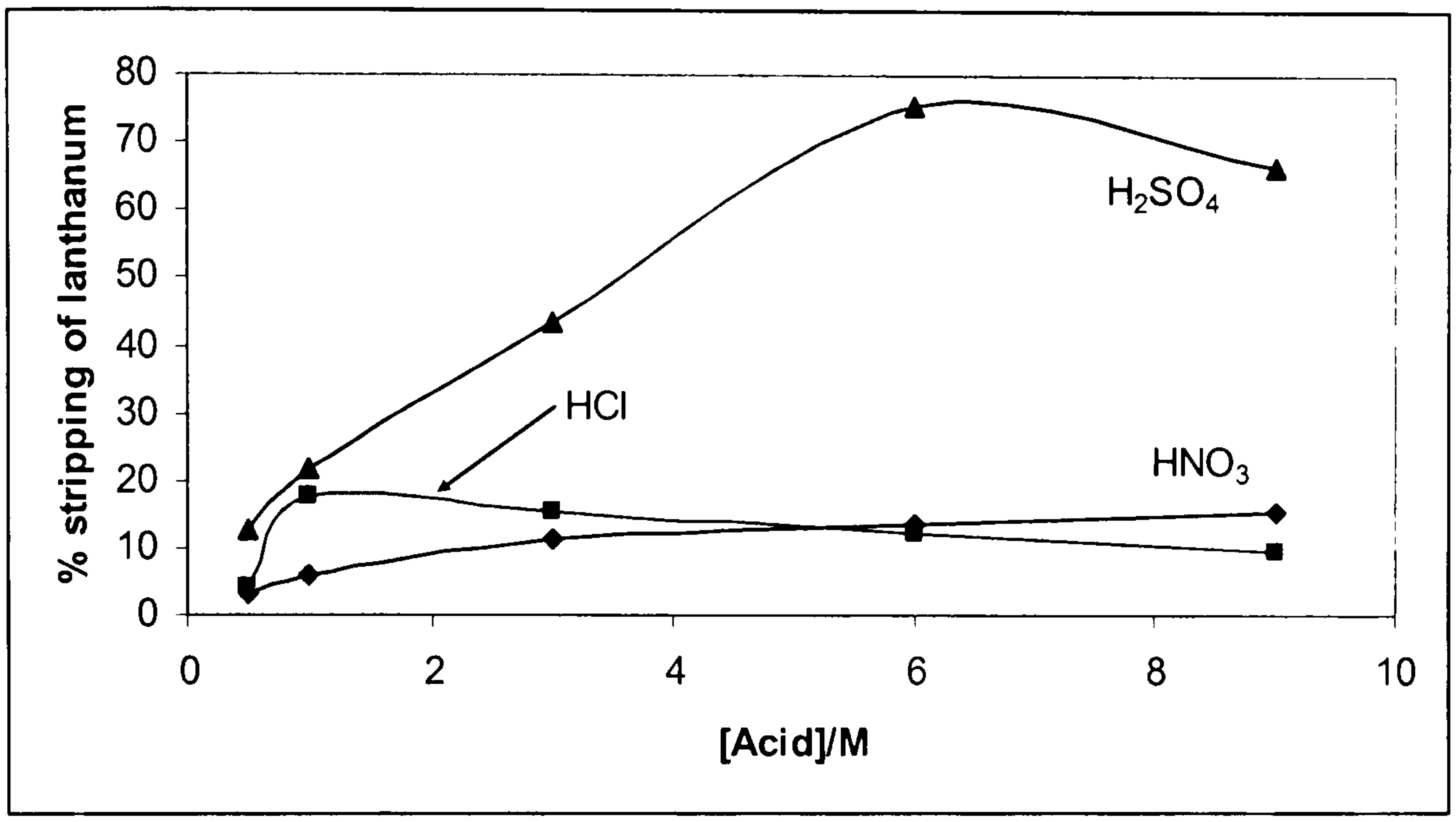


Figure 4.14: Effect of different acids (H_2SO_4, HNO_3, and HCl) on the stripping of lanthanum.

4.2.3.4 Effect of equilibration time on the stripping of lanthanum.

The effect of equilibration time on the attainment of an equilibrium state has been studied at the time interval 1 to 30 minutes, while the other factors were kept at 6M H_2SO_4, 1:1 (v/v) aqueous to organic phase ratio and room temperature. The results obtained are given in Table 4.14 and shown in Fig. 4.15. It is obvious that a contact time of 5 minutes is sufficient for lanthanum stripping from loaded solvent. Indeed, at higher contact times stripping decreases, and this behaviour is similar to that explained in section 3.6.

Table 4.14: Effect of equilibration time on the stripping of lanthanum.

Time/minutes	Lanthanum % stripping
1	70.18
5	75.82
10	66.04
20	54.23
30	53.44

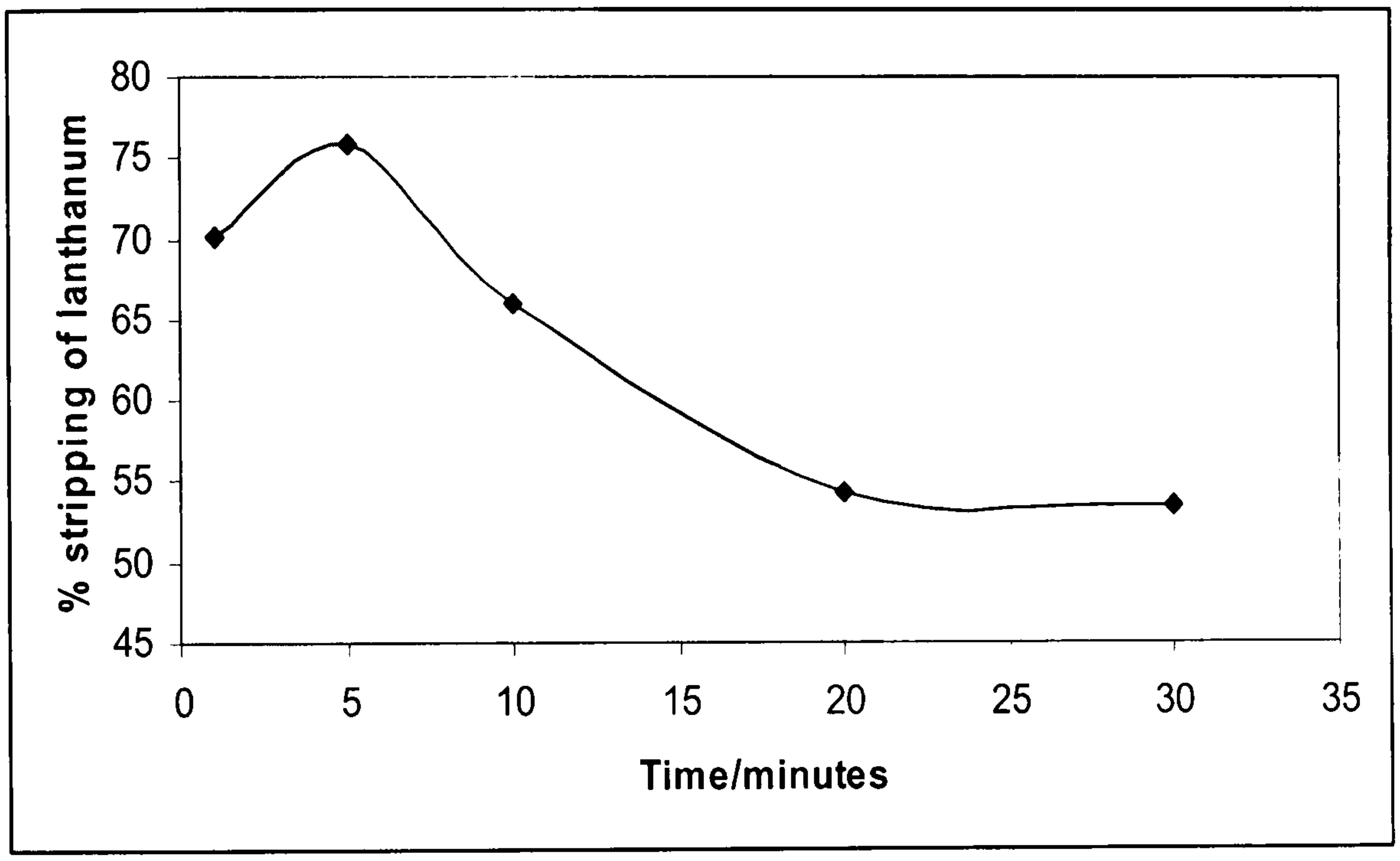


Figure 4.15: Effect of mixing time on the stripping efficiency of lanthanum.

4.2.4 Conclusions

A study of the liquid-liquid extraction of lanthanum using different amines such as tri-*iso*octylamine, tri-n-octylamine, tris(2-aminoethyl)amine, and triethylamine has been described. The experiments indicate that tri-*iso*octylamine (TiOA) gives the highest distribution coefficient efficiency. The optimum conditions for solvent extraction of lanthanum from sulfate solution by using (TiOA) dissolved in carbon tetrachloride have been investigated. The optimum conditions are: concentration of TiOA 0.1M, contact time 5 minutes, pH 1.1, the best diluent is carbon tetrachloride, room temperature, and 2M H_2SO_4 as an aqueous composition. Also, there is synergistic effect when using D2EHPA, which is useful in the separation of lanthanum from light rare earth elements. Scrubbing the loaded solvent can be achieved with distilled water. The optimum conditions for the stripping of lanthanum are: 6M H_2SO_4 and contact time 5 minutes.

The separation of rare earth elements into individual elements is very difficult to achieve, due to the very low separation factors involving the adjacent rare earth elements. The liquid-liquid extraction of lanthanum was different from that of Ce(III) and Y(III) because there are systematic differences in their basicity, which decreases from Lanthanum to Y(III). (19) So, the acidity of these elements that increases from lanthanum to Y(III) is related to a systematic and smooth decrease in ionic radii of rare earth elements, known as the lanthanide contraction, which increases with the atomic number in the lanthanide series. (4, 5)

By comparison the data of liquid-liquid extraction of lanthanum, Ce(III) and Y(III), the experiments indicate that TiOA gives the highest distribution coefficient at 0.08M, 0.1M and 0.1M for Y(III), Ce(III) and lanthanum respectively. The best diluent is carbon tetrachloride for both Y(III) and lanthanum but Ce(III) is chloroform. The stripping of lanthanum is carried out by 6M H_2SO_4 while 10M H_2SO_4 is the optimum concentration for Y(III) stripping. Also, 3M HNO_3 is the best stripping agent concentration for Ce(III). However, they are all similar in equilibration time that 5 minutes is quite adequate for highest extraction and room temperature is suitable and economic for the process of solvent extraction. Attempts to use these differences to separate mixtures of these elements are described in subsequent chapters.

4.2.5 References

1 Y. Nagaosa, Y. Binghua, *Sep. Sci. Technol.*, (1997) **32**, 1053.

2 P. Maestro, D. Hugenin, *J. Alloys Compd.*, (1995) **25**, 520.

3 J. M. Sànchez, M. hidalgo, V. Salvadò, *Solv. Extr. Ion Exch.*, (1999) **17**, 455.

4 K. A. Gschneider jr., Symposium on Speciality Inorganic Chemistry, The Royal Society of Chemistry, London, (1980), 403.

5 C. V. Sundaram, *Trans. Indian Inst. Met.*, (1987) **40**, 457.

6 Ramakul, parkorn; Panchareon, Ura. Proceedings of the Kasetstart University Annual Conference, 41st, Bangkok, Thailand, Feb.3-7, 2003, (2003).

7 Y. K. Agrawal; S. B. Vora; G. Shah, *Indian Journal of Chemistry*, (2005), **44** A(3), 497.

8 Md. I. Salah, Md. F. Bari, B. Saad *J. Hydrometallurgy*, (2002) **63**, 75.

9 C. A. Morais, V. S. T Ciminelli *J. Hydrometallurgy*, (2004) **73**, 237.

10 M. Curtui, I. Haiduc *J. Radioanal. Nucl. Chem.*, (1992) **164**, 91.

11 J. Noro, T. Sekine, *Bulletin of the Chemical Society of Japan*, (1993) **66**, 2564.

12 S. B. Savvin, Organic Reagents of the Arsenazo III Group, Atomizdat, Moscow, (1971).

13 W. Youshao, S. Chaohong, S. Guoxin, Z. Jiankang, and B. Borong; Pro. of the Int. Conf. on Uranium Extraction, China, (1996) 84.

14 T. Cecconie, H. freiser, *Anal. Chem.*, (1990) **62**, 622.

15 C. Deptula, S. Minc, *J. Inorg. Nucl. Chem.*, (1967) **29**, 159.

16 D. Nucciarone, C. D. Pagnucco, B. Jakovljevic, W. A. Rickelton, Solvent Extraction Conference-ISEC'99, Proceedings Vol. 2, Society of Chemical Industry-SCI, London, (2001), 1133.

17 M. Majdan, *Hydrometallurgy*, (1994) **35**, 179.

18 J. N. Mathur, G. R. Choppin, *Solv. Extr. Ion Exch.*, (1998) **16**, 739.

19 L. –F. Qiu, X. –H. Kang, and T. –S. Wang, *Sep. Sci. Technol.*, (1991) **26**, 199.

Chapter Five

Liquid-liquid extraction of binary and ternary element systems

5.1 Introduction.

The separation of the rare earth elements poses one of the most difficult problems in inorganic chemistry. Due to the great similarity of their chemical properties, the methods available are generally not very selective. In a few cases, much better separation can be achieved by conversion to another oxidation state of adequate stability ($Ce^{3+} \rightarrow Ce^{4+}$, $Eu^{3+} \rightarrow Eu^{2+}$). A further difficulty is presented by the unfavourable distribution of concentrations of individual rare earth metals in the common minerals. The method of separation must therefore be selected to suit the existing ratios. The first step is a preliminary separation into groups of elements that resemble each other very closely.

5.1.1 Principles of Separation. (1)

Two principal types of process are used for the extraction of rare earth elements. Solid–liquid systems use fractional precipitation or crystallization, or ion exchange. Ion exchange processes are used in the production of small quantities of higher value heavy rare earth elements. Second, liquid–liquid systems using solvent extraction. This process is the most commonly used commercial process for the extraction of rare earth elements.

The distribution of two rare earth elements RE_A and RE_B between the two phases is given by the equilibrium constants K_A and K_B:

$$K_A = \frac{\overline{[RE_A]}}{[RE_A]} \text{ and } K_B = \frac{\overline{[RE_B]}}{[RE_B]} \tag{1}$$

where $[RE]$ and $\overline{[RE]}$ represent the concentrations in the aqueous and non-aqueous phase, respectively. The selectivity of this separation system is given by the separation factor $\alpha_{RE_B} / _{RE_A}$ where

$$\alpha_{RE_B} / _{RE_A} = K_B/K_A \tag{2}$$

More correctly, activities should be used instead of concentrations. In practice, apparent equilibrium constants based on concentrations are adequate because work is carried out at low concentration. In the following discussion, these apparent constants are used throughout. The processes of fractional crystallization or fractional precipitation are now mainly having historic interest only. The separation factor corresponds to the solubility ratio of the two rare earth elements in the aqueous phase. In the case of ion exchange or liquid–liquid extraction, the ratio of the distribution coefficients is a measure of the different affinities of the rare earth metals for the two phases.

For the trivalent ions of neighbouring rare earth elements, the separation factor is low for all methods. For precipitation or crystallization, $\alpha = 1.1$ to 5; for separation by ion exchange with addition of complexing agents, $\alpha = 1.1$ to 10; and for liquid–liquid extraction, $\alpha = 1.1$ to 5. For an effective separation, many repetitions of a single separation operation are necessary, which can be carried out batch-wise or continuously. With ion exchange separation, although the establishment of equilibrium is continually repeated, the overall process is discontinuous, since continuous feeding is not possible. However, it has the advantage that several rare earth elements can be separated at the same time.

A fully continuous liquid–liquid extraction process in counter current flow with partial recycle enables separation to be achieved into two groups or two individual rare earth elements of high purity. The production of three pure rare earth elements requires two batteries of separation equipment. This limitation is, however, compensated for by the advantage of continuous operation. A further characteristic of a separation process is the size of the apparatus required. This depends on the concentration of the rare earth elements in the two phases. Cationic ion exchangers have a high capacity (ca. 150 g REO/L), but elution in the presence of complexing agents requires very dilute solutions (ca. 5–10 g REO/L). These separation plants are therefore very bulky. In the liquid–liquid extraction process, the capacity of the solvent can be very high (170–90 g REO/L), and it is therefore often possible to work with aqueous solutions with concentrations of 100–140 g REO/L, i.e., approaching saturation. The equipment is therefore compact.

5.1.2 Separation by Classical Methods. (2-4)

5.1.2.1 Fractional Crystallization. (1)

Fractional crystallization was the first process for separating the rare earth elements, both in the laboratory and on an industrial scale. It is no longer of importance.
The purification effect decreases with increasing purity of the crystals, so the final purity achievable by this method is therefore limited. Also, many intermediate fractions are produced that must be reprocessed. In general, this process is more problematic for the yttrium earths than the cerium earths (yttrium and cerium earths are described previously in chapter (3) and reported in Table 3.1). The cerium earths were therefore separated by fractional crystallization and the yttrium earths by ion exchange. The cerium earths were converted to nitrates after oxidation of the cerium to the tetravalent state, and the double nitrates $NH_4NO_3{\cdot}RE(NO_3)_3{\cdot}4H_2O$ were crystallized. Pechiney Saint Gobain produced 99.9 % pure lanthanum in five crystallization stages, this salt being the most soluble. Yttrium was first precipitated as its dichromate and then purified by ion exchange.

5.1.2.2 Separations Based on Oxidation State Changes.

Cerium(IV) or europium(II) can be economically separated from the other rare earth metals by precipitation, ion exchange, or liquid–liquid extraction. Cerium can be oxidized by oxidizing agents such as hypochlorite, hydrogen peroxide, atmospheric oxygen, or electrolytically at a suitable pH, precipitating it as cerium(IV) oxide hydrate. By adding chlorine and sodium hydroxide solution to a solution of cerium earth chlorides, cerium(IV) oxide hydrate is precipitated. This can be converted to a 90 % pure cerium oxide that is suitable for use as a polishing material. The separation of tetravalent cerium from the trivalent rare earth elements by liquid–liquid extraction is described in previous works. (5-7)

Divalent europium has properties similar to those of the alkaline earths, especially strontium (insoluble sulfate, soluble hydroxide, etc.). The rare earth metals are usually reduced in hydrochloric acid solution by zinc amalgam or sodium amalgam. The subsequent precipitation of europium sulfate from the very dilute solution can be improved by co precipitation of strontium or barium sulfate. The europium can be further purified by precipitating trivalent elements as their hydroxides using ammonia. Under these conditions, Eu^{2+} remains in solution. (8) The separation of divalent europium from the trivalent rare earth elements by liquid–liquid extraction is described. The main problem in separating europium is its low content in the ores compared with the other rare earth metals. The classical minerals such as bastnaesite contain only 0.12 % Eu_2O_3 based on total REO content. Therefore a strongly enriched solution must first be prepared, from which the europium can be precipitated as its sulfate after first converting it to the divalent state. The process used by Molycorp, Inc. is shown in Fig. 5.1. (9) The extraction consists of two consecutive cycles with several separation units operating with DEHPA. These concentrate the europium by a factor of 100 before it is precipitated.

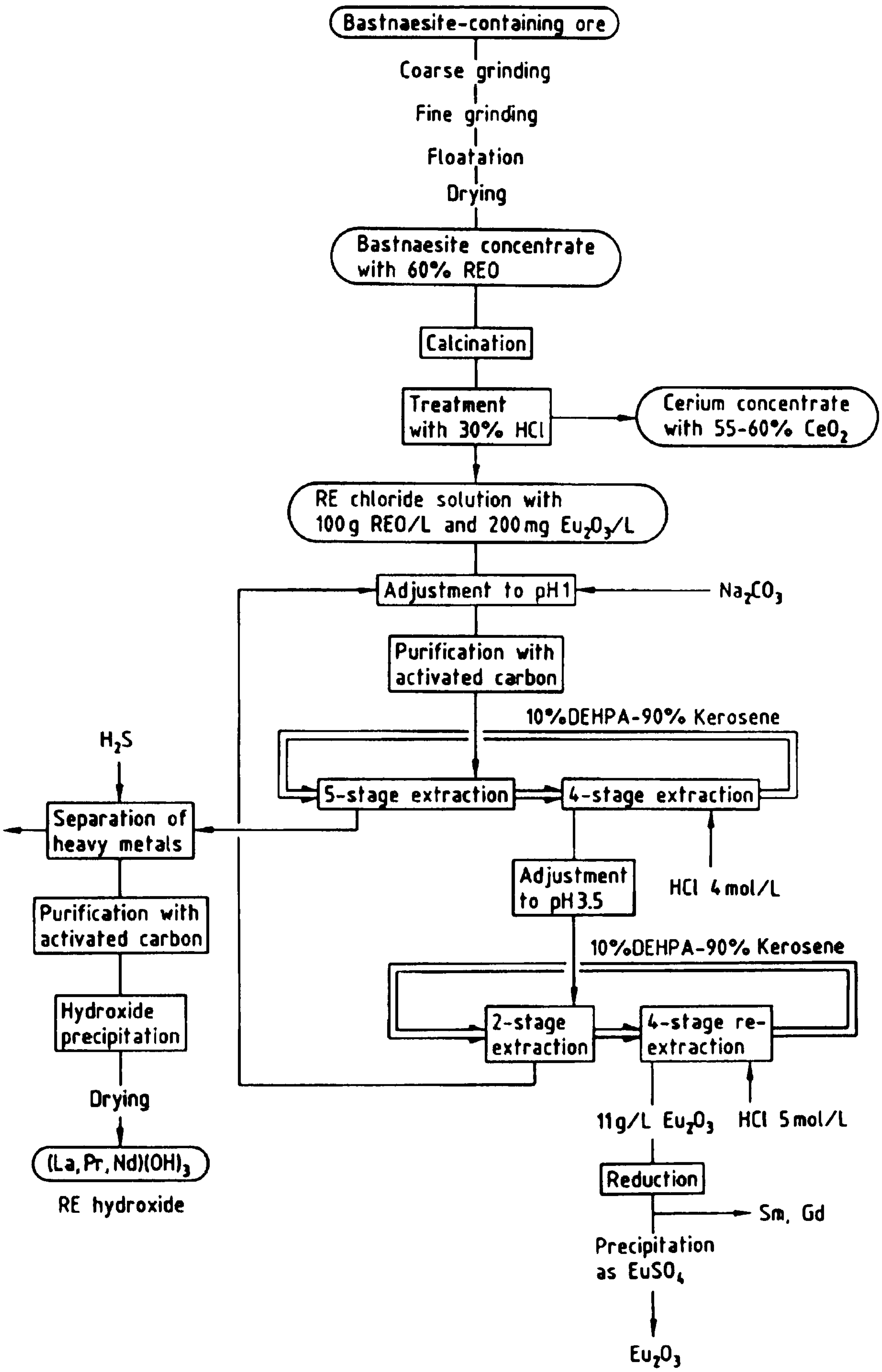


Figure 5.1: Molycorp process for the production of europium oxide.(9)

5.1.3 Separation by Ion Exchange.

This process is based on work carried out on the separation of rare earth elements produced by uranium fission, and formed part of the Manhattan Project (1943 – 1947). The principles of separation by elution were developed by Boyed and co-workers in the Oak Ridge National Laboratory. (1) The Ames Laboratory, Iowa State University, under the leadership of Spedding, investigated the production of rare earth metals on a large scale by displacement elution. Spedding and Powell have provided review of the developments up to 1950. (10, 11) Attempts to develop ion exchange column chromatography into a continuous process were realized with the development of the continuous annular chromatograph (CAC) by researchers at Oak Ridge Laboratory in the mid 1970s. However, the process was designed for analytical requirements with low loading of the columns and was therefore not commercialized. (12-14) A more recent development, known as continuous displacement chromatography (CDC), (15) shows greater promise for surpassing present industrial, batch, and fixed-column displacement ion exchange processes.

5.1.3.1 Ion Exchange with Chelating Agents.

Sulfonated polystyrene ion exchange resins, which possess high chemical stability, can combine with 0.5 – 0.8 mol of rare earth elements per 1 mol resin. However, differences in the affinities of the rare earth elements for the resin are very small, and the separation factor for two neighbouring rare earth elements is only *ca.* 1.08. (16) However, this can be considerably improved by the addition of chelating agents. The separation factor $F_{RE_B} / _{RE_A}$ for two rare earth elements RE_A and RE_B between an aqueous solution and the cation exchanger (concentrations marked with a bar) is

$$F_{\mathrm{RE_B/RE_A}} = \frac{\left[\overline{\mathrm{RE_B^{3+}}}\right] \cdot \left[\mathrm{RE_A^{3+}}\right]}{\left[\overline{\mathrm{RE_A^{3+}}}\right] \cdot \left[\mathrm{RE_B^{3+}}\right]} \qquad (3)$$

On the addition of a chelating agent L, the equilibrium constants in solution are given by:

$$K_A = \frac{[RE_A L]}{[RE_A L].[L]} \quad K_B \frac{[RE_B L]}{[RE_B L].[L]} \tag{4}$$

The constants depend on conditions in the medium, especially the pH of the aqueous phase. For large values of K_B and K_A and an excess of chelating agent (the concentration of the unchelated rare earth metals then being negligible), a new separation factor $F^{*}_{RE_B/RE_A}$ can be defined:

$$F^{*}_{RE_B/RE_A} \approx F \cdot \frac{K_B}{K_A} \tag{5}$$

Separation can therefore be much improved by using a chelating agent whose equilibrium constants K_A and K_B are very different from each other. Certain carboxylic acids form 1:1 chelates over a large pH range with K values that differ considerably for neighbouring rare earth elements and which are sufficiently soluble in water. Citric acid is only of historical interest; it was used in the Ames Laboratory to prepare rare earth oxides in kilogram quantities with a purity of 99.9 % in 1947.

Later, polycarboxylic acids were replaced by aminocarboxylic acids, which form chelates with considerably improved stability, selectivity, and solubility. Fig. 5.2 shows the K values as a function of the atomic numbers of the rare earth elements. They vary between 10^{10} and 10^{20}. The selectivity F_L also varies widely, and can have values of between 1 and 10 for neighbouring elements. For ethylenediaminetetraacetic acid (EDTA) and 1,2-diaminocyclohexanetetraacetic acid (DCTA), the selectivity for the cerium earths is much higher than for the yttrium earths. The position of yttrium (dashed lines) varies with the chelating agent over a range from Pr to Dy.

Rare Earth Elements

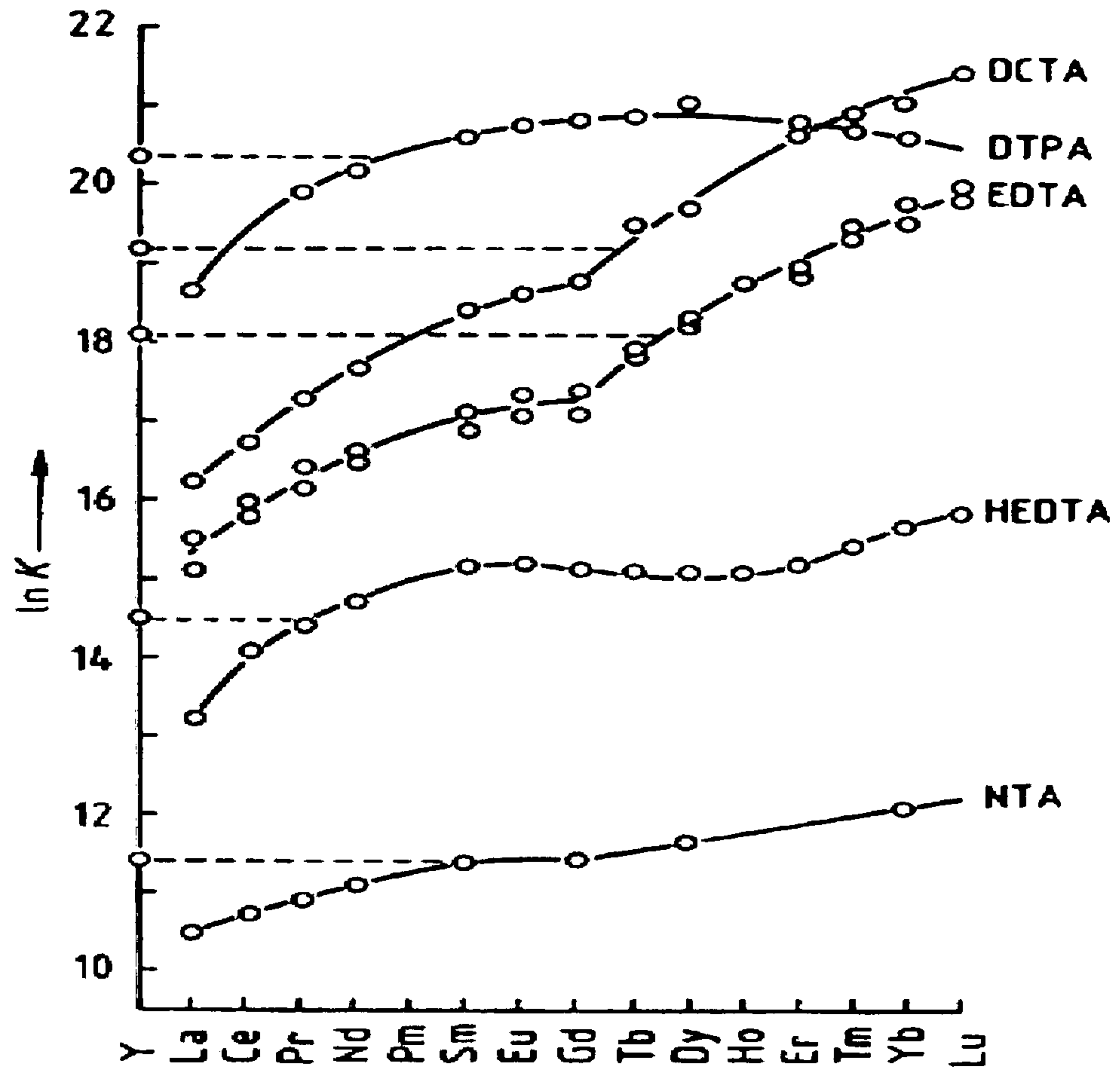


Figure 5.2: Stability constants *K* of selected rare earth chelates. (1)

– – – Position of yttrium.

The disadvantage of using chelates is their lower solubility. The most soluble chelates such as *N*-(hydroxyethyl)ethylenediaminetriacetic acid (HEDTA) or diethylenetriaminepentaacetic acid (DTPA) reach concentrations of *ca.* (2 – 2.5) × 10^{-2} mol/L at 25 °C.

5.1.4 Thermodynamics of liquid-liquid extraction.

Triangular diagrams (Fig. 5.3) are used for representing three component systems. Every possible composition of the ternary mixture corresponds to a point in the diagram. Each corner of the triangle represents a pure component and its designated is marked at this corner, on the side opposite to this corner the mass fraction of this component is zero. The sides of the triangle represent the corresponding two-component systems. The proportions of the individual components in a mixture are obtained as follows: the mass fraction of each component is given by lines parallel to the side opposite to the corner which represents the pure component, from 0 kg/kg at this opposite side to1 kg/kg at the corner. The numbering can be placed at the edges of the triangles in which case it is advisable to extend the lines. The numbers can also be inserted in the middle of the lines. The point P has the composition 0.5 kg/kg C, 0.2 kg/kg A, and 0.3 kg/kg B.

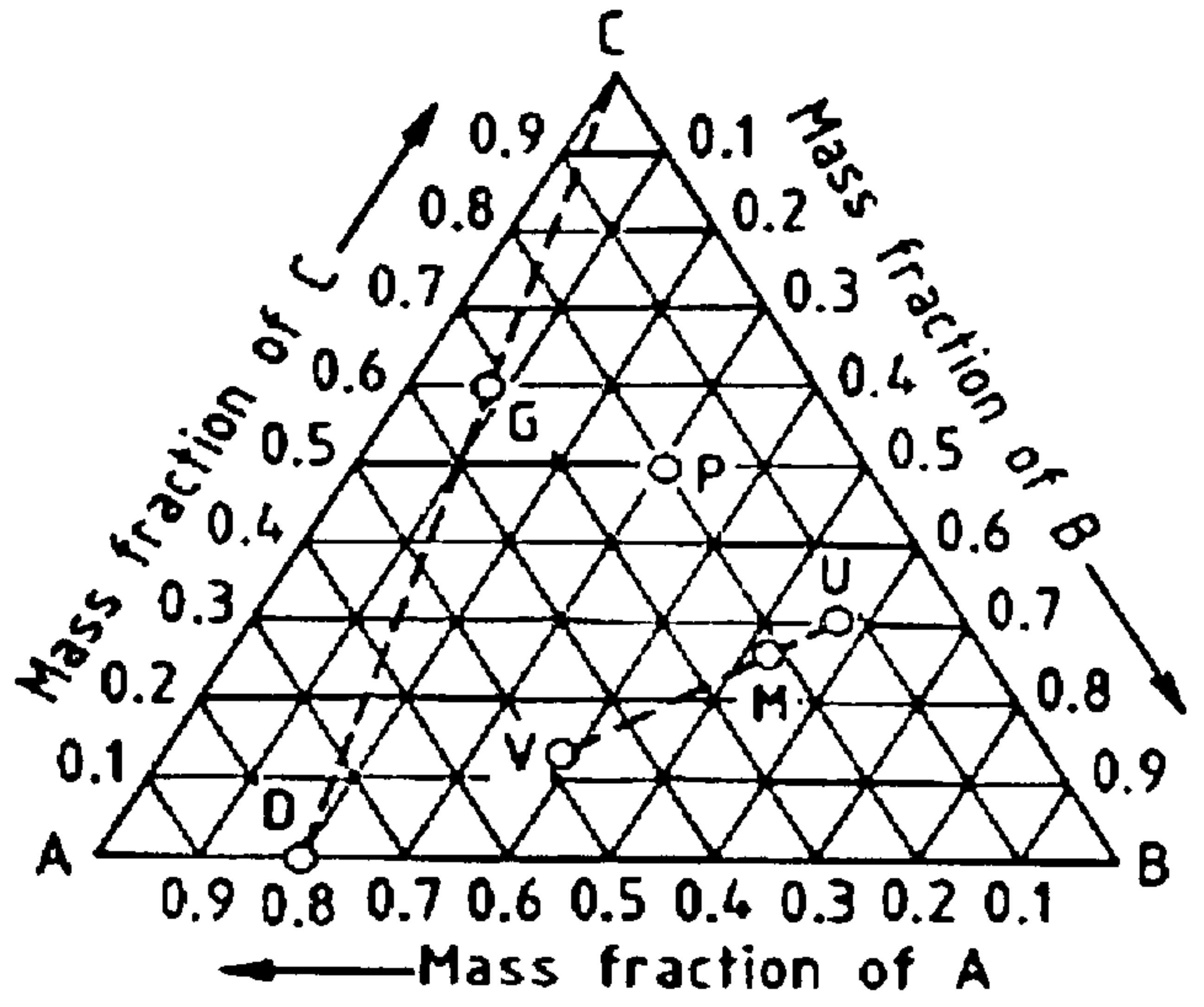


Figure 5.3: Triangular diagram for representation of a three-component system. (1)

The following rules apply in the triangular diagram: if component C is added to a mixture of 0.8 kg/kg A and 0.2 kg/kg B represented by the point D, then the composition of the new mixture follows the path of the straight line DC, on this straight line, and on all straight lines which pass through a corner, the ratio between the two other components that do not form the corner is constant.

If a mixture of composition U and one of composition V are combined then the resulting mixture lies on the straight connecting line UV. The concentration data obtained from the triangular diagram (e.g., point G: 0.6 kg/kg C, 0.08 kg/kg B, 0.32 kg/kg A; B: A = 1:4) apply to the total quantity of resulting mixture regardless of whether it is homogeneous or separated into several phases, as every point in a triangular corresponds to a composition there is no coordinate free for another reference variable. It is only possible to plot parameters such as lines of equal density, boiling points or other physical data, lines of equal activity coefficients or lines of phase boundaries. Only ternary systems with miscibility gaps are suitable for extractions, and the boundary line between the liquid single-phase region(s) and the two phase region is particular important. This boundary line is called the "binodal curve" (Fig. 5. 4).

A) Phase equilibria; B) Mass fractions

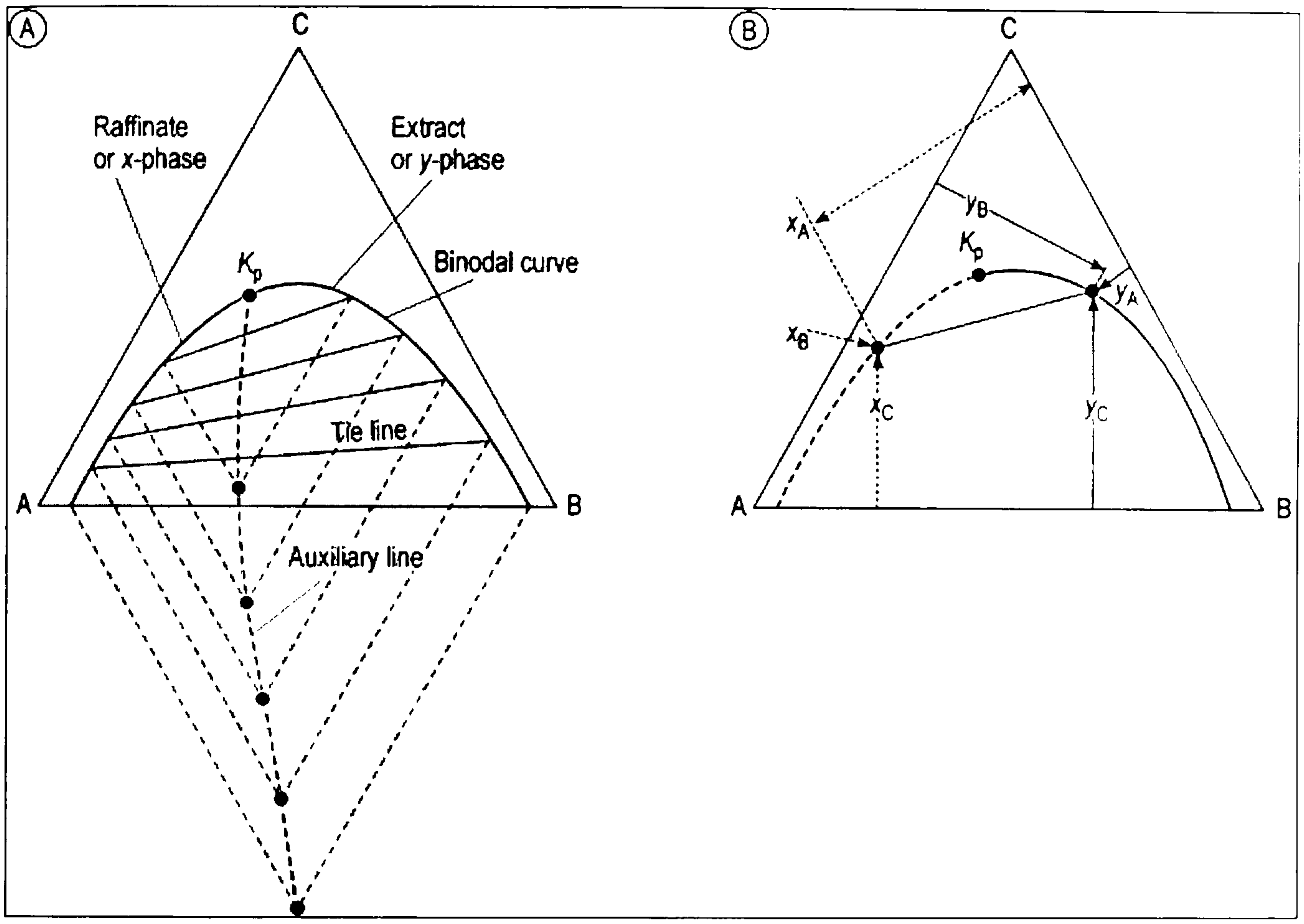


Figure 5.4: Definitions of phase equilibria and mass fractions in a triangular diagram. (1)

5.2 Results and discussion.

5.2.1 Liquid-liquid extraction of binary element systems.

In order to obtain an efficient and economic separation of yttrium from lanthanum as binary mixtures, it has been necessary to study the relevant factors affecting the liquid-liquid extraction process to determine the optimum conditions for this separartion from sulfate liquor. These factors include pH and D2EHPA concentration. Scrubbing using different concentrations of HNO_3, H_2SO_4, and HCl and in addition, the synergistic effect of using primene JMT/D2EHPA and primene JMT/TiOA to enhance the separation of yttrium from lanthanum, have been investigated along with use of the water-soluble complexing agent EDTA to enhance the separation. The stripping process depends on a number of factors, which have to be studied to obtain the best stripping efficiency that matches at the same time economic considerations. The factors under consideration are the effects of different reagents (strip solutions) such as H_2SO_4, HNO_3, and HCl, and the effect of different reagent concentrations.

5.2.1.1 The effect of pH on the extraction of Y/La from 1M H_2SO_4.

The extraction process has been studied by varying the pH values of the sulfate liquor (Y/La each element initial concentration 5.22×10^{-3} $Mol.dm^{-3}$) from 0.44 to 6.00, using either sulfuric acid or sodium hydroxide. Other factors were fixed at 1:1 (v/v) organic to aqueous phase ratio, 0.1M TiOA in carbon tetrachloride, contact time 10 minutes and the experiments were carried out at room temperature. The results obtained are given in Table 5.1 and shown in Fig. 5.5. It is clear that at lower pH (1.6) of the sulfate liquor, the separation of yttrium from lanthanum can be maximised. This indicates the possbility of separating heavy lanthanides (yttrium) from lanthanum (light lanthanides). (17) This increase on percent extraction with increasing atomic number of lanthanum to yttrium was also reported by Koopman *et al* (18) for the extraction of lanthanides with di(2-ethylhexyl)phosphoric acid from phosphoric acid solution. The increased affinity for extraction across the lanthanide series reflects their decreasing ionic radii from 1.06 Å for La and 0.88 Å for Y. (19)

Table 5.1: Effect of different pH on the extraction of Y/La.

pH	% E_Y	D_Y	% E_{La}	D_{La}
0.44	94.80	18.23	87.80	7.19
0.90	95.20	19.83	88.40	7.62
1.20	95.60	21.73	88.70	7.85
1.60	96.00	24.00	89..00	8.09
2.60	96.40	26.78	89.20	8.26
3.40	97.00	32.33	94.00	15.67
4.60	97.20	34.71	94.60	17.52
6.00	97.30	36.04	94.80	18.23

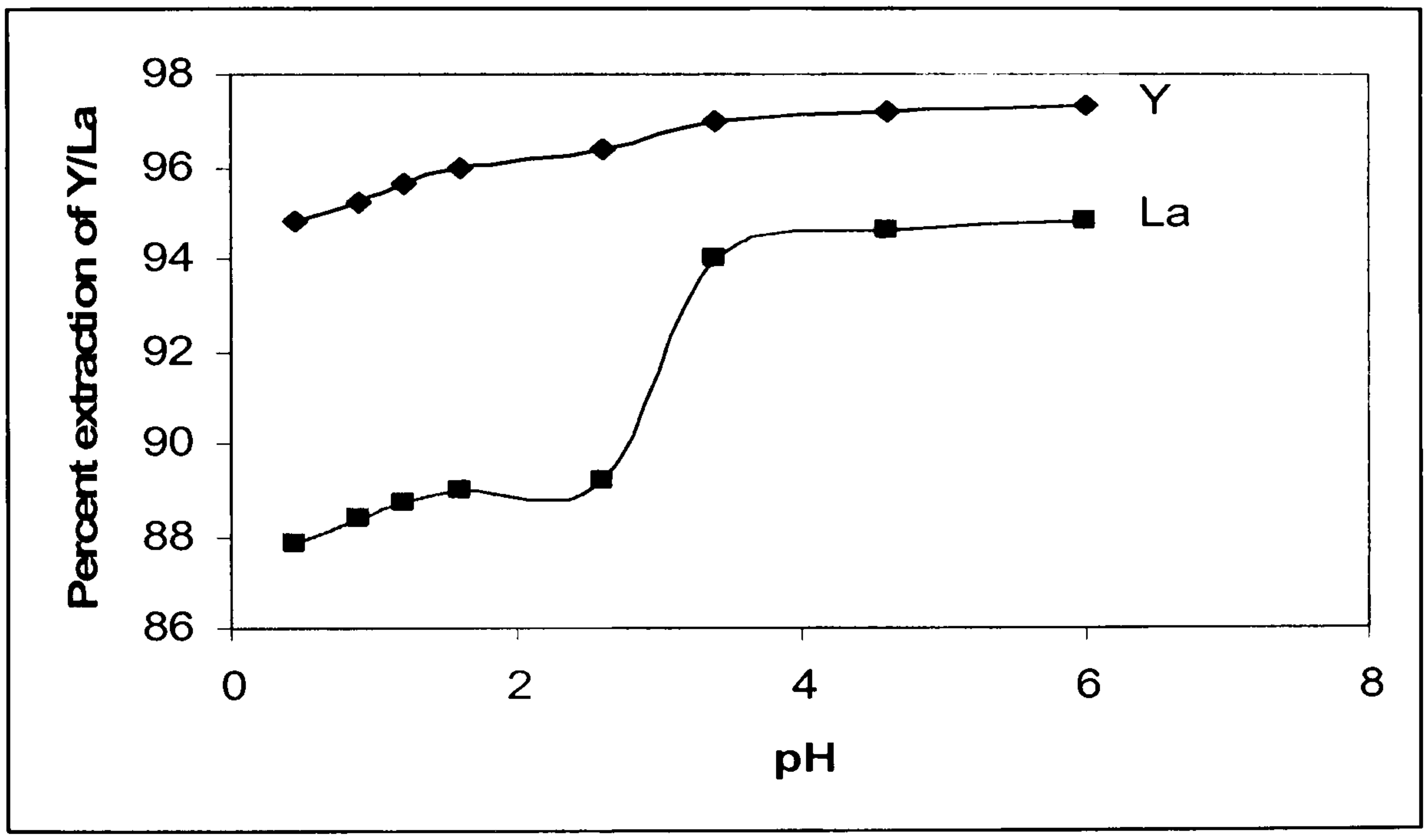


Figure 5.5: Effect of pH on the extraction of Y/La.

5.2.1.2 Effect of different concentrations of D2EHPA/CCl_4 on the extraction of Y/La from 1M H_2SO_4.

To 10 ml of the sulfate liquor (lanthanum, yttrium) at pH 4.6, 10 ml of a solution of D2EHPA in CCl_4 was added with concentration ranging from 0.05 to 0.5M, and then the solution was shaken for 10 minutes at room temperature to attain equilibrium state. By increasing the concentration of D2EHPA/CCl_4 the percent extraction of both elements increases in parallel. For economic reasons the optimum value of a

0.5M solution of D2EHPA in CCl_4 was chosen from the data reported in Table 5.2 and represented in Fig. 5.6.

Table 5.2: Effect of D2EHPA/CCl_4 concentration on the extraction of Y/La.

[D2EHPA]/M	% E_Y	D_Y	% E_{La}	D_{La}
0.05	**96.60**	**28.41**	**95.00**	**19.00**
0.1	**97.20**	**34.71**	**95.40**	**20.74**
0.2	**97.60**	**40.66**	**95.80**	**22.81**
0.3	**98.00**	**49.00**	**96.20**	**25.32**
0.5	**98.40**	**61.50**	**96.60**	**28.41**

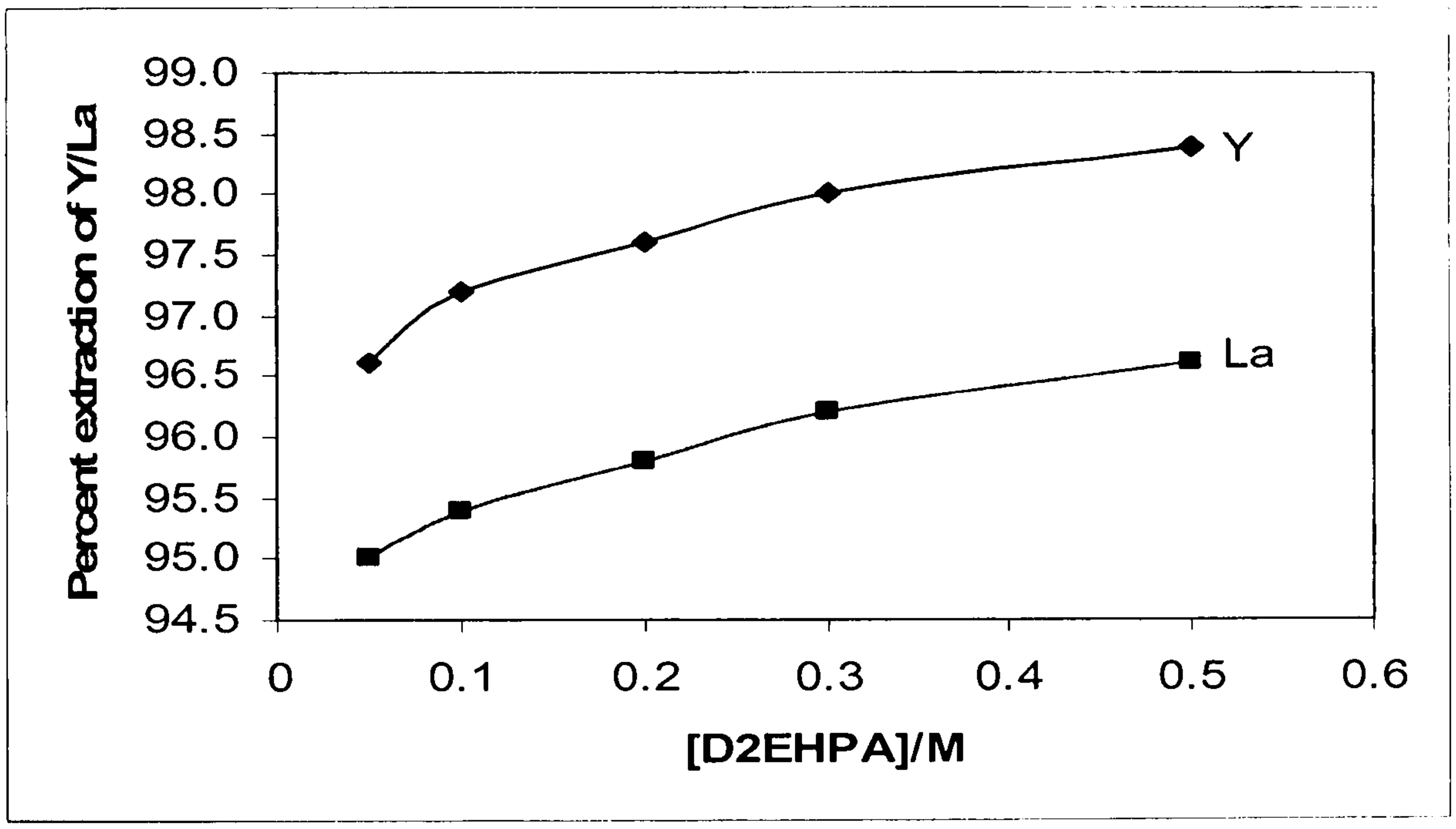


Figure 5.6: Effect of D2EHPA/CCl_4 concentration on the extraction of Y/La.

5.2.1.3 Effect of different HNO_3 concentrations on the scrubbing of Y/La.

A series of scrubbing experiments were carried out, using HNO_3 solutions of concentration ranging from 0.1M to 1M, while the contact time was 10 minutes and phase ratio 1:1 organic/aqueous, 0.1M TiOA in carbon tetrachloride and room temperature. The obtained results are given in Table 5.3 and shown in Fig. 5.7. It is clear from the results that scrubbing efficiency by HNO_3 increased with increasing the concentration of HNO_3 up to 0.4M, and then decreased. The optimum concentration of HNO_3 for scrubbing can therefore be taken as 0.4M.

Table 5.3: Effect of HNO_3 concentration on the scrubbing of Y/La.

$[HNO_3]$/M	Y % scrubbing	La % scrubbing
0.1	45.00	52.26
0.2	50.52	57.45
0.3	55.00	62.50
0.4	85.00	98.45
1.0	66.00	74.32

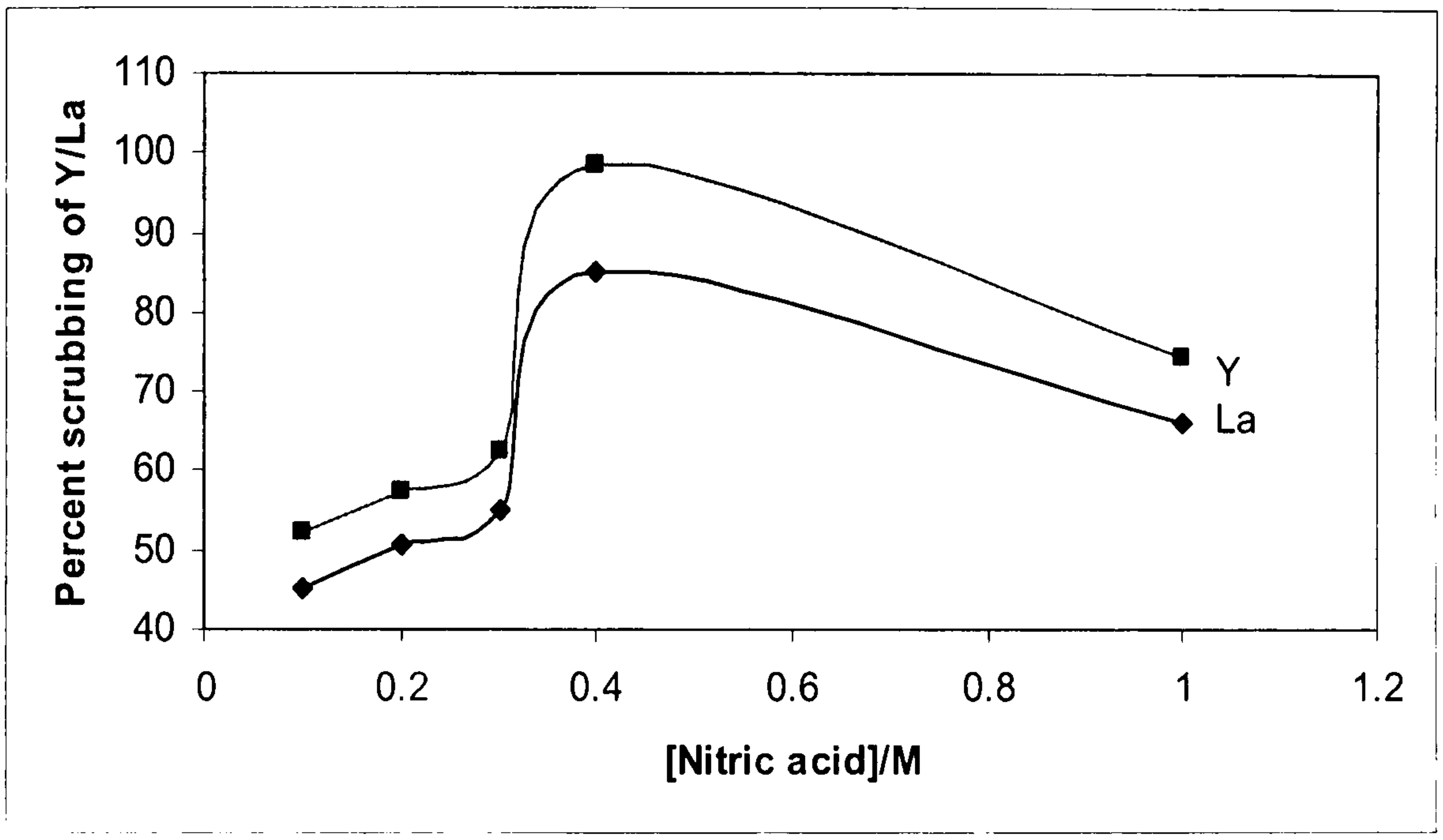


Figure 5.7: Effect of HNO_3 concentration on the scrubbing of Y/La.

5.2.1.4 Effect of different H_2SO_4 concentrations on the scrubbing of Y/La.

A series of scrubbing experiments were carried out, using H_2SO_4 solutions of concentration ranging from 0.1M to 1M, while the contact time was 10 minutes and phase ratio 1:1 organic/aqueous, 0.1M TiOA in carbon tetrachloride and room temperature. The obtained results are given in Table 5.4 and shown in Fig. 5.8. It is clear from the results that scrubbing efficiency by H_2SO_4 decreased with increasing concentration of H_2SO_4 up to 0.4M, and then showed an increase with increasing concentration. For separation of the elements a concentration H_2SO_4 of 0.1M is optimum.

Table 5. 4: Effect of H_2SO_4 concentration on the scrubbing of Y/La.

$[H_2SO_4]$/M	Y % scrubbing	La % scrubbing
0.1	39.52	44.72
0.2	20.52	25.09
0.3	20	24.06
0.4	20	23.58
1.0	39.48	42.31

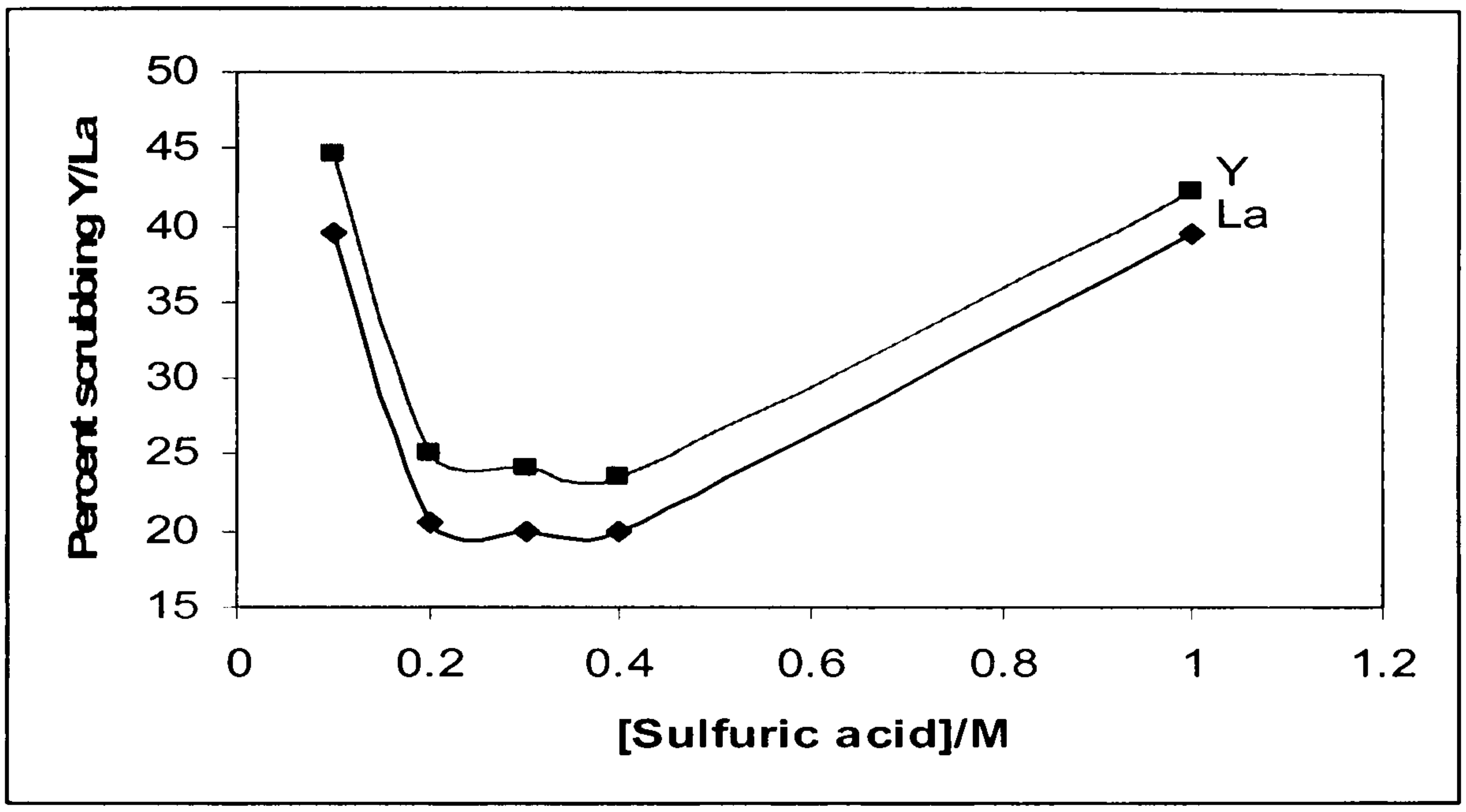


Figure 5.8: Effect of H_2SO_4 concentration on the scrubbing of Y/La.

5.2.1.5 Effect of different HCl concentrations on the scrubbing of Y/La.

A series of scrubbing experiments were carried out, using HCl solution of concentration ranging from 0.1M to 1M, while the contact time was 10 minutes and phase ratio 1:1 organic/aqueous, 0.1M TiOA in carbon tetrachloride and room temperature. The obtained results are given in Table 5.5 and shown in Fig. 5.9. It is clear from the results that scrubbing efficiency by HCl increased by increasing the concentration of HCl up to 0.3M then begins to decrease. But 0.3M HCl is the optimum for maximum separation.

Table 5.5: Effect of HCl concentration on the scrubbing of Y/La.

[HCl]/M	Y % scrubbing	La % scrubbing
0.1	65.10	81.60
0.2	74.90	92.47
0.3	65.40	93.98
0.4	41.10	67.60
1.0	36.00	56.02

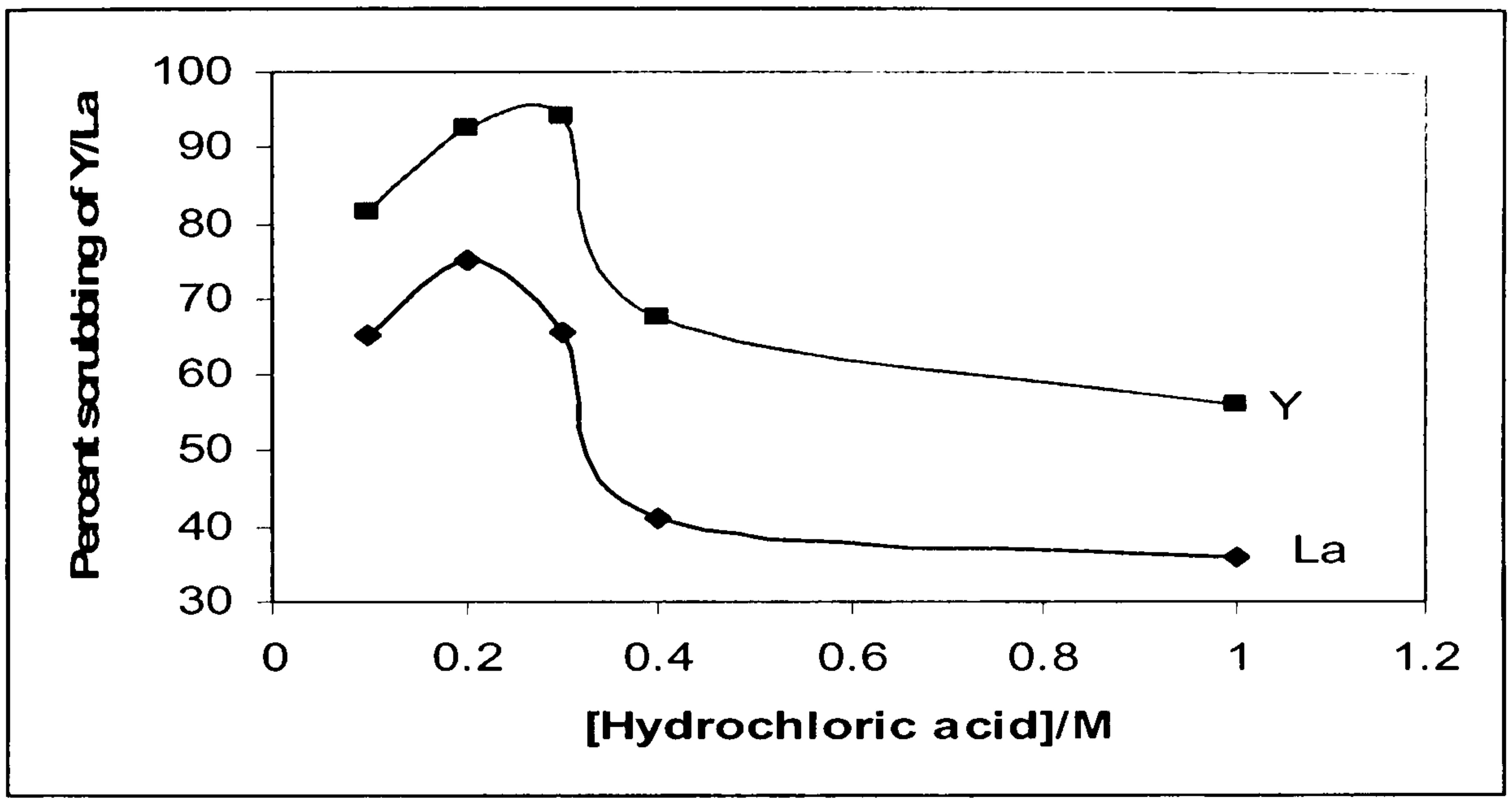


Figure 5.9: Effect of HCl concentration on the scrubbing of Y/La.

5.2.1.6 Effect of different amounts of primene JMT added to D2EHPA on enhancement of the separation factors of Y/La.

A stock solution of 0.5M primene JMT (a primary amine) in carbon tetrachloride was added to 0.5M D2EHPA/carbon tetrachloride in different amounts. Table 5.6 and Fig. 5.10 shows that by increasing the percentage of primene JMT there is a decrease in the extraction of yttrium/lanthanum. This means that primene JMT gives antisynergistic enhancement in the extraction of yttrium/lanthanum. However, by increasing the concentration of primene JMT added to D2EHPA, extraction of La decreases strongly but Y does not, which means that, the separation factor sharply increases. Primene JMT-D2EHPA is the most effective system for the separation of yttrium from lanthanum and better than systems containing thenoyltrifluoroacetone

(TTA) in combination with neutral (TBP, TOPO) or basic (amines or quaternary ammonium salt) extracting agents. (20)

Table 5.6: Effect of different amount of primene JMT added to D2EHPA on the enhancement of the separation factors of Y/La.

Primene JMT % by volume	Y % extraction	La % extraction
10	98.10	75.95
20	95.65	46.00
30	95.00	45.25
40	94.15	40.60
100	94.85	35.88

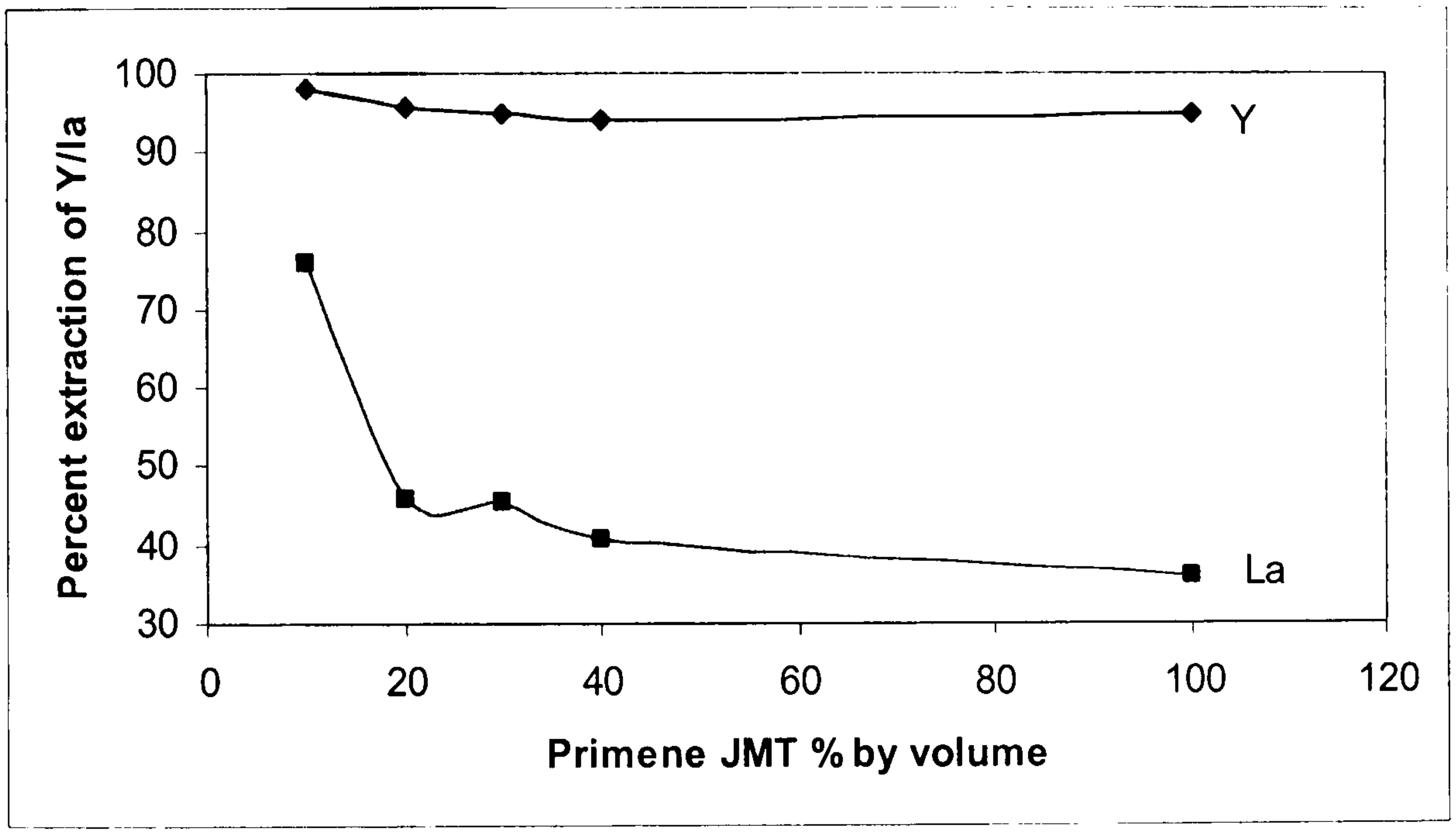


Figure 5.10: Effect of different amount of primene JMT added to D2EHPA on the enhancement of the separation factors of Y/La.

5.2.1.7 Effect of different amounts of primene JMT added to TiOA on enhancement of the separation factors of Y/La.

A stock solution of 0.5M primene JMT in carbon tetrachloride was added to 0.1M TiOA/carbon tetrachloride in different amounts. Table 5.7 and Fig. 5.11 show that by increasing the percentage of primene JMT there is an increase in the extraction of yttrium/lanthanum, reaching complete recovery in 30 % and 40 %. This means that primene JMT is promising a synergistic enhancement in the extraction of yttrium/lanthanum. However, at this concentration it is not possible to separate the two elements. The data show a concentration of 10 % primene JMT gives the best separation of the two elements from each other.

Table 5.7: Effect of different amount of primene JMT added to TiOA on the enhancement of the separation factors of Y/La.

Primene JMT % by volume	Y % extraction	La % extraction
10	86.20	13.28
20	92.05	50.20
30	100.00	100.00
40	100.00	100.00
50	95.70	83.45

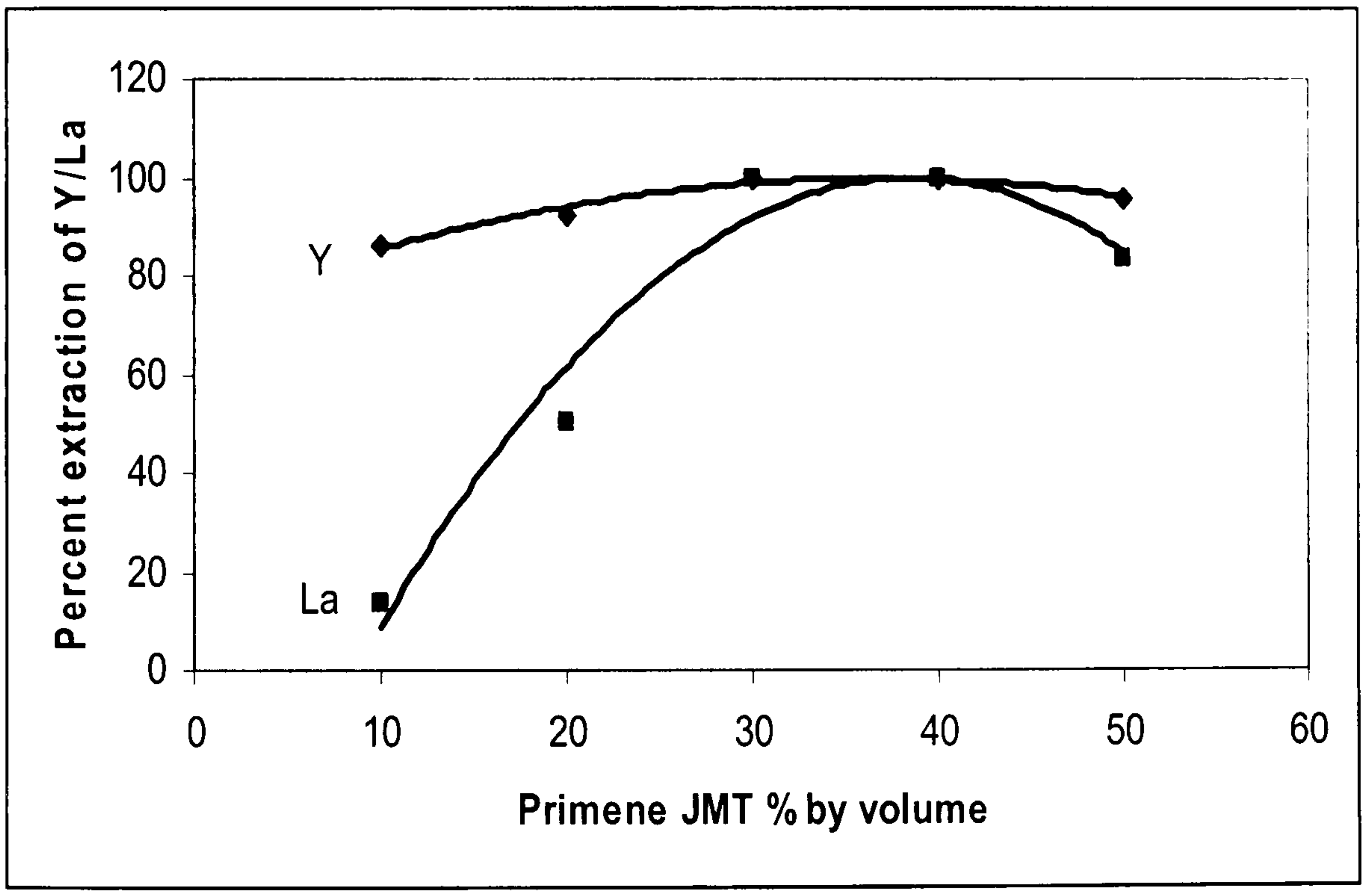


Figure 5.11: Effect of different amount of primene JMT added to TiOA on the enhancement of the separation factors of Y/La.

5.2.1.8 Effect of EDTA added to the aqueous phase on enhancement of the separation factors of Y/La.

The relatively low values of separation factor in rare earth element extraction by amines may be enhanced by addition of a complexing agent, provided the difference in the stability constants for individual REE is sufficiently high. (21) Inczedy (22) in his monograph gave comprehensive description of a whole set of REE complex compounds as well as their possible utilization in the extraction process.

A stock solution of 0.01M EDTA was prepared and added to the aqueous phase in different amounts as a water-soluble masking agent using 0.1M TiOA/carbon tetrachloride as extractant. Table 5.8 and Fig. 5.12 show that by increasing the amount of EDTA added there is a small increase in the extraction of yttrium and lanthanum. There doesn't seem to be a big increase however, and at low % (5) there is a decrease. This means that EDTA provides a promising enhancement in the separation factors of yttrium/lanthanum, especially at 5 % that gives the highest separation factor. It may be concluded that two favorable effects take place during the extraction of La and Y by TiOA/CCl_4 in the presence of EDTA: preferential extraction of Y and preferential complex formation of La, keeping it in the aqueous phase. Summation of both factors should lead to an increase in the separation factor, which has actually been observed and can be seen in Fig. 5.12. (21)

Table 5.8: Effect of EDTA added to an aqueous phase on the enhancement of the separation factors of Y/La.

EDTA % by volume	Y % extraction	La % extraction
0	94.25	23.85
5	93.35	15.75
10	95.00	38.53
15	95.10	39.95
20	95.10	40.01

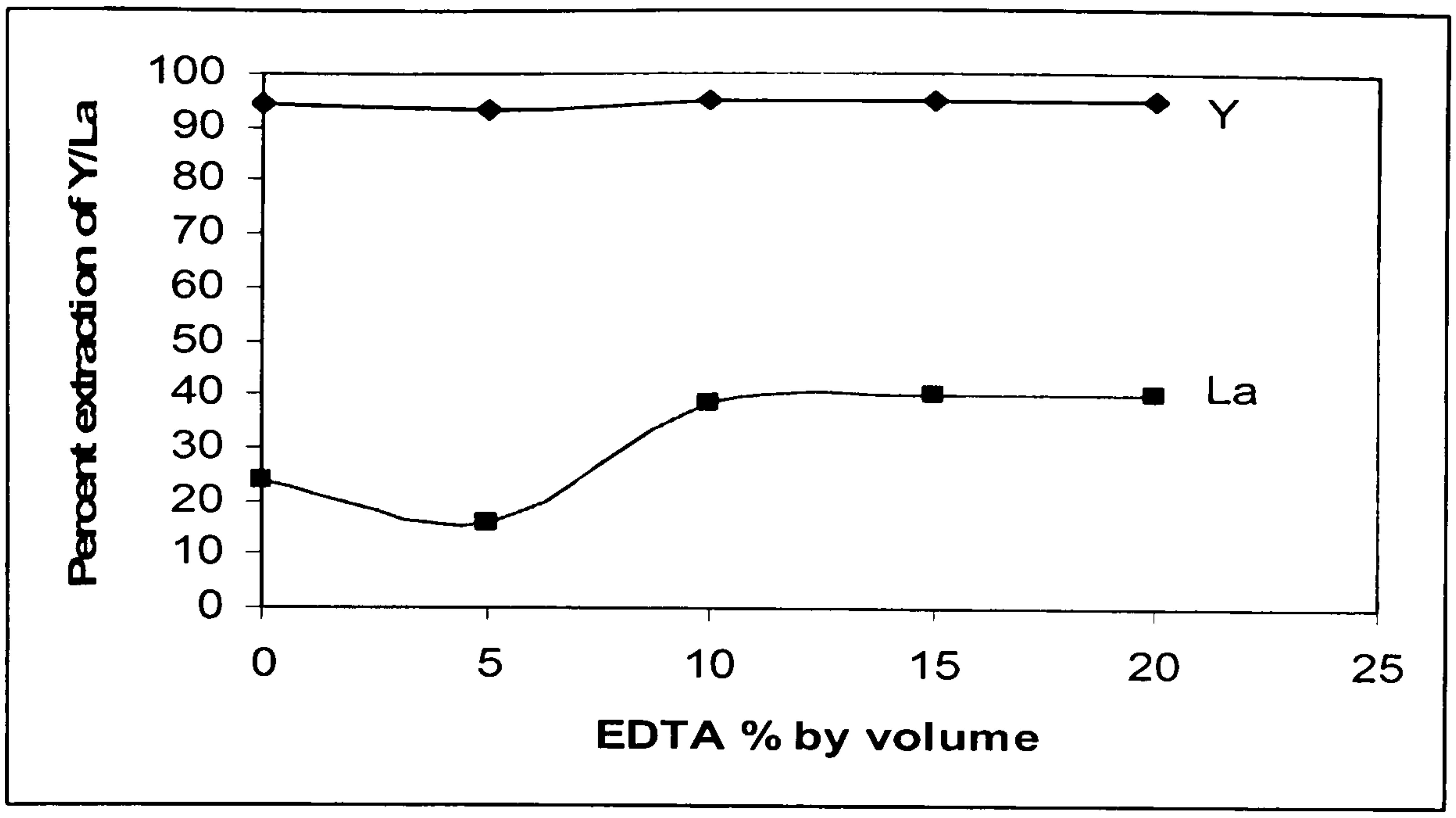


Figure 5.12: Effect of EDTA added to an aqueous phase on the enhancement of the separation factors of Y/La.

5.2.1.9 Effect of different sulfuric acid concentrations on the stripping of Y/la.

A series of stripping experiments were carried out, using H_2SO_4 solutions of concentration ranging from 0.2M to 6M while the contact time was 10 minutes and phase ratio 1:1 organic/aqueous, 0.1M TiOA in carbon tetrachloride and room temperature. The obtained results are given in Table 5.9 and shown in Fig. 5.13. It is clear from the results that stripping by 0.4M H_2SO_4 gives the best Y/La re-extraction percent, while the contact time was 10 minutes and phase ratio 1:1 organic/aqueous, room temperature.

Table 5.9: Effect of sulfuric acid concentration on the stripping of Y/La.

[H_2SO_4]/M	Y % stripping	La % stripping
0.2	17.50	79.76
0.4	18.50	85.44
1.0	14.00	62.00
3.0	10.45	51.86
6.0	8.50	42.58

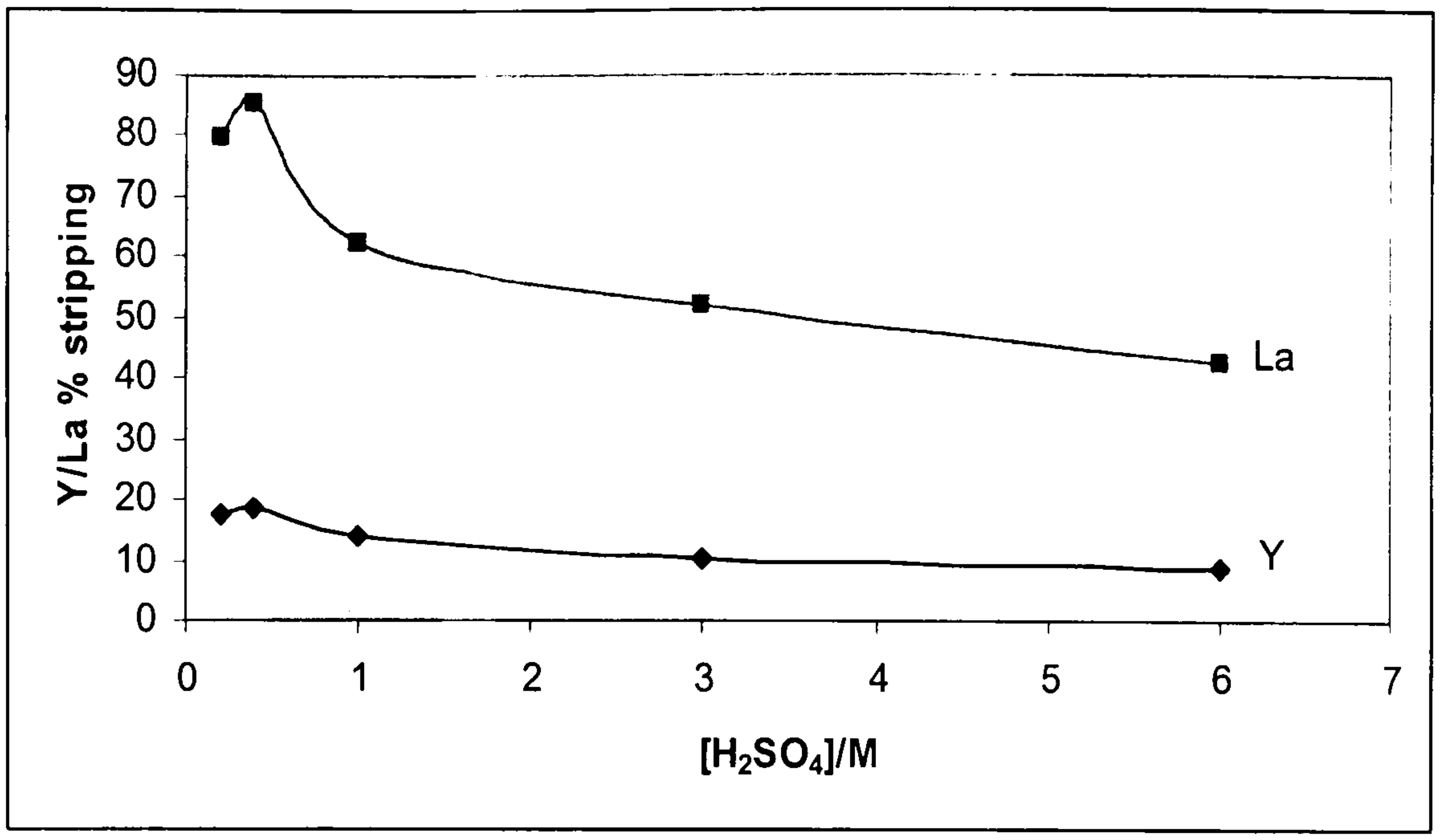


Figure 5.13: Effect of H_2SO_4 concentration on the stripping of Y/La.

5.2.1.10 Effect of different HCl concentrations on the stripping of Y/la.

A series of stripping experiments were carried out, using HCl solutions of concentration ranging from 0.1M to 3M, while the contact time was 10 minutes and phase ratio 1:1 organic/aqueous, 0.1M TiOA in carbon tetrachloride and room temperature. The obtained results are given in Table 5.10 and shown in Fig. 5.14. It is clear from the results that stripping by 0.1M HCl gives the best Y/La re-extraction percent.

Table 5.10: Effect of hydrochloric acid concentration on the stripping of Y/La.

[HCl]/M	Y % stripping	La % stripping
0.1	17.5	81.12
0.2	17.5	74.64
0.4	13.5	48.68
1.0	10.0	41.98
3.0	7.5	30.40

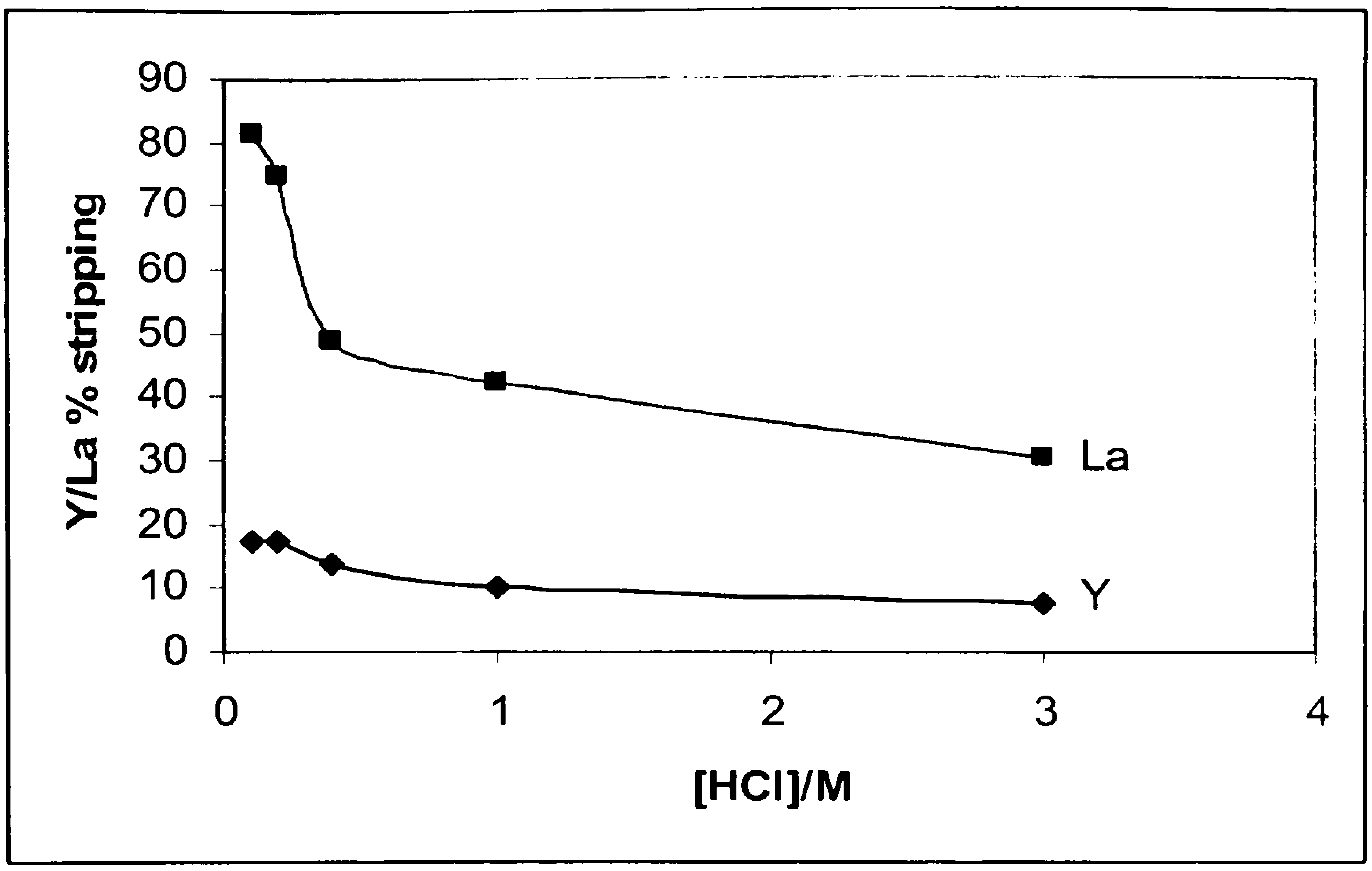


Figure 5.14: Effect of HCl concentration on the stripping of Y/La.

5.2.1.11 Effect of different nitric acid concentrations on the stripping of Y/la.

A series of stripping experiments were carried out, using HNO_3 solutions of concentration ranging from 0.1M to 3M while the contact time was 10 minutes and phase ratio 1:1 organic/aqueous, 0.1M TiOA in carbon tetrachloride and room temperature. The obtained results are given in Table 5.11 and shown in Fig. 5.15. It is clear from the results that stripping by 0.2M HNO_3 gives the best Y/La re-extraction percent.

Table 5.11: Effect of nitric acid concentration on the stripping of Y/La.

$[HNO_3]$/M	Y % stripping	La % stripping
0.1	3.00	15.52
0.2	14.80	65.40
0.4	14.00	54.88
1.0	12.50	50.60
3.0	11.35	42.40

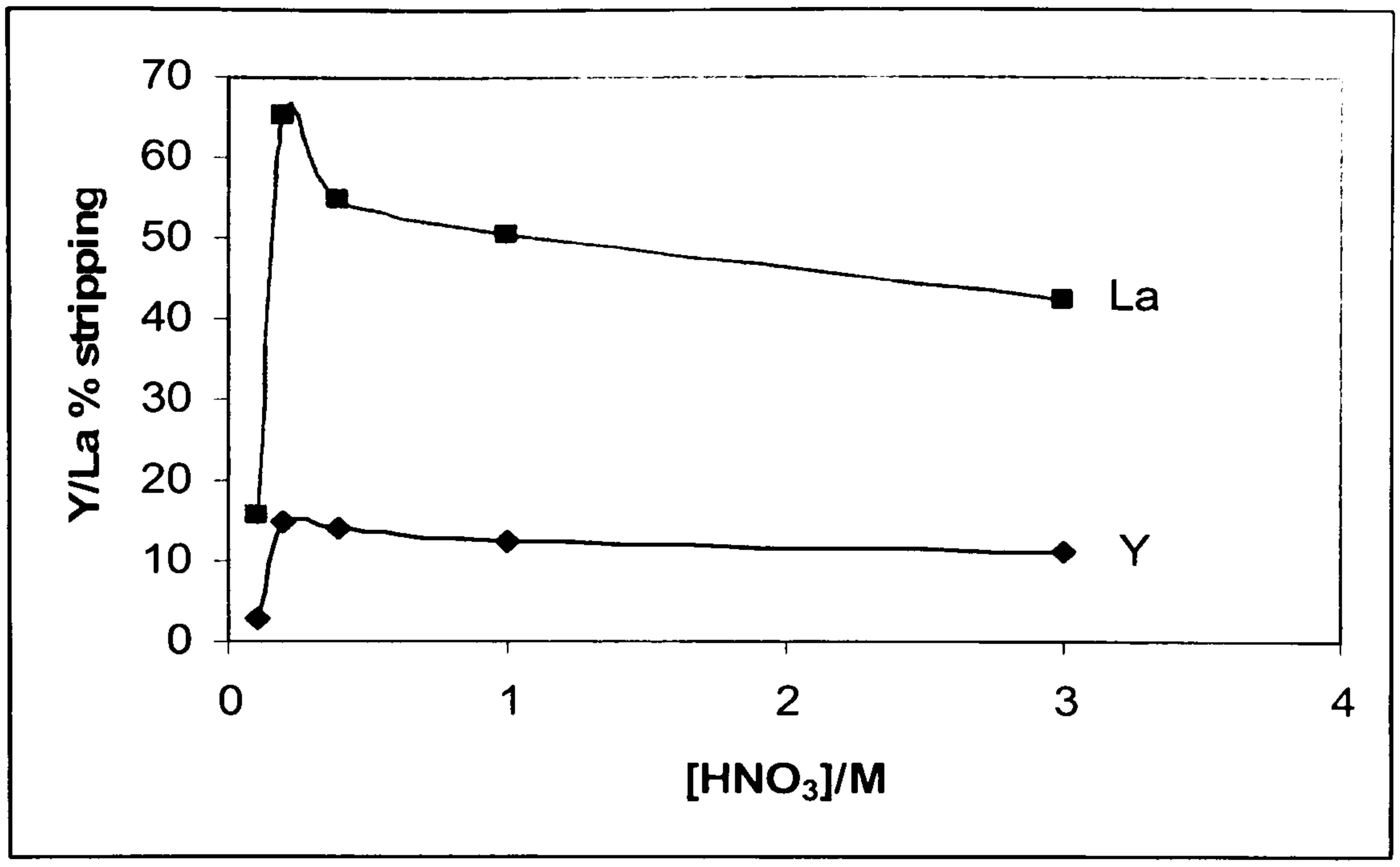


Figure 5.15: Effect of HNO_3 concentration on the stripping of Y/La.

5.2.1.12 Conclusions.

The utilization of solvent extraction in order to obtain an efficient and economic separation of yttrium from lanthanum as binary mixtures has been investigated. The optimum conditions for the separation of yttrium from lanthanum from sulfate liquor using TiOA/CCl_4 were at pH 1.6. Addition of 0.5M solution of D2EHPA/CCl_4 enhances the separation. Suitable conditions for scrubbing of the loaded solvent (TiOA/CCl_4) were 0.4M HNO_3, 0.1M H_2SO_4, and 0.3M HCl. In addition, the synergistic effect of using primene JMT/D2EHPA and primene JMT/TiOA were investigated. Using a water-soluble complexing agent EDTA enhanced the separation of yttrium from lanthanum. The optimum conditions for the stripping of the two elements were, 0.4M H_2SO_4, 0.1 M HCl, and 0.2M HNO_3.

This part of Chapter 5 gave a new approach about the possible extraction and separation of Y from La from sulfuric acid system that is complicated by the presence of sulfate-bisulfate equilibrium. Extraction of lanthanides (III) with organophosphorous esters (D2EHPA, TBP, and TOPO), chelating extractant thenoyltrifluoroacetone (HTTA), and benzo-15-crown-5 as well as with mixture of HTTA and various synergistic agents has been studied by many authors. (23, 24) No investigations, however have been published for the extraction separation of Y from La using primene JMT-D2EHPA/CCl_4 and primene JMT-TiOA/CCl_4 systems as new synergistic mixtures which is promising. Also, using water complexing agent EDTA with TiOA/CCl_4 enhanced the separation of Y from La and works better than EDTA as complexing agent in the system La and Sm nitrates, with $NaNO_3$ and HNO_3 as aqueous phase and benzyldibutylamine (BDBA) in benzene as organic phase. (22)

5.2.2 Liquid-liquid extraction of ternary element systems.

5.2.2.1 Results and discussion.

In order to obtain an efficient and economic separation of Nd-La-Y ternary mixtures, it has been necessary to study the relevant factors affecting the liquid-liquid extraction process to determine the optimum conditions for this separartion from sulfate liquor. These factors include different concentrations of primene JMT, pH, temperature and diluents. The stripping process depends on a number of factors, which have to be studied to obtain the best stripping efficiency that matches at the same time economic considerations. The factors under consideration are effect of different reagents (strip solution) such as H_2SO_4, HNO_3, $HClO_4$, CH_3COOH, and HCl, effect of different reagent concentrations as acidic stripping. Also, alkaline stripping by NaOH and Na_2CO_3, and different contact times.

5.2.2.2 Effect of different concentrations of primene JMT (not treated) in carbon tetrachloride on the extraction of Nd-La-Y.

High molecular amines extract metals by ion-pair formation. Cations and anions are extracted from an aqueous phase into an organic phase and because such extraction is energetically very unfavourable, it is necessary to neutralise the ionic charge prior to extraction. This neutralisation is achieved either by forming organic-soluble neutral complexes between cations and anions in the aqueous phase or by direct reaction between the ionic species of interest and an appropriate organic compound to form a neutral species soluble in the organic phase. (25) High molecular amines are currently finding a wide range of applications in the technologies of production of Zn, U, Co, Ni, W, and V. Also there is a possibility to use high-molecular amines like primene JMT to separate elements from the group of lanthanides. (26, 27) However, there is no evidence of an industrial application of primene JMT, all the suggested technologies have only been tested in semi commercial scale plants. The primary amine primene JMT was tested for the separation of Th form sulfate solutions containing Fe, U, and some lanthanides. (28) The objective of these experiments is to test and to see the behaviour of primene JMT in extraction of ternary system. Firstly the solvent must be equilibrated by contacting it with sulfuric acid solution (pH 4.5) for 10 minutes. To 10 ml of the sulfate liquor (Nd-La-Y initial concentration of each element 5.22×10^{-3}

Mol.dm^{-3}) at pH 4.5, 10 ml of a solution of primene JMT in CCl_4 was added with concentration ranging from 0.1 to 0.5M, and then the solution was shaken for 10 minutes at room temperature to attain equilibrium state. The optimum value of a 0.3M solution of primene JMT in CCl_4 was chosen from the data reported in Table 5.12 and represented in Fig. 5.16.

Table 5.12: Effect of concentration of primene JMT/carbon tetrachloride on the extraction of Nd-La-Y from sulfuric acid medium.

[Primene JMT]/ M	Y % extraction	La % extraction	Nd % extraction
0.1	86.50	66.33	61.55
0.2	87.00	67.54	63.22
0.3	89.50	73.60	70.42
0.4	88.00	69.83	65.33
0.5	86.00	65.00	62.12

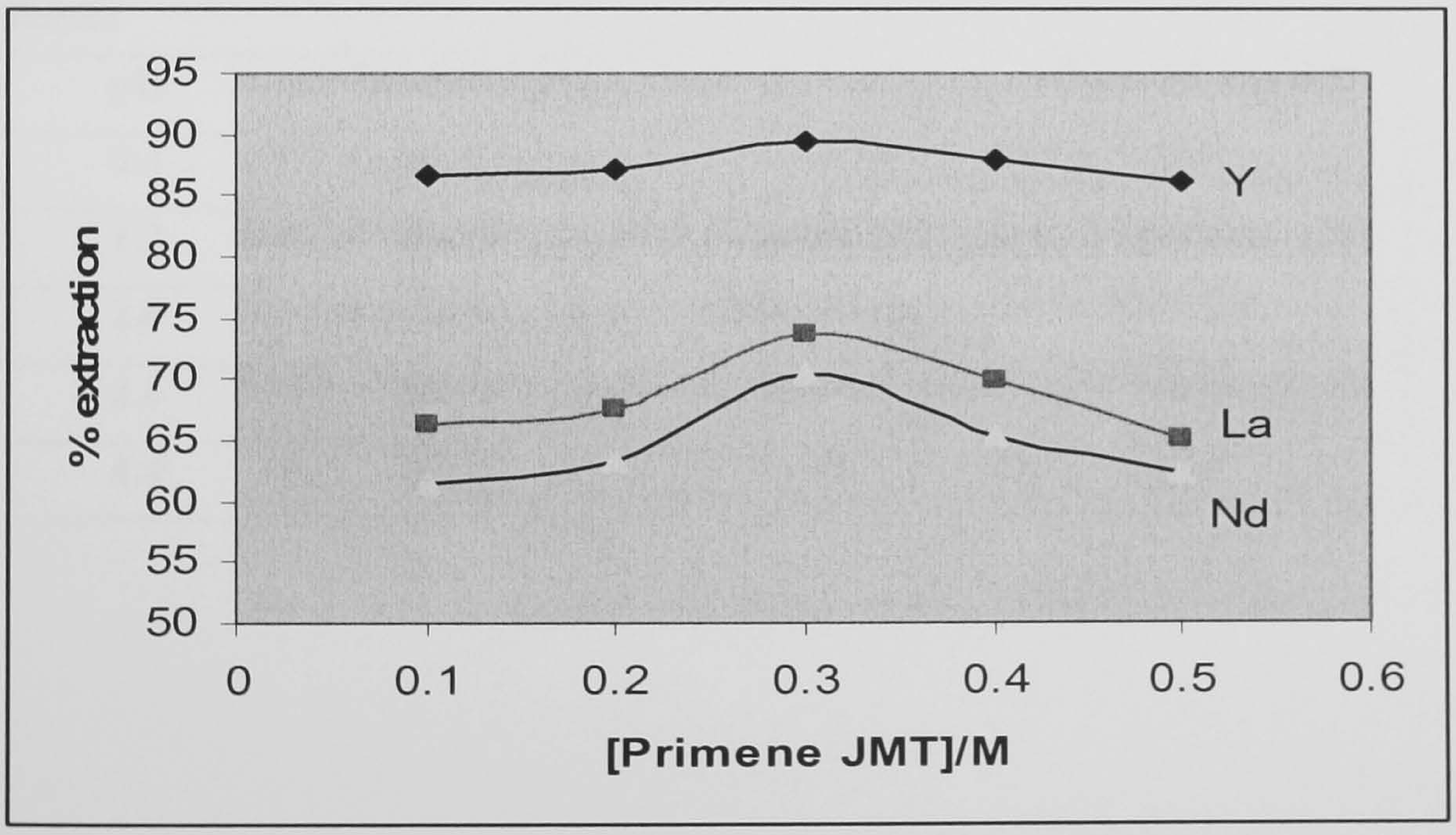


Figure 5.16: Extraction percent of Nd-La-Y as a function of primene JMT concentration.

5.2.2.3 Effect of pH on the extraction of Nd-La-Y.

The extraction process has been studied by varying the pH values of the sulfate liquor from 0.4 to 4.4, using either sulfuric acid or sodium hydroxide. Other factors were fixed at 1:1 (v/v) organic to aqueous phase ratio, 0.3M primene JMT in carbon tetrachloride, contact time 10 minutes and the experiments were carried out at room temperature. The results obtained are given in Table 5.13 and shown in Fig. 5.17. It is clear that the pH 2 of the sulfate liquor can be taken as an optimum pH value for maximum extraction, but not for separation. pH 0.4 is the best for the separation of yttrium from lanthanum and neodymium. The reason for ease of separation of Y from La and Nd was attributed by decreasing pH (increasing hydrogen ion concentration) the sulfate concentration increased and result in the appearance of free sulfuric acid in the system, which can force out the La and Nd from the organic phase due to a competition extraction. (29-31)

Table 5.13: Variation of Nd-La-Y percent extraction with the pH of the sulfate liquor.

pH	Y % extraction	La % extraction	Nd % extraction
0.4	85.30	0.09	20.00
1.2	99.15	89.15	86.43
2.0	99.75	96.50	95.82
3.0	99.75	96.50	95.85
4.4	99.75	96.50	95.95

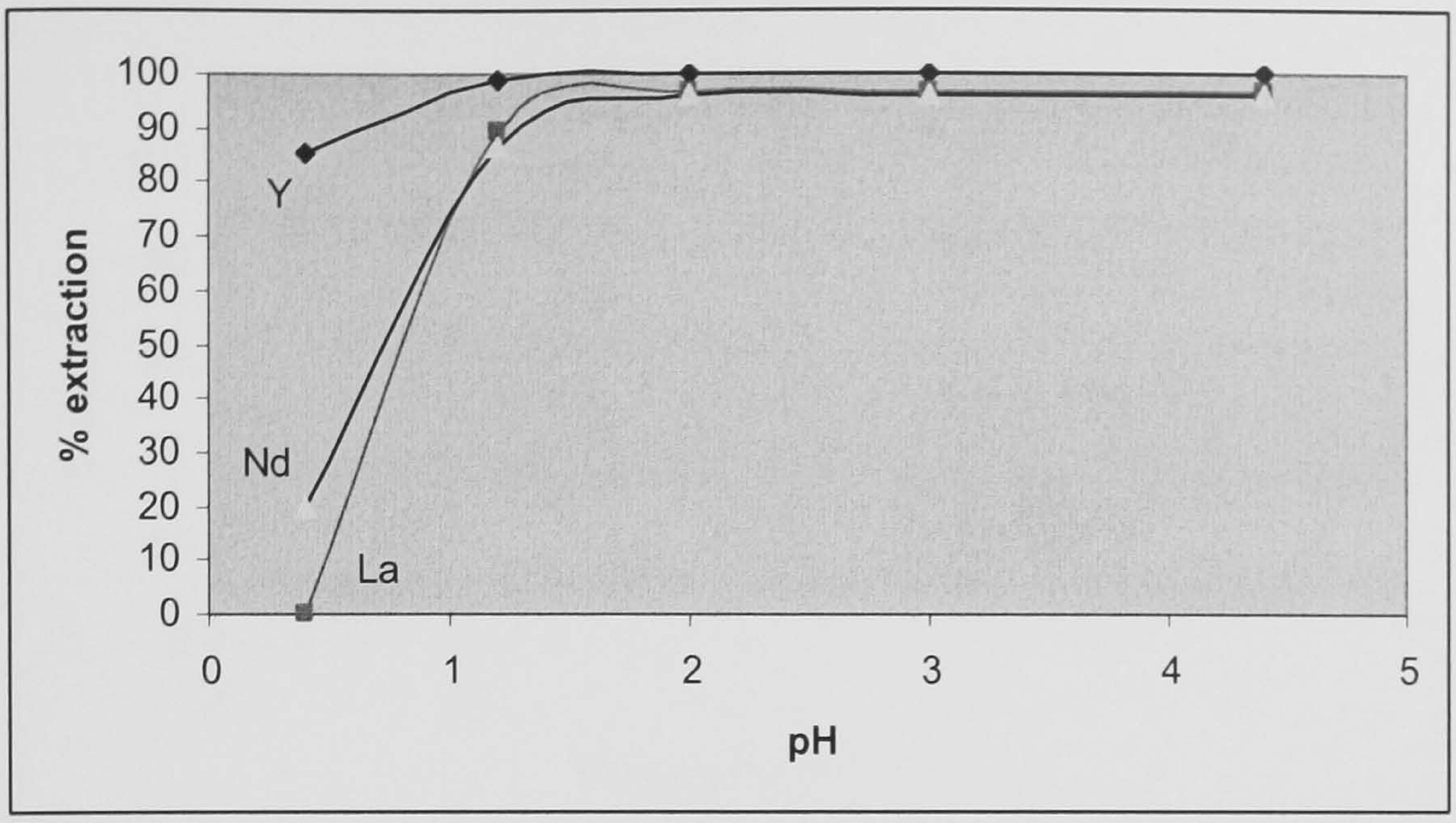


Figure 5.17: Extraction percent of Nd-La-Y as a function of pH.

5.2.2.4 Effect of different temperatures on the extraction of Nd-La-Y from sulfate solution.

For studying the effect of temperature on distribution coefficient and extraction percent, experiments were carried out in oil bath using an electric thermostat, the temperature of which was regulated from 25–50°C. The following factors were kept constant at 1:1 (v/v) organic to aqueous phase ratio, pH 2.0, contact time 10 minutes and 0.3M solution of primene JMT/carbon tetrachloride.

From the obtained results shown in Fig. 5.18 it is clear that there is almost no change in distribution coefficient with increasing temperature. This means that the extraction process is probably diffusion controlled. The phenomenon is similar to that occurring with other amide extractants, (2, 3) although this is not clear from the graph as all three lines elements overlap. The reason for this different behaviour compared to TiOA extractions, which are exothermic, is unknown.

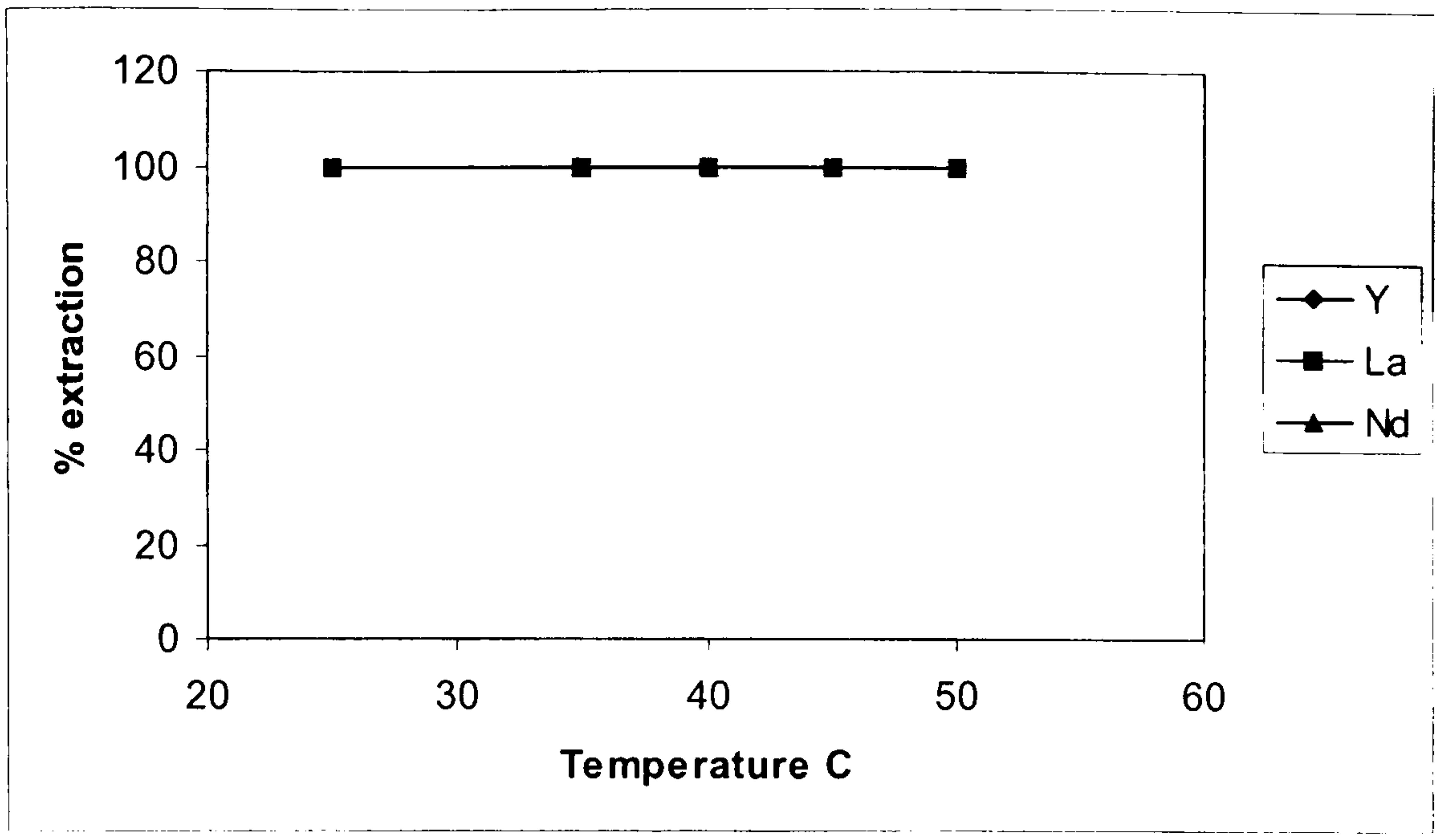


Figure 5.18: Extraction percent of Nd-La-Y as a function of temperature.

5.2.2.5 Effect of different diluents on the extraction of Nd-La-Y.

The extraction of ternary system components has been studied using different organic diluents namely, chloroform (1), carbon tetrachloride (2), toluene (3), benzene (4), *o*-xylene (5), dichloromethane (6), and kerosene (7). The other studied factors were fixed at the values at which maximum extraction occurred i.e. 1:1 (v/v) organic to aqueous phase ratio, room temperature, 0.3M primene JMT in all diluents, and contact time 10 minutes. Results are presented in Table 5.14 and shown in Fig. 5.19. It is obvious that non-aromatic diluents such as carbon tetrachloride, chloroform, and dichloromethane give quantitative extraction of yttrium, lanthanum, and neodymium.

Table 5.14: Effect of different diluents on the extraction of Nd-La-Y.

Diluents	Y % extraction	La % extraction	Nd % extraction
Chloroform (1)	100	100	95.75
Carbon tetra chloride (2)	100	100	98.66
Toluene (3)	85.17	71.54	81.53
Benzene (4)	88.30	74.23	83.42
O- xylene (5)	87.19	72.32	80.25
Dichloromethane (6)	100	100	98.9
Kerosene (7)	73.14	69.29	65.32

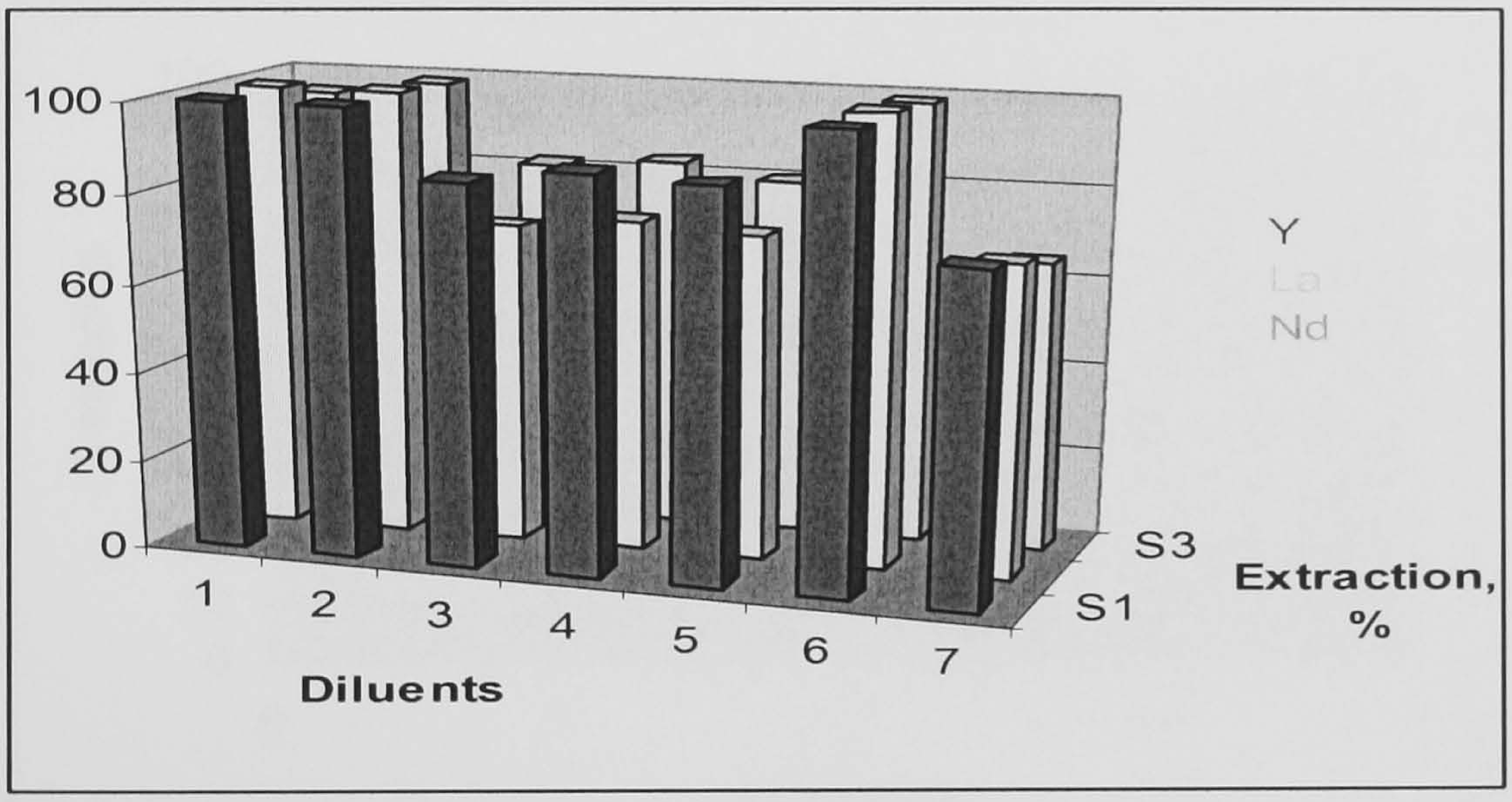


Figure 5.19: Extraction percent of Nd-La-Y as a function of diluents.

5.2.2.6 Acidic stripping:

5.2.2.6.1 Effect of different concentrations of H_2SO_4 on the stripping of Nd-La-Y from 0.3M primene JMT loaded solution.

A series of stripping experiments were carried out, using H_2SO_4 solutions of concentration ranging from 0.1M to 3M while the contact time was 10 minutes and phase ratio 1:1 organic/aqueous, room temperature. The obtained results are given in Table 5.15 and shown in Fig. 5.20. It is clear from the results that stripping by 0.1M

H_2SO_4 gives the best La-Y re-extraction percent, but for Nd the stripping efficiency increases with increasing H_2SO_4 concentration.

Table 5.15: Effect of sulfuric acid concentration on the stripping of Nd-La-Y.

[H_2SO_4]/M	Y % stripping	La % stripping	Nd % stripping
0.1	16.40	97.95	35.93
0.5	7.80	43.29	45.82
1.0	7.50	41.65	64.45
2.0	7.20	40.20	73.33
3.0	6.50	39.20	87.98

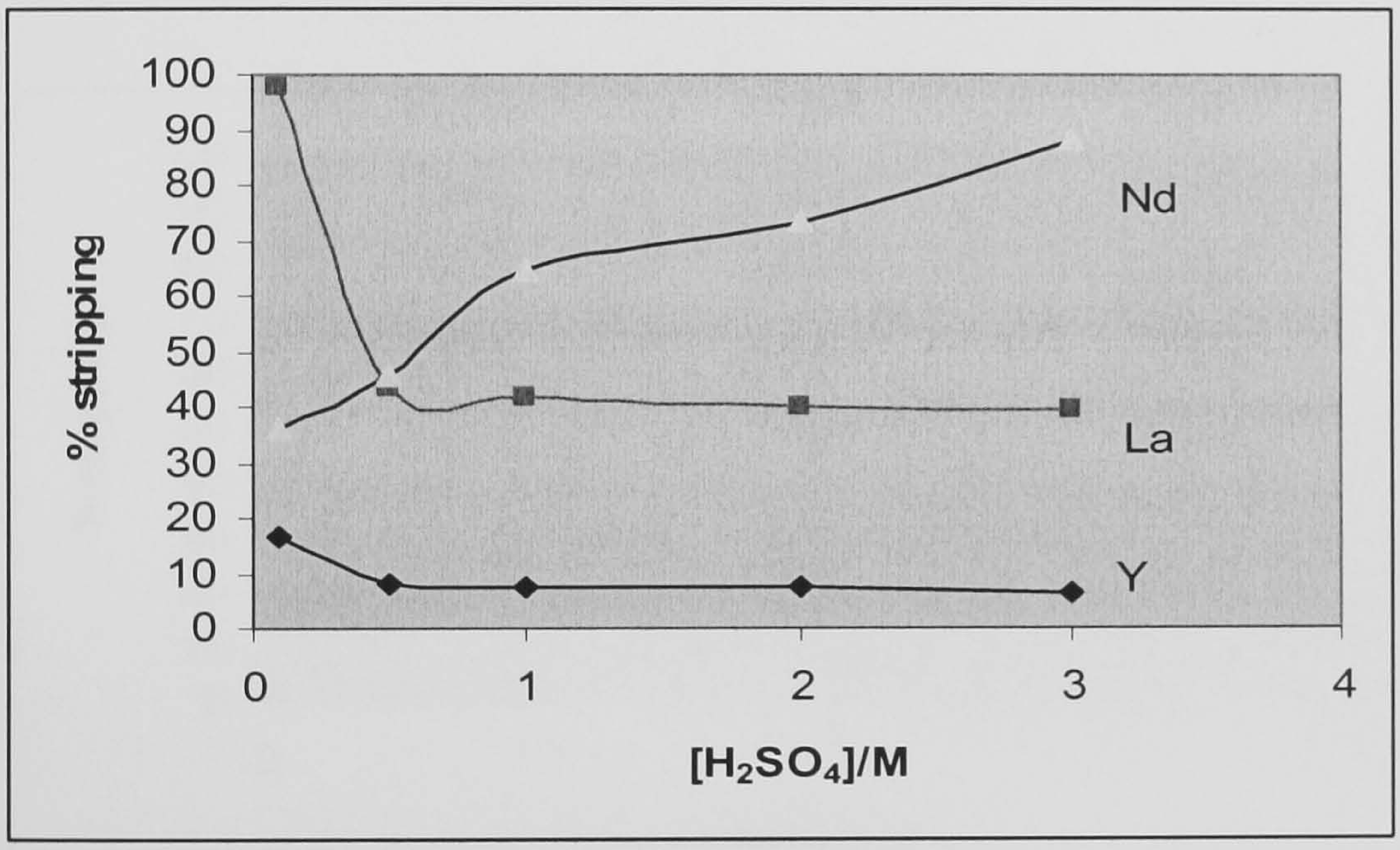


Figure 5.20: Effect of sulfuric acid concentration on the stripping of Nd-La-Y.

5.2.2.6.2 Effect of different concentrations of HNO_3 on the stripping of Nd-La-Y from 0.3M primene JMT loaded solution.

A series of stripping experiments were carried out using HNO_3 solutions of concentration ranging from 0.1M to 3M while the contact time was 10 minutes and phase ratio 1:1 organic/aqueous, room temperature. The obtained results are given in Table 5.16 and shown in Fig. 5.21. It is clear from the results that stripping by 0.1M

HNO_3 gives the best La-Y re-extraction percent but not in comparison with H_2SO_4 that gives a higher stripping efficiency. However 1M HNO_3 gives the highest stripping for Nd.

Table 5.16: Effect of nitric acid concentration on the stripping of Nd-La-Y.

[HNO_3]/M	Y % stripping	La % stripping	Nd % stripping
0.1	15.95	83.3	44.82
0.5	13.35	81.81	85.24
1.0	7.90	46.55	95.77
2.0	5.85	32.58	72.95
3.0	4.80	27.04	65.37

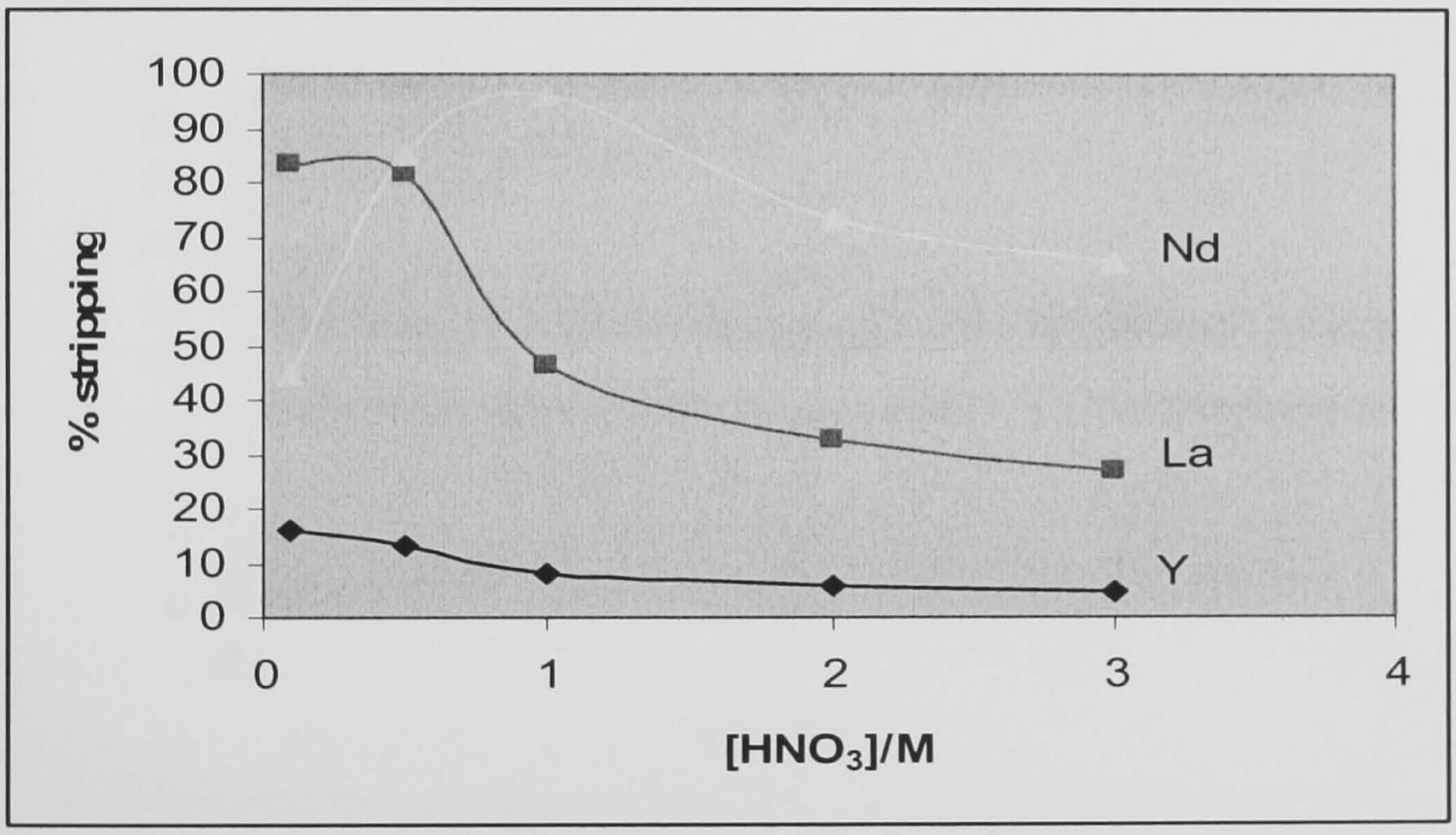


Figure 5.21: Effect of nitric acid concentration on the stripping of Nd-La-Y.

5.2.2.6.3 Effect of different concentrations of HCl on the stripping of Nd-La-Y from 0.3M primene JMT loaded solution.

A series of stripping experiments were carried out, using HCl solutions of concentration ranging from 0.1M to 3M while the contact time was 10 minutes and phase ratio 1:1 organic/aqueous, room temperature. The obtained results are given in Table 5.17 and shown in Fig. 5.22. It is clear from the results that stripping by 0.1M

HCl gives the best La-Y re-extraction percent, but not in comparison with H_2SO_4, which gives highest stripping efficiency. In the case of Nd 1M HCl gives the highest stripping but is much lower than that achieved with HNO_3.

Table 5.17: Effect of hydrochloric acid concentration on the stripping of Nd-La-Y.

[HCl]/M	Y % stripping	La % stripping	Nd % stripping
0.1	11.15	64.45	20.49
0.5	7.50	49.00	45.28
1.0	6.50	37.90	78.35
2.0	5.40	31.29	72.95
3.0	4.85	27.61	70.43

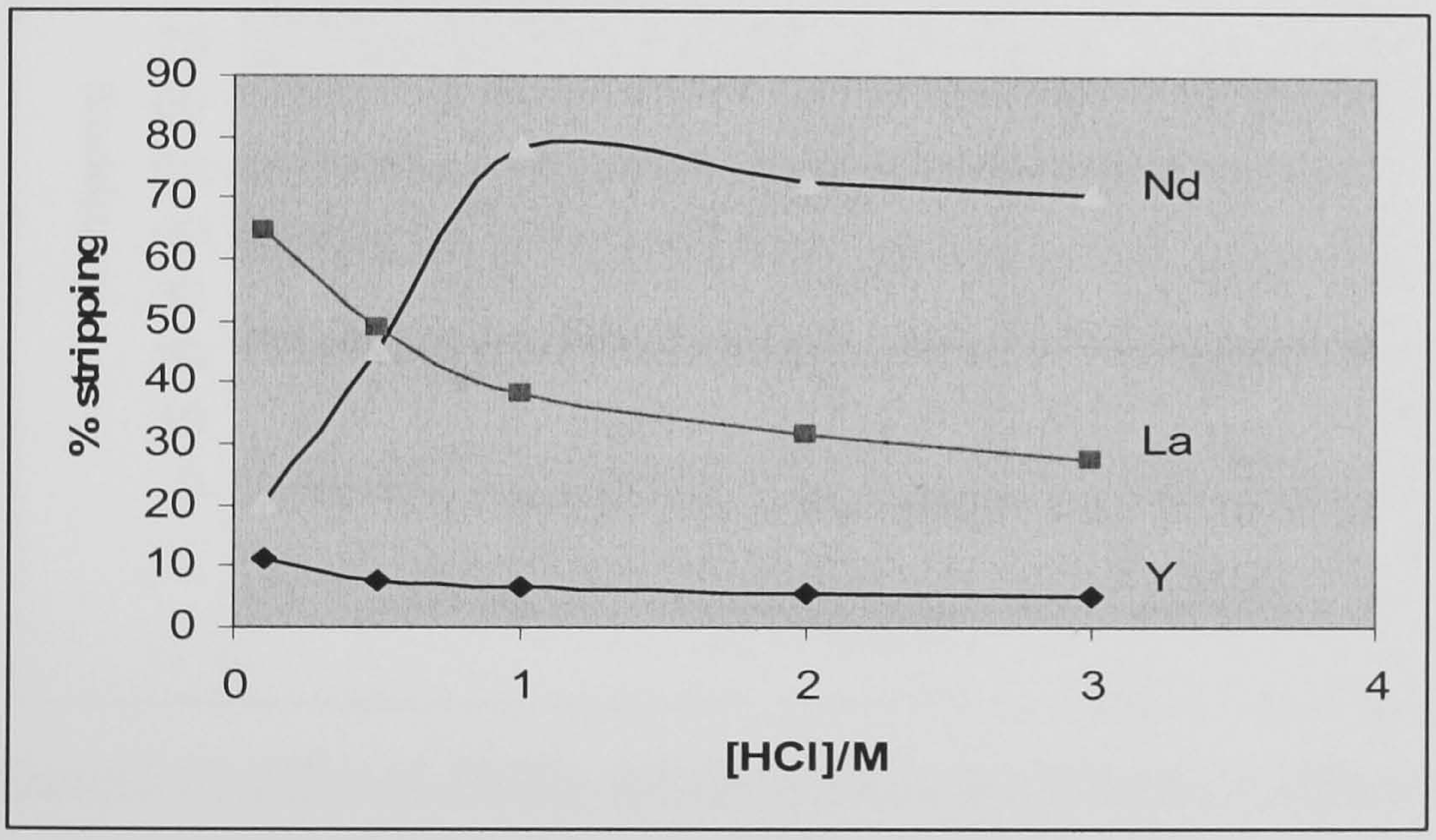


Figure 5.22: Effect of hydrochloric acid concentration on the stripping of Nd-La-Y.

5.2.2.6.4 Effect of different concentrations of $HClO_4$ on the stripping of Nd-La-Y from 0.3M primene JMT loaded solution.

A series of stripping experiments were carried out, using $HClO_4$ solutions of concentration ranging from 0.1M to 3M while the contact time was 10 minutes and phase ratio 1:1 organic/aqueous, room temperature. The obtained results are given in Table 5.18 and shown in Fig. 5.23. It is clear from the results that stripping by 0.1M

$HClO_4$ gives the best La-Y re-extraction percent, but not in comparison with H_2SO_4, and that 1M $HClO_4$ gives the highest extraction for Nd, but not compared with HNO_3.

Table 5.18: Effect of $HClO_4$ concentration on the stripping of Nd-La-Y.

$[HClO_4]$/M	Y % stripping	La % stripping	Nd % stripping
0.1	12.35	65.56	18.35
0.5	12.15	54.02	42.59
1	8.30	40.86	76.54
2	6.90	38.12	71.19
3	5.95	33.03	71.22

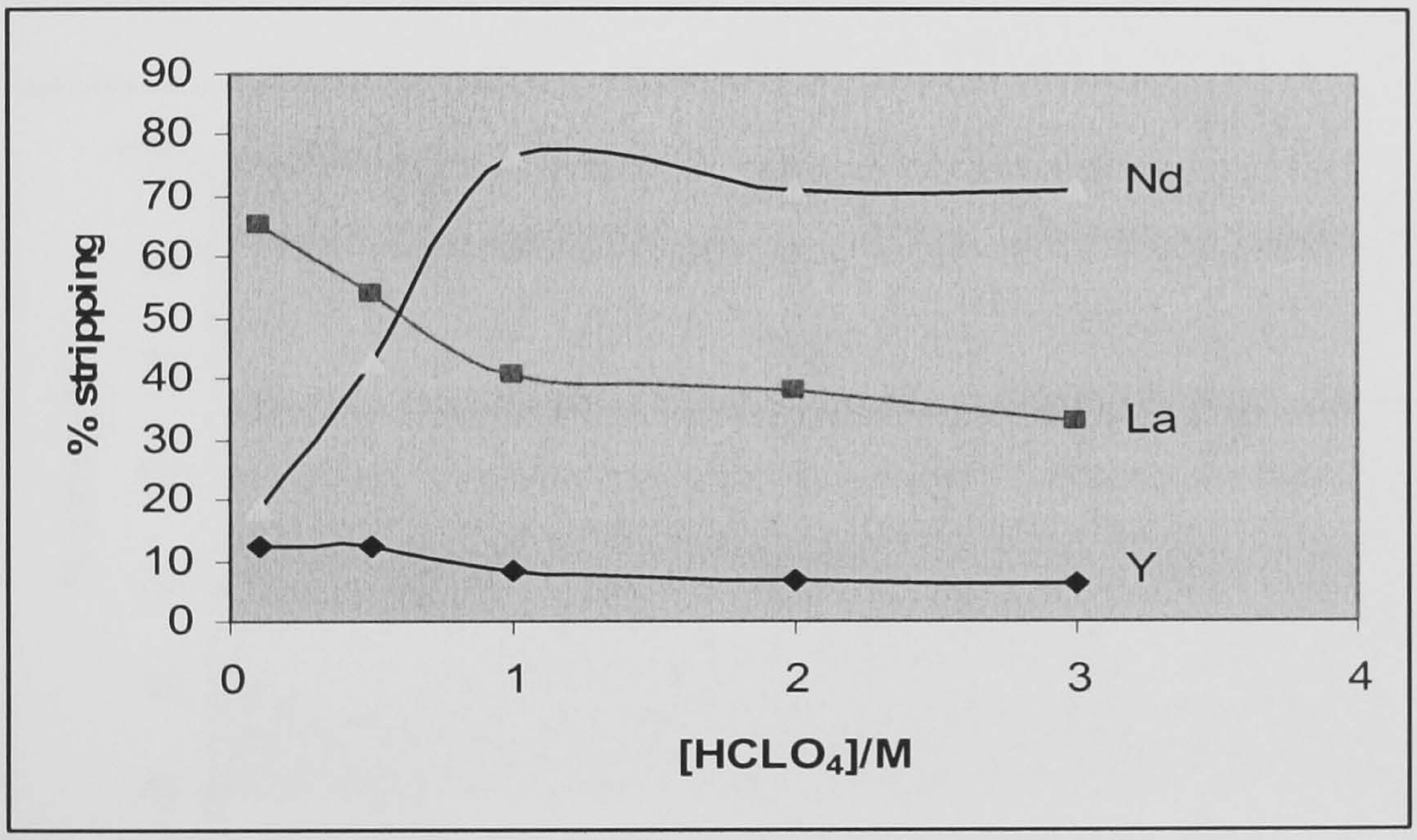


Figure 5.23: Effect of $HClO_4$ concentration on the stripping of Nd-La-Y.

5.2.2.6.5 Effect of different concentrations of CH_3COOH on the stripping of Nd-La-Y from 0.3M primene JMT loaded solution.

A series of stripping experiments were carried out, using acetic acid solutions of concentration ranging from 0.1M to 3M while the contact time was 10 minutes and phase ratio 1:1 organic/aqueous, room temperature. The obtained results are given in Table 5.19 and shown in Fig. 5.24. It is clear from the results that stripping by

2M CH_3COOH gives the best La re-extraction percent, in comparison with HCl, HNO_3, H_2SO_4, and $HClO_4$. In the case of Nd, and Y acetic acid gave lower stripping efficiency.

Table 5.19: Effect of CH_3COOH concentration on the stripping of Nd-La-Y.

[CH_3COOH]/M	Y % stripping	La % stripping	Nd % stripping
0.1	0.50	3.16	4.95
0.5	1.05	6.08	9.74
1	2.00	11.66	13.42
2	16.00	98.25	21.55
3	16.50	99.22	25.78

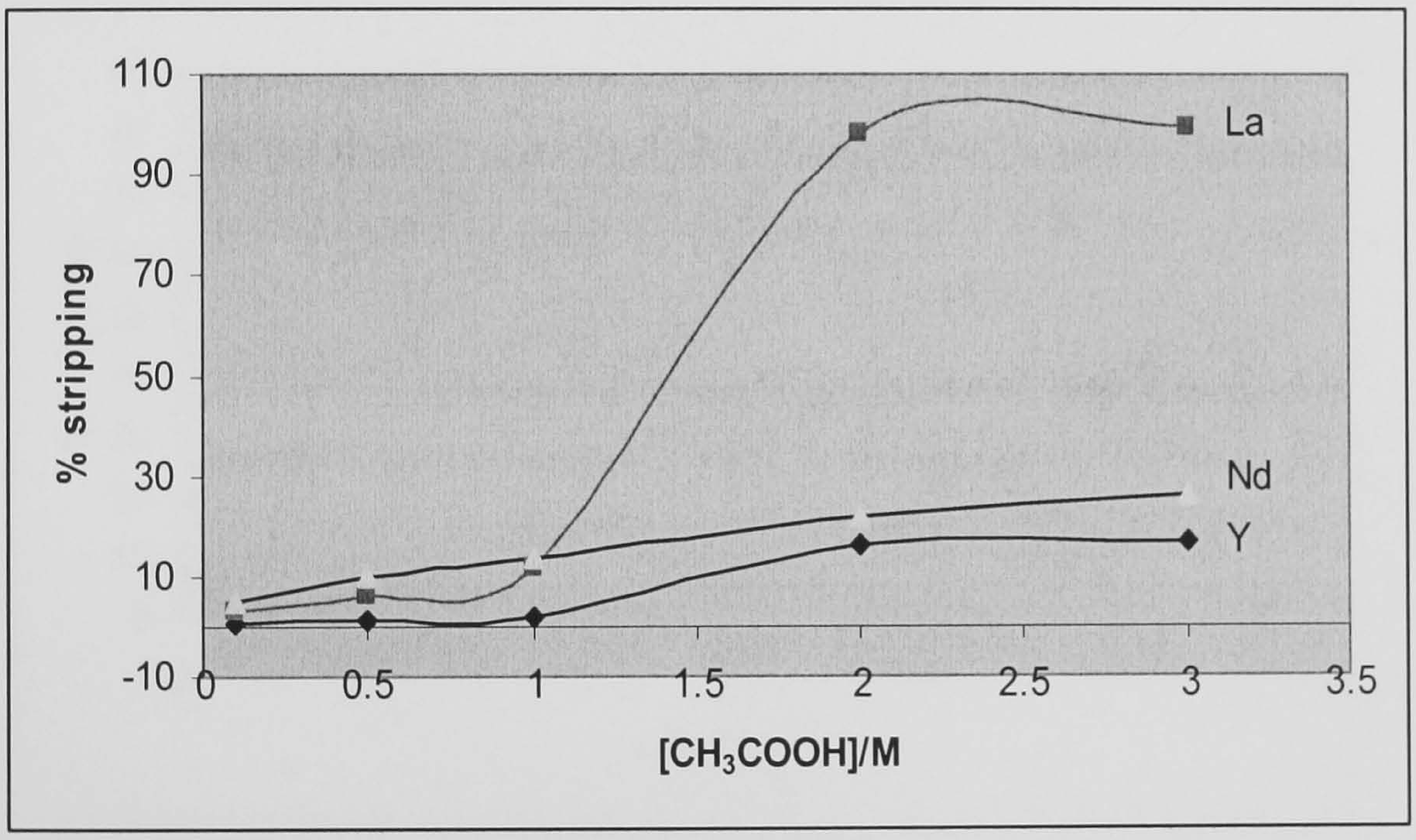


Figure 5.24: Effect of CH_3COOH concentration on the stripping of Nd-La-Y.

5.2.2.7 Alkaline stripping.

5.2.2.7.1 Effect of different concentrations of NaOH on the stripping of Nd-La-Y from 0.3M primene JMT loaded solution.

A series of stripping experiments were carried out, using NaOH solutions of concentration ranging from 0.1M to 1M while the contact time was 10 minutes and phase ratio 1:1 organic/aqueous, room temperature. The obtained results are given in

Table 5.20 and shown in Fig. 5.25. It is clear from the results that stripping by 0.1M NaOH gives the best Nd-La-Y re-extraction percent. However, in comparison, stripping by acidic reagents gave a higher much efficiency stripping.

Table 5.20: Effect of NaOH concentration on the stripping of Nd-La-Y.

[NaOH]/M	Y % stripping	La % stripping	Nd % stripping
0.1	9.40	79.23	4.72
0.3	2.60	15.97	3.89
0.5	2.00	12.37	2.18
0.8	1.75	9.80	1.89
1.0	1.45	9.02	1.77

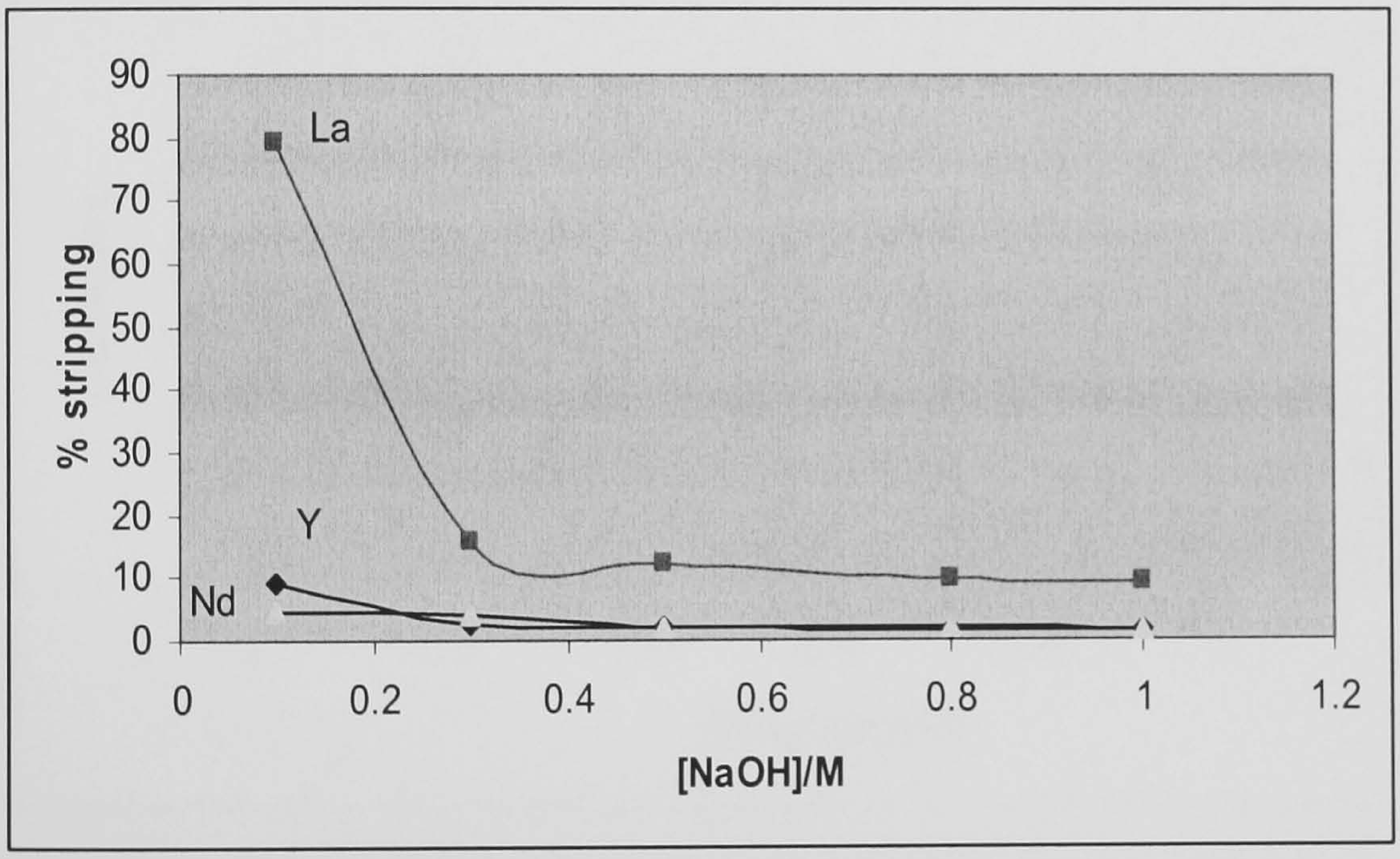


Figure 5.25: Effect of NaOH concentration on the stripping of Nd-La-Y.

5.2.2.7.2 Effect of different concentrations of Na_2CO_3 on the stripping of Nd-La-Y from 0.3M primene JMT loaded solution.

A series of stripping experiments were carried out, using Na_2CO_3 solutions of concentration ranging from 0.1M to 1M while the contact time was 10 minutes and phase ratio 1:1 organic/aqueous, room temperature. The obtained results are given in Table 5.21 and shown in Fig. 5.26. It is clear from the results that stripping by 0.1M

NaOH gave a higher Nd-La-Y re-extraction percent than 1M Na_2CO_3, but not in comparison to acidic stripping which gave the highest stripping efficiency.

Table 5.21: Effect of Na_2CO_3 concentration on the stripping of Nd-La-Y.

$[Na_2CO_3]$/M	Y % stripping	La % stripping	Nd % stripping
0.1	0.50	3.11	2.45
0.3	1.00	6.05	4.99
0.5	1.90	11.81	10.78
0.8	3.95	23.91	21.33
1.0	4.85	29.52	25.89

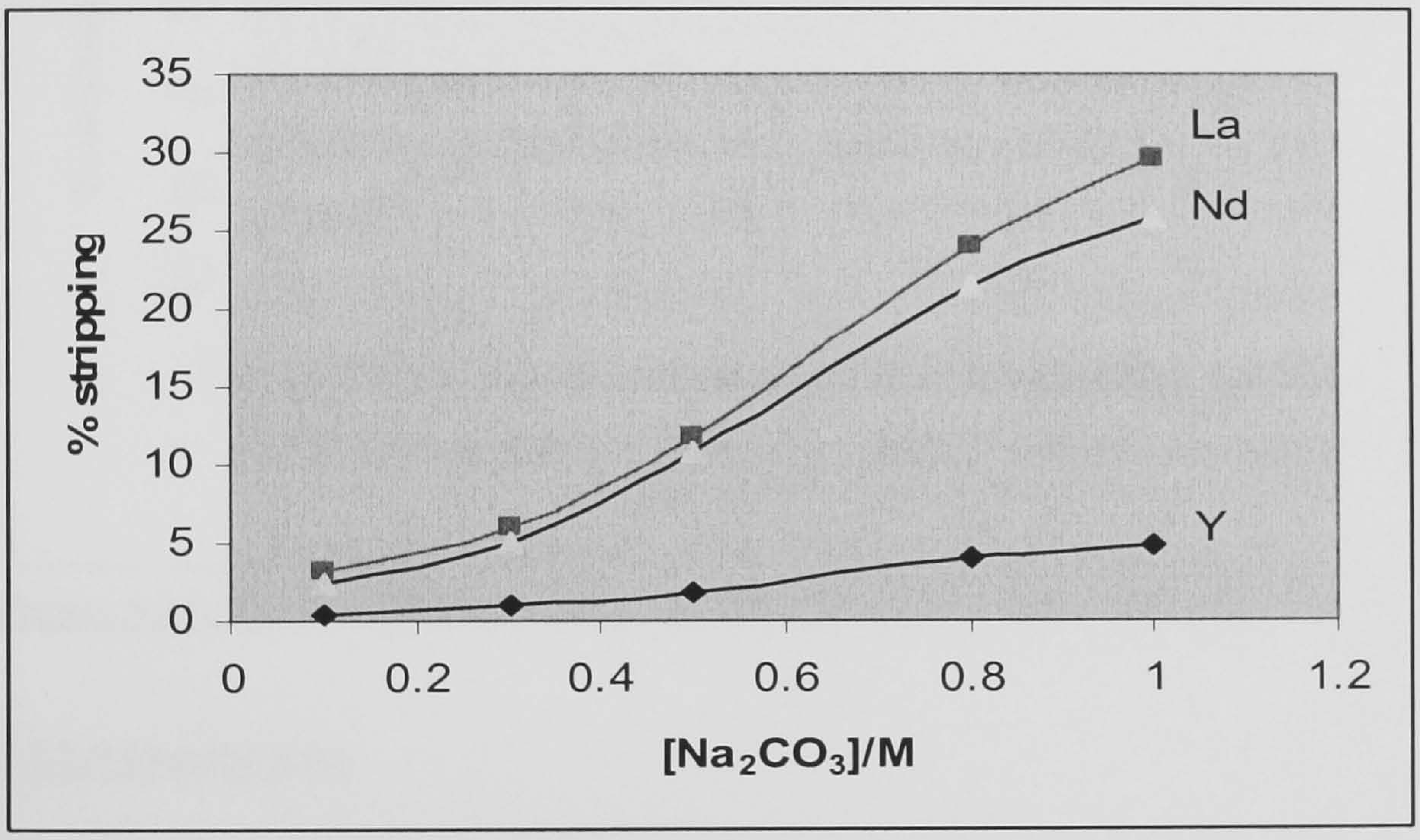


Figure 5.26: Effect of Na_2CO_3 concentration on the stripping of Nd-La-Y.

5.2.2.8 Effect of equilibration time on the stripping of Nd-La-Y.

The effect of equilibration time on the attainment of an equilibrium state has been studied at the time interval 1 to 30 minutes, while the other factors were kept at 0.1M H_2SO_4 and 1:1 (v/v) aqueous to organic phase ratio and the experiments were carried out at room temperature. The results obtained are given in Table 5.22 and shown in Fig. 5.27. It is obvious that contact time of 10 minutes is sufficient for stripping from 0.3M primene JMT loaded solvent.

Table 5.22: Effect of equilibration time on the stripping of Nd-La-Y.

Time/minutes	Y % stripping	La % stripping	Nd % stripping
1	8.40	83.71	32.42
5	10.23	85.23	36.12
10	16.50	97.90	34.02
15	15.75	97.70	34.09
30	15.65	97.55	34.10

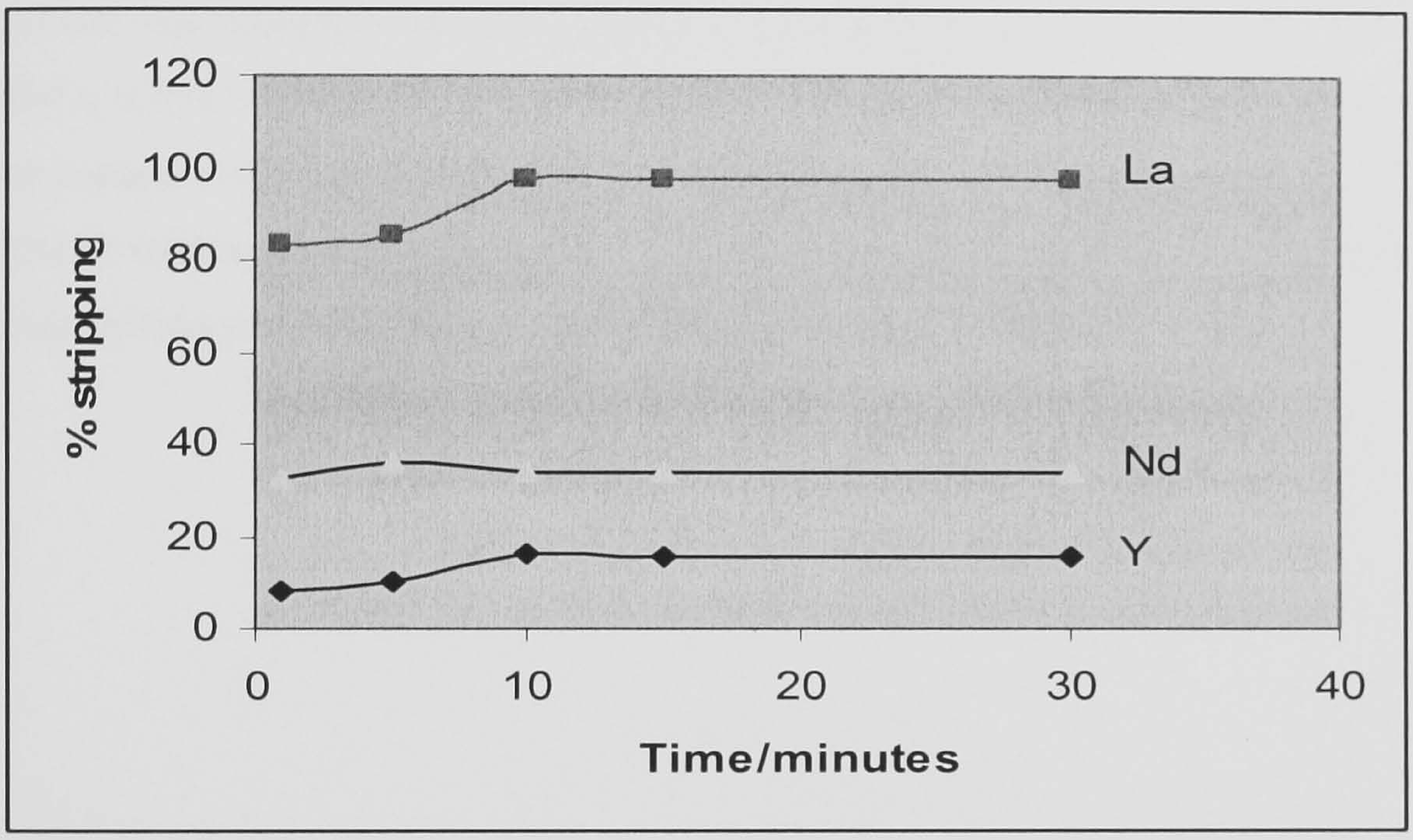


Figure 5.27: Effect of equilibration time on the stripping of Nd-La-Y.

5.2.2.9 Conclusions.

The utilization of solvent extraction in order to obtain an efficient and economic separation of Nd-La-Y as ternary mixtures has been studied. The optimum conditions for this separation from sulfate liquor was 0.3M primene JMT/CCl_4, at pH 2.0, no change in extraction by applying different temperature, and CCl_4 was the best diluents. Suitable conditions for stripping were 0.1M H_2SO_4 for La-Y but in case of Nd increasing the sulfuric acid concentration increased the stripping. 0.1 M HNO_3 gave the highest stripping efficiency for La-Y but 1M HNO_3 the highest for Nd, and the same results with HCl and $HClO_4$. In comparison H_2SO_4 gave a higher stripping than other acids. Acetic acid gave about 99 % stripping for La only so, it is easy to use acetic acid for selective separation of La from the ternary mixtures. Alkaline stripping (NaOH and Na_2CO_3) gave efficiency lower than the acidic stripping.

The primary amine primene JMT was tested for the separation of Th from sulfate solutions containing Fe, U, and some lanthanides. (28) However, no data about using primene JMT in extraction separation of individual lanthanides like Nd-La-Y from sulfate solutions were available before this study. Primene JMT quantitavely extracts Nd-La-Y ternary systems from sulfuric acid solution and, after extraction, the loaded solvent was stripped by different agents to separate the individual elements. 1M HNO_3 selectively stripped Nd from the loaded organic phase while acetic acid gave the highest stripping efficiency for La. Finally we added 5 % oxalic acid to precipitate yttrium oxalate. Our future plan is to take the advantages of primene JMT from bench scale (laboratory) to industrial semi commercial scale plants.

5.2.2.10 References.

1 I. McGill, Ullmann's Encyclopedia of Industrial Chemistry, Second Edition, (2002).

2 R. E. Treybal "*Liquid extraction*", McGraw-Hill, New York-Toronto-London 1963.

3 J. Rydberg, C. Musikas, G. R. Choppin(eds.) "*Principles and Practises of Solvent Extraction*" M. Dekker, Inc., New York 1992.

4 J. D. Gdfrey, M. J. Slater(eds.) "*Liquid –liquid Extraction Equipment*, J. Wiley & Sons, New York 1994.

5 E. Blass, W. Goettert, M. J. Hampe "*Liquid –liquid Extraction Equipment*, J. Wiley& Sons, New York 1994.

6 I. Wagner, Ph. D. Thesis, Technische Universität München, (1999).

7 M. Henschke, Ph. D. Thesis, RWTH Aachen, (1995).

8 E. Aufderheide, Ph. D. Thesis, Technische Universität Clausthal (Fed. Rep. of Germany) (1985).

9 K. Koppers, Hydrocarbon Process, (1973) **52**, 139.

10 T. C. Lo, M. H. I. Baird, C. Hanson (eds.): *Handbook of Solvent Extraction*, Wiley-Interscience, New York, (1983).

11 W. Pietzsch, Ph. D. Thesis, Technische Universität München (Fed. Rep. of Germany) (1984).

12 H. Haverland, Ph. D. Thesis, Technische Universität Clausthal (Fed. Rep. of Germany) (1988).

13 K. H. Rreissinger, Ph. D. Thesis, Technische Universität Graz (Austria) (1985).

14 R. Berger, K. Walter, Chem. Eng. Sci. (1985) **40**, 2175.

15 H. Zimmermann, Ph. D. Thesis, Technische Universität München (Fed. Rep. of Germany) 1981.

16 Th. Pilhofer, Chem. Ing. Tech. (1976) **48**, 237.

17 A. A. Abdeltawab, S. Nii, F. Kawaizumi, and K. Takahashi, *Proceedings of the International Solvent Extraction Conference, ISEC,* (2002).

18 C. Koopman, G. J. Witkamp, and G. M. Van Rosmalen, *Sep. Sci. Technol*, (1999) **34**, 2997.

19 J. Rydberg, C. Muskas, and G. R. Choppin, *Principles and Practices of Solvent Extraction*, Mercel Dekker, New York, (1992).

20 V. Jedinakova, P. Vanura, J. Zilkova, V. Bilek, F. Touti, *J. of Radioanal. and Nucl. Chem.*, (1992) **162**, 267.

21 J. Kovalancik, and M. Galova, *J. of Radioanal. and Nucl. Chem.*, (1992) **162**, 35.

22 J. Inczedy, *Analytical Applications of Complex Equilibria*, Akademiai Kiado, Budapest, (1976).

23 I. L. Dukov, V. M. Jordanov, *Solvent Extr. Ion Exch.* (1998) **16**, 1151.

24 I. L. Dukov, V. M. Jordanov, *Monash. Chem.* (1999) **130**, 865.

25 P. Nekovar, D. Schrotterova, and M. Mrnka, , *J. of Radioanal. and Nucl. Chem.*, (1997) **223**, 17.

26 K. S. Chou, and C. C. Lin, *Hydrometallurgy*, (1986) **15**, 39.

27 L. E. Schultze, J. A. Eisele, M. T. Morimoto, and D. T. Bauer, U.S. Bur. Mines Rept. Invest, (1979) 1.

28 G. M. Ritcey, A. W. Ashbrook, *Solvent Extraction Principles and Applications to Process Metallurgy*, Elsevier, Amesterdam, (1979).

29 A. M. Cekmarev, S. V. Cizev, M. Mrnka, and D. Schrotterova, *Proc. Int. Solv. Extr. Conf., ISEC'88*, Vol. 3, Moscow, (1988).

30 M. Mrnka, D. Schrotterova, and P. Nekovar, Scientific Papers of the Prague Institute of Chemical Technology, B29 (1984) 229.

31 M. Mrnka, D. Schrotterova, and V. Bizek, *Zh. Neorg. Khim* (1984) **29**, 2068.

Chapter Six

Novel extractants and their uses in liquid-liquid extraction of rare earth elements

6.1 Introduction.

Recently there has been a significant increase in the use and demand for rare earth element compounds, particularly high purity rare earth elements. Liquid-liquid extraction of the rare earth elements has been studied extensively since the 1950's, and this technique is now widely accepted in the commercial processing of certain rare earth elements. In recent years, amides have been proposed as alternatives for phosphorous-containing compounds as extractants in the nuclear fuel reprocessing because of several advantages, such as complete incinerability, high chemical and radiolytic stability, simplicity of synthesis and easy removal of the degradation products. (1-3)

The structures of extractants have been a major concern in the development of new extractants with a potential high extracting power for metal ions. Yuan, Xu *et al* (4, 5) pointed out that electron density at the active site, steric effects and lipophilicity of an extractant are the main factors affecting the extracting power for metal ions.

6.1.1 Recent ligand design for solvent extraction of metal salts.

To make solvent extraction of metal salts viable, highly selective ligands that can complex both the metal cation and the attendant anion(s) are required. Design of these ligands should focus on producing separate cation- and anion-binding sites otherwise the anion could be bound directly to the metal centre. To facilitate stripping procedures, it is desirable to have separated binding sites in the extractant. There are examples of this type of ditopic ligand in the literature. Reinhoudt and co-workers constructed a ligand that contained two cation-binding crown ether groups and two anion-binding amide moieties, which were aided in their role by a lewis acidic UO^{2+} group in relatively close proximity (6) (Fig. 6.1). The receptor successfully complexed both potassium and dihydrogenphosphate ions.

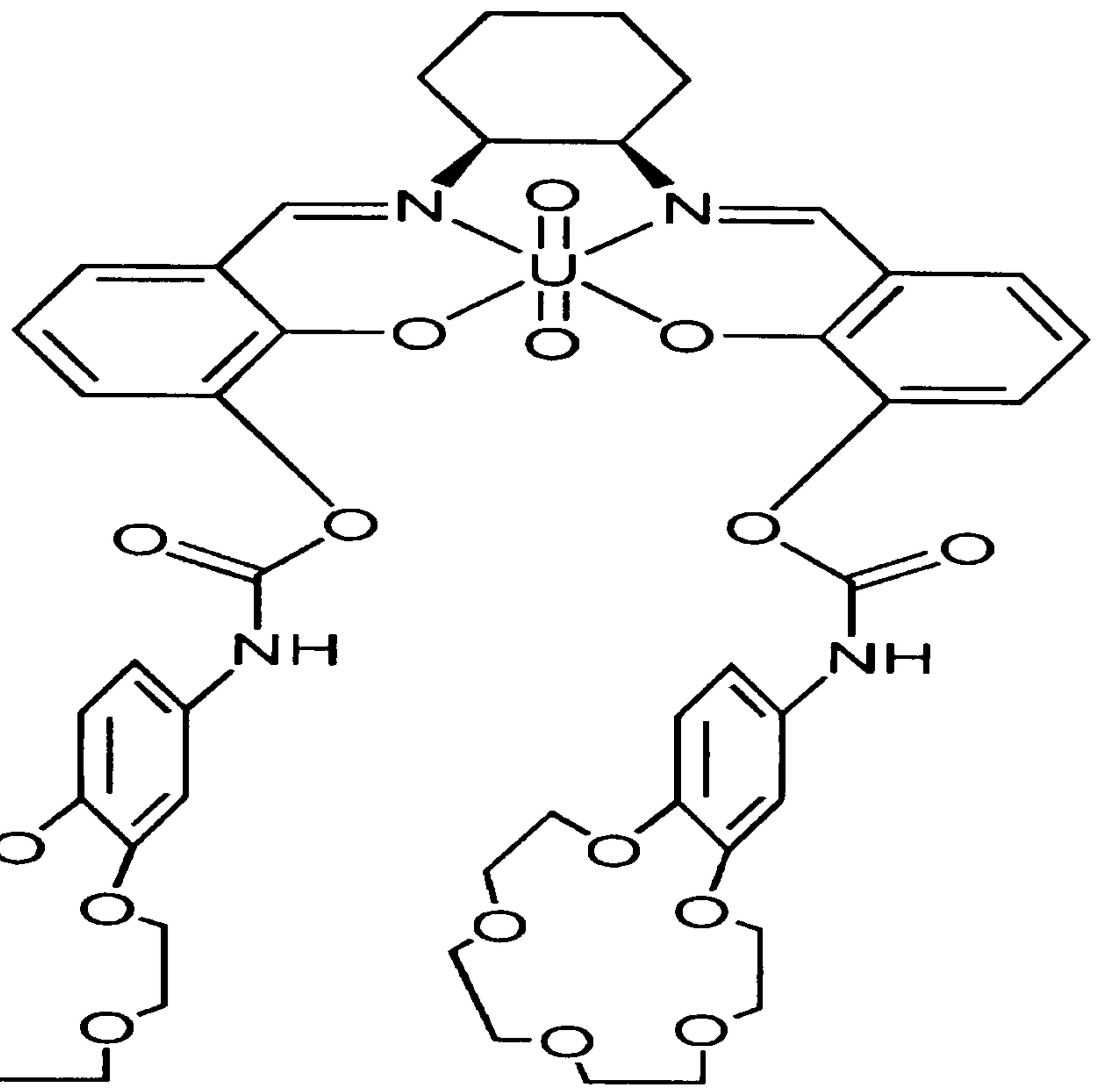


Figure 6.1: Ditopic ligand developed by Reinhoudt and co-workers to bind $K^+/H_2PO_4^-$.$^{(6)}$

Another example of this type of ligand was reported by Beer *et al.* in which the receptor contained two benzo[15] crown-5 moieties attached to the lower rim of calix[4]arene through an amide linker $^{(7)}$ (Fig. 6.2). In the absence of alkali metal cations, the amide groups bound no anions, but on addition of potassium ions a sandwich complex was formed between the two crown ether units. This templated the formation of an anion-binding site by bringing the amide moieties closer together. The system showed particular selectivity for the dihydrogen phosphate anion. This system demonstrates the benefit of using ditopic ligands with separate binding sites. Cooperative binding can be achieved using cation complexation to facilitate anion binding.

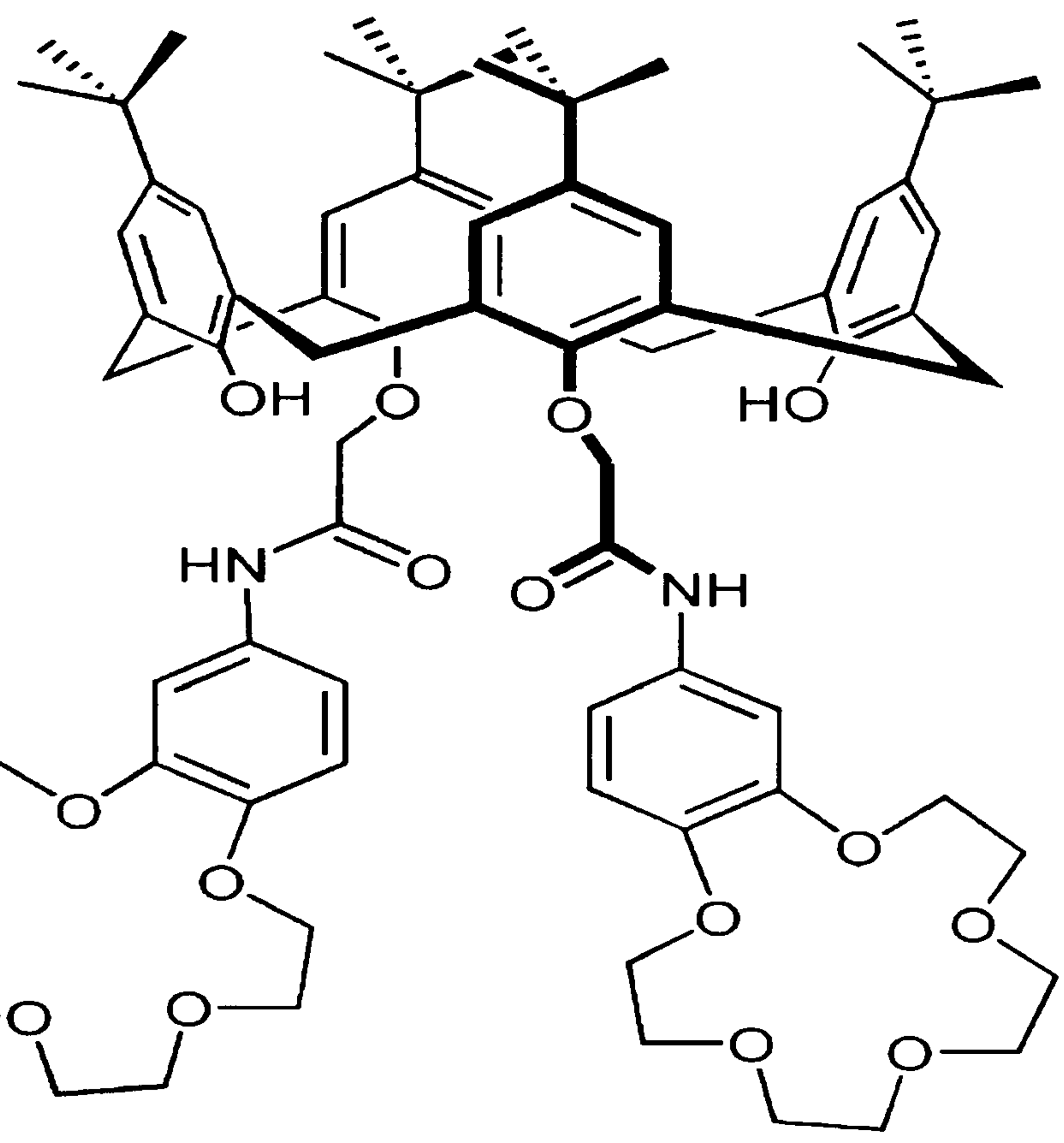


Figure 6.2: Calixarene-based ditopic receptor developed by Beer *et al.* (7)

It is important to consider the behaviour of ligands in the non-polar solvents used in industrial solvent extraction when designing extractants. Intra- and intermolecular interactions, such as hydrogen bonds, become increasingly significant and can be instrumental in controlling the efficiency of complexation and extraction. An example of this uses the well-known phenolic oxime extractants. (8) These are used in hydrocarbon solvents for the recovery of copper. Intermolecular hydrogen bonds between the oxime OH group and the phenolate oxygen atoms lead to the formation of *pseudo*-macrocyclic copper complexes (9) (Fig. 6.3) of high stability, which contribute to the efficiency of the process.

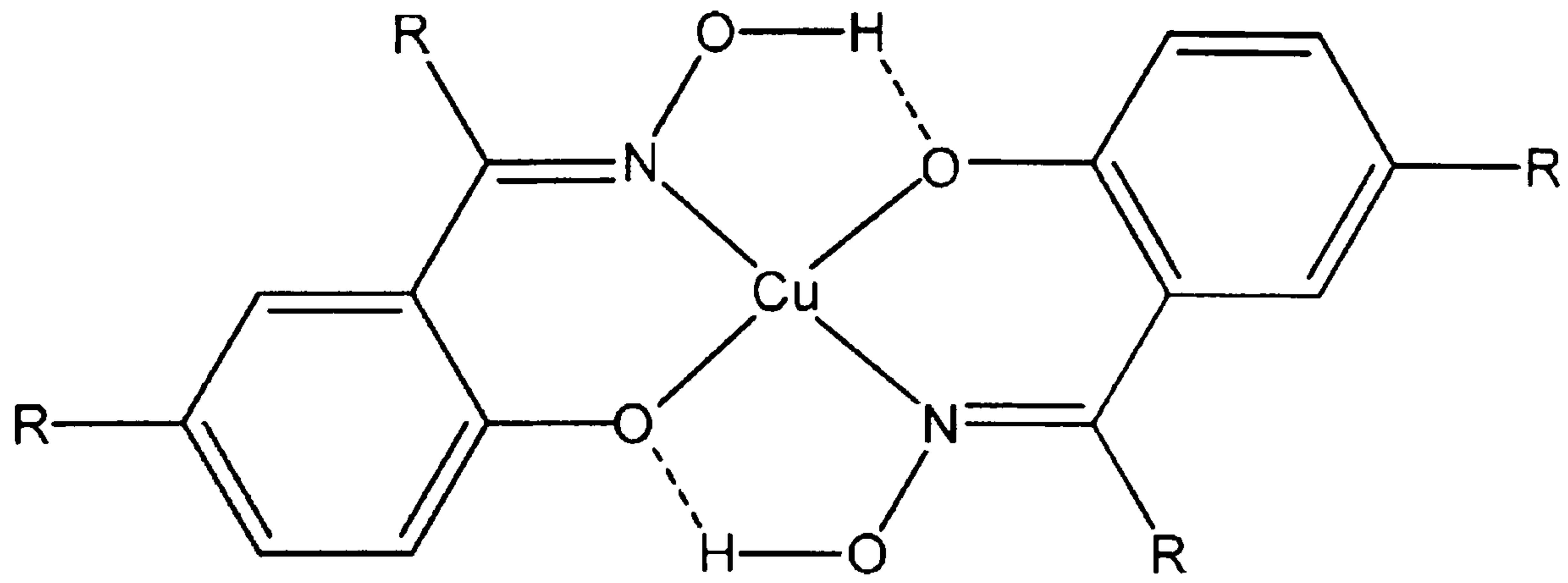


Figure 6.3: Phenolic-oxime *pseudo*-macrocyclic copper complex. (9)

In another example, the organophosphorus acid metal extractants show very strong interligand hydrogen bond causing the formation of dimers in hydrocarbon solvents. (10) The eight-membered rings in the dimers are retained upon metal complexation, in the presence of excess extractant (Fig. 6.4). This has important consequences as the bite angle defined by the *pseudo*-chelate rings favours tetrahedral coordination and allows the selective extraction of metals such as zinc. For example, di(2-ethylhexyl)phosphoric acid (D2EHPA) extracts Zn^{2+} more strongly than other first row transition metal ions. (10, 11) Ditopic ligands have been designed in the Tasker group (12) to transport metal salts. The metals that were targeted for extraction were copper and nickel and the anion chosen was sulfate, the anion present in many pregnant leach solutions. A salen-based binding site (salen = N,N-(salicylilene)ethylenediamine dianion) was used as a coordination site for the metal (Fig. 6.4) as it is known to bind strongly to nickel and copper. (13, 14)

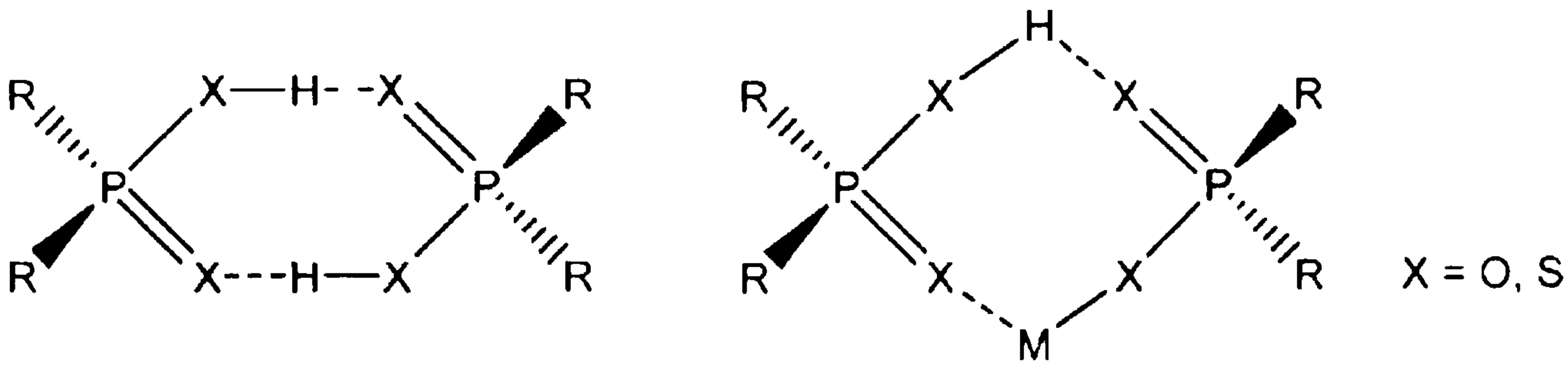
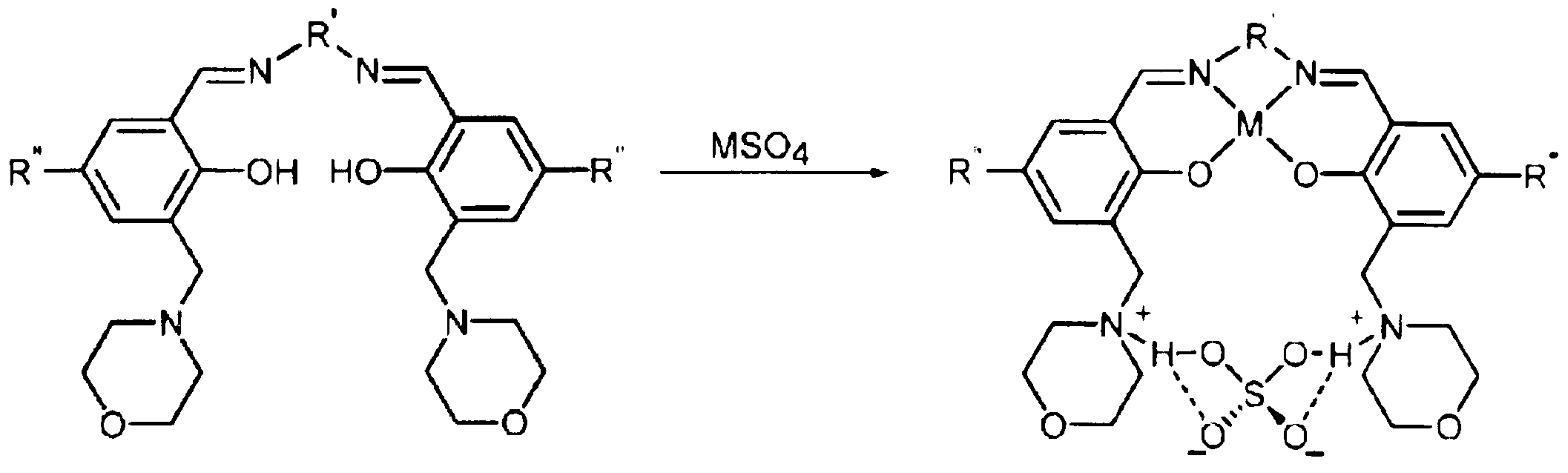


Figure 6.4: Organophosphorous acid extractants and their mode of metal binding. (11)



R' – -$(CH_2)_2$-(A), *o*-C_6H_4(B), (+)-*trans*-1,2-cyclohexane (C)

R'' = Bu^t, branched nonyl (used for solvent extraction to increase organic solubility)

Figure 6.5: Prototype ditopic ligands for the transport of metal sulfate. (11)

The prototype ligands (12) (Fig. 6.5) also have two pendant tertiary amines that are capable of capturing the protons released from the phenolic oxygen atoms upon metal complexation giving the ligand a zwitterionic form (positive and negative sites are present but the molecule is overall charge-neutral). These arms are templated by the coordination of a metal ion to create a dicationic-binding site for anions. This is important for the encapsulation of the sulfate anion in the solid state (12) and is also essential for the efficient solvent extraction of sulfate. (15) The anion-binding site also has the ability to hydrogen bond to the captured anion. These types of interactions are important to the efficiency of transport in solvent extraction processes. An advantage of the ligand's zwitterionic form is that no acid is lost to the aqueous phase upon formation of a complex with a metal salt so the pH of the raffinate is similar to that of the feed solution. The overall charge neutrality of the complex is also important for solubility in hydrocarbons or other solvents of low polarity. These design features open up the possibility for the ligand to be used in hydrometallurgy operations in sulfate media (Fig. 6.6). A practicable metal salt extractant must bind the targeted metal cation and anion(s) strongly and selectively. This could be performed by a variety of methods such as using the coordination of a metal cation to template the formation of the anion-binding site or by taking advantage of the importance of hydrogen-bond interactions in non-polar solvents. To develop highly selective systems for the desired metal cation and anion(s), convenient methods to assess selectivity are required.

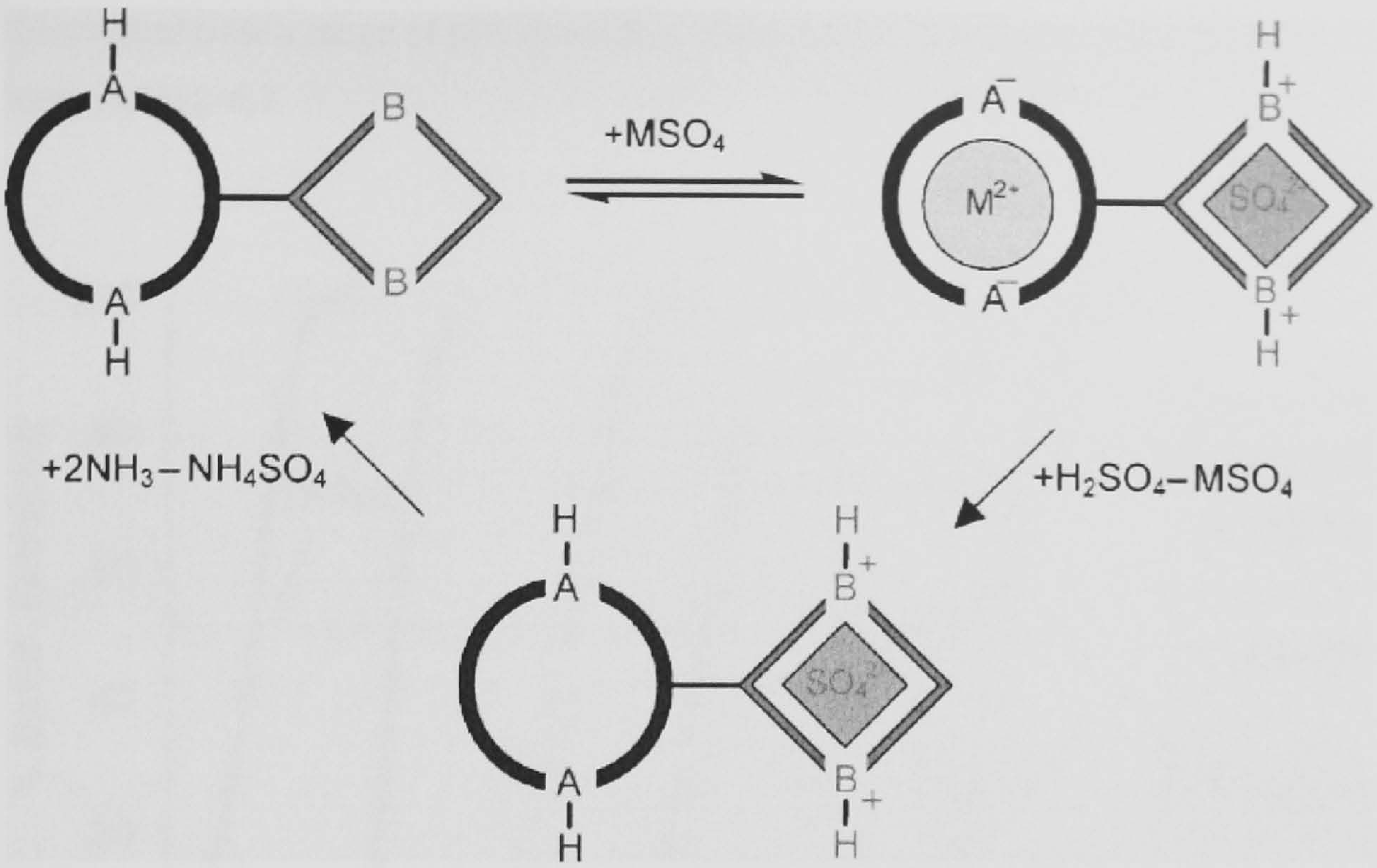


Figure 6.6: Application of zwitterionic ditopic ligands with dicationic/dianionic sites for the transport of metal sulfates.

6.1.2 Metal and anion detection methods for assessing selectivity.

Reliable analytical techniques are needed to obtain accurate data for the amount of metal and anion extracted or the relative strength of their binding. Metal ions can be detected by a variety of methods (16) (e.g. inductively coupled plasma optical emission spectroscopy (ICP-OES), atomic absorption spectroscopy, UV-Vis spectroscopy), which can be used to determine the selectivity of their extraction. ICP-OES is very good for accurately analysing samples for metal content (less than 10ppb detection limits) (16) and in solvent extraction experiments it can be used to analyse both the organic and the aqueous phase to check for materials balance.

In hydrometallurgy, a common way of comparing the "strengths" of organic acid (LH) extractants is by measuring the $pH_{1/2}$, which is the pH associated with 50% loading of the extractant at a stated concentration and for a defined composition of aqueous feed. (11) Conventionally, for the extraction of metal ions, the lower the $pH_{1/2}$ the stronger the metal complexations. If the metal content of the organic phase is determined over a range of pH, then $pH_{1/2}$ values can be obtained and selectivity's assigned Fig. 6.7.

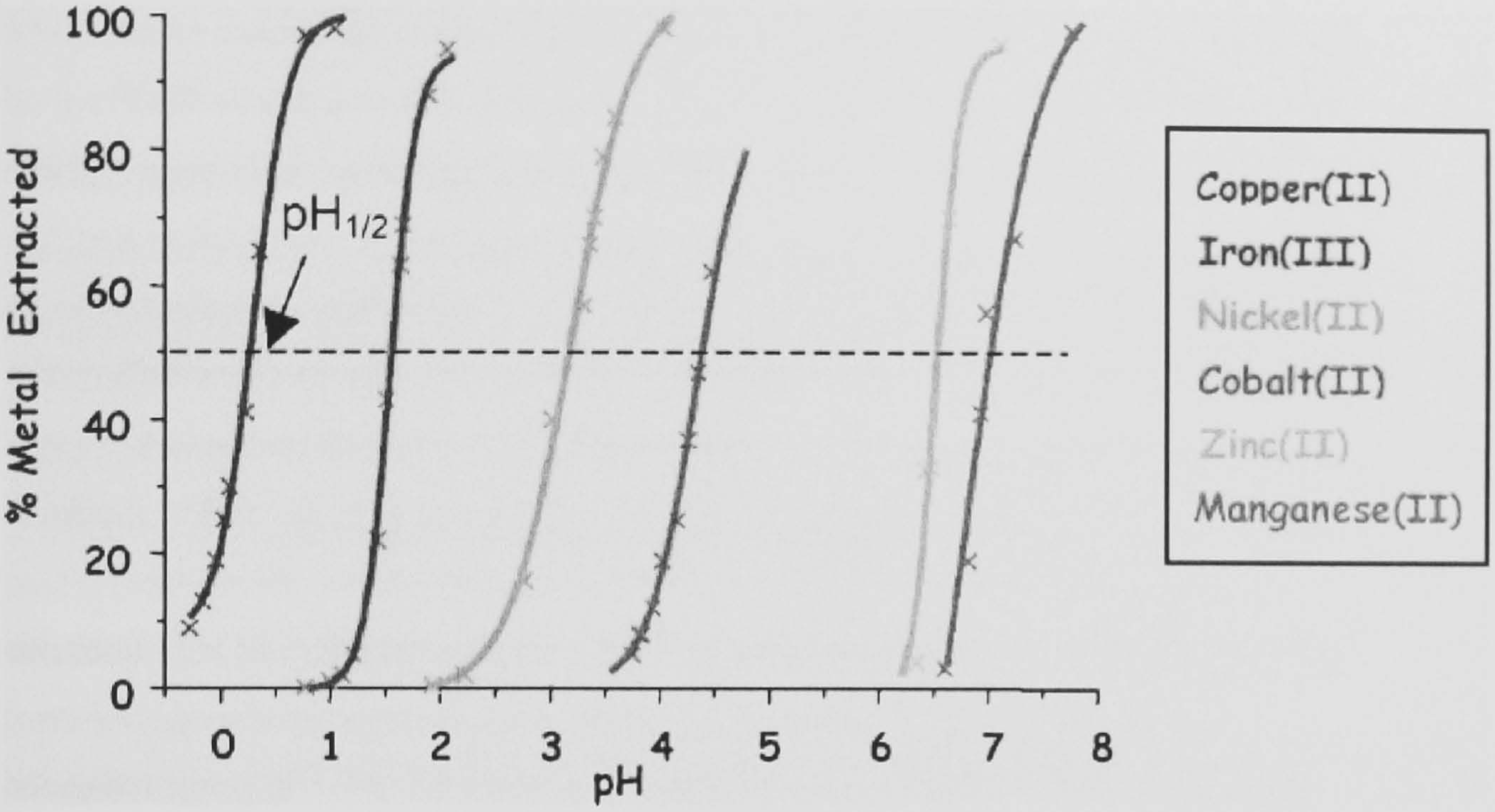


Figure 6.7: The $pH_{1/2}$ of metals with p50-oxime (a phenolic oxime) copper extractant. (8)

The stability of anion complexation is examined in a number of different ways in the literature but most have involved a single-phase system. One popular method is based on potentiometry, or more specifically pH-meter. (17, 18) This technique is nearly always carried out using a glass pH electrode and, to be effective, it needs to relate the consumption or release of protons in the complexation process to the concentration of the anion-receptor complex formed. However, as ligands and anions can often capture protons independently, the first step in the procedure is usually to determine the basicity constants of the ligand and anion separately. (19) Once these are known, an alkali or mineral acid is titrated into a solution of the ligand, anion and protons, and the variation in the free hydrogen ion concentration is monitored. The stability constants of anion complexation can then be determined by computer programs. (19) This technique has been used successfully to generate anion selectivity data. To date, most of the studies have been carried out in water alone.

NMR is probably the most widely used technique for the determination of anion binding constants in non aqueous-solvents. (20) It has also provided some of the most important structural information on the solution behaviour of anion receptors. The experimentally measurable parameters (chemical shifts, coupling constant, etc.) in NMR can be used to determine complex stability constants. These parameters depend on the NMR-sensitive nuclei present and their chemical environments as well as the reaction rates of the exchange taking place between them. Slow or fast exchange gives different information: in the case of slow exchange, the amount of free and complexed species present in equilibrium can be determined from integration of signal area which allows an estimate of the stability constants. Under fast exchange average signals of chemical shift are obtained and these can be used to calculate equilibrium constants. NMR can also give information on the solution structure as NMR-sensitive nuclei most heavily involved in anion binding will exhibit the largest changes in chemical shift and relaxation times. The disadvantages of NMR are that it can suffer from low sensitivity resulting from the high association, and relatively high concentrations (10^{-2} -10^{-3}) of both host and guest are required to obtain appreciable NMR signals. (21) NMR also cannot be used in the presence of some paramagnetic nuclei (e.g. Cu^{2+}).

Anion coordination can also affect the electromagnetic (absorption) spectrum of the anion and/or the receptor in the 10^{-8}-10^{-4} m wavelength region, which allows the use of UV-Vis spectrophotometry and IR spectroscopy. Both of these techniques use the Beer-Lambert-Bouger law,

$$A_p = \sum \varepsilon_{ip} I C_i \qquad (1)$$

where A_p and ε_{ip} are, respectively, the absorbance of the solution and the molar absorption coefficient of the species at the wavelength denoted by the index p, C_i is the concentration of the species and I is the optical path length. (19) This relates the absorption data obtained to concentration, which can subsequently be used to calculate equilibrium constants for anion binding. UV-Vis and IR have been used as the dominant techniques (21, 22) because studies can take place at low and high pH and there is no restriction to aqueous solution.

A rapidly growing and popular way of monitoring anion concentration is the use of anion selective electrodes. (19) There are several different metal ion selective electrodes available but the range of anion selective electrodes is still relatively small. Those for halides are now widely available and successfully used, often in combination with a glass electrode, to give information on the free concentration of the anion under study and the hydrogen ion concentration. (23) For analysis by ICP-OES, elements generally require one or more atomic or ionic emission lines in the 160 to 900nm region to be detected accurately. The sulfate anion can therefore be analysed as it has emission lines at low wavelength (180-190nm) capable of giving reliable results. In metal salt extraction this allows the amount of metal and sulfate extracted by ligand to be analysed simultaneously as the ICP-OES can perform multi-element analysis.

The selectivity of metal ion extraction can be assessed by the determination of differences in $pH_{1/2}$ values (Fig. 6.7). (8) If $pH_{1/2}$ values for sulfate complexation can be obtained by monitoring the extraction of sulfate over a range of pH, then they could be used to assess the strength of the sulfate binding in two-phase extraction experiments. In this case the higher the $pH_{1/2}$, the stronger the binding as complexation will only occur when protonation of the anion-binding site (e.g. tertiary amine groups) is favourable. This is shown hypothetically in Fig. 6.8 for a system in which Cl^- is extracted at a higher pH than $H_2PO_4^-$ and SO_4^{2-}, indicating the strength of Cl^- binding is greater. This novel approach to assessing anion selectivity should allow rapid and efficient determinations of the strength of complexation in a two-phase solvent extraction system.

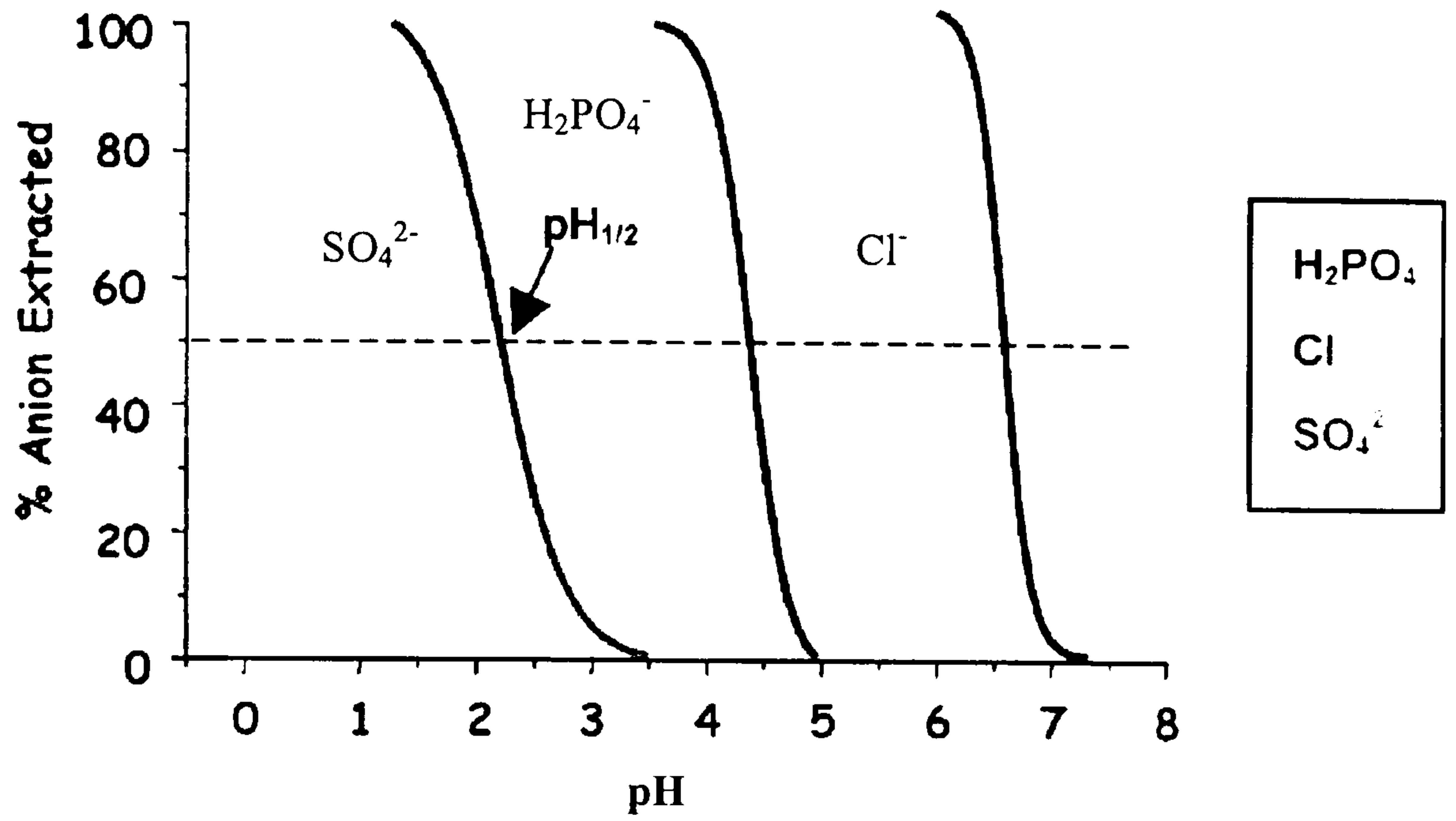


Figure 6.8: Schematic representation of how anion selectivity could be measured in solvent extraction experiments. (24)

6.1.3 Developing sulfate-selective anion receptors.

New methods are required for the treatment of metal sulfates and one potential strategy involves the development of extractants for metal sulfates. This is complicated because selective binding is needed for both the targeted metal cation and the sulfate anion to maintain good materials balances. The more challenging of these targets is to design sulfate-selective anion receptors.

Anion coordination chemistry is an emerging area of supramolecular chemistry. Cation recognition is already very well developed and it has taken time for the coordination chemistry of anions to receive a significant level of interest. (19) The main reason that less attention has been given to the design of anion receptors is its challenging nature. Anions are larger than their isoelectronic cations (Table 6.1), resulting in a lower charge-to-radius ratio. (25) This means that they are more difficult to bind electrostatically (cations are much smaller so their charge is more concentrated). Also, they are subject to protonation as the pH is lowered. Receptors must therefore be designed to work in a specific pH range as the anion's charge will decrease with pH.

Table 6.1: Radii of selected isoelectronic cations and anions. (25)

Cation	r (A°)	Anion	r (A°)
Na^+	1.16	F^-	1.19
K^+	1.52	Cl^-	1.67
Rb^+	1.66	Br^-	1.82
Cs^+	1.81	I^-	2.06

Anionic species also have a variety of different structures. The design of receptors is therefore specific for the anion's particular geometry and is far more complicated than for the inherently spherical cations (Fig. 6.9).

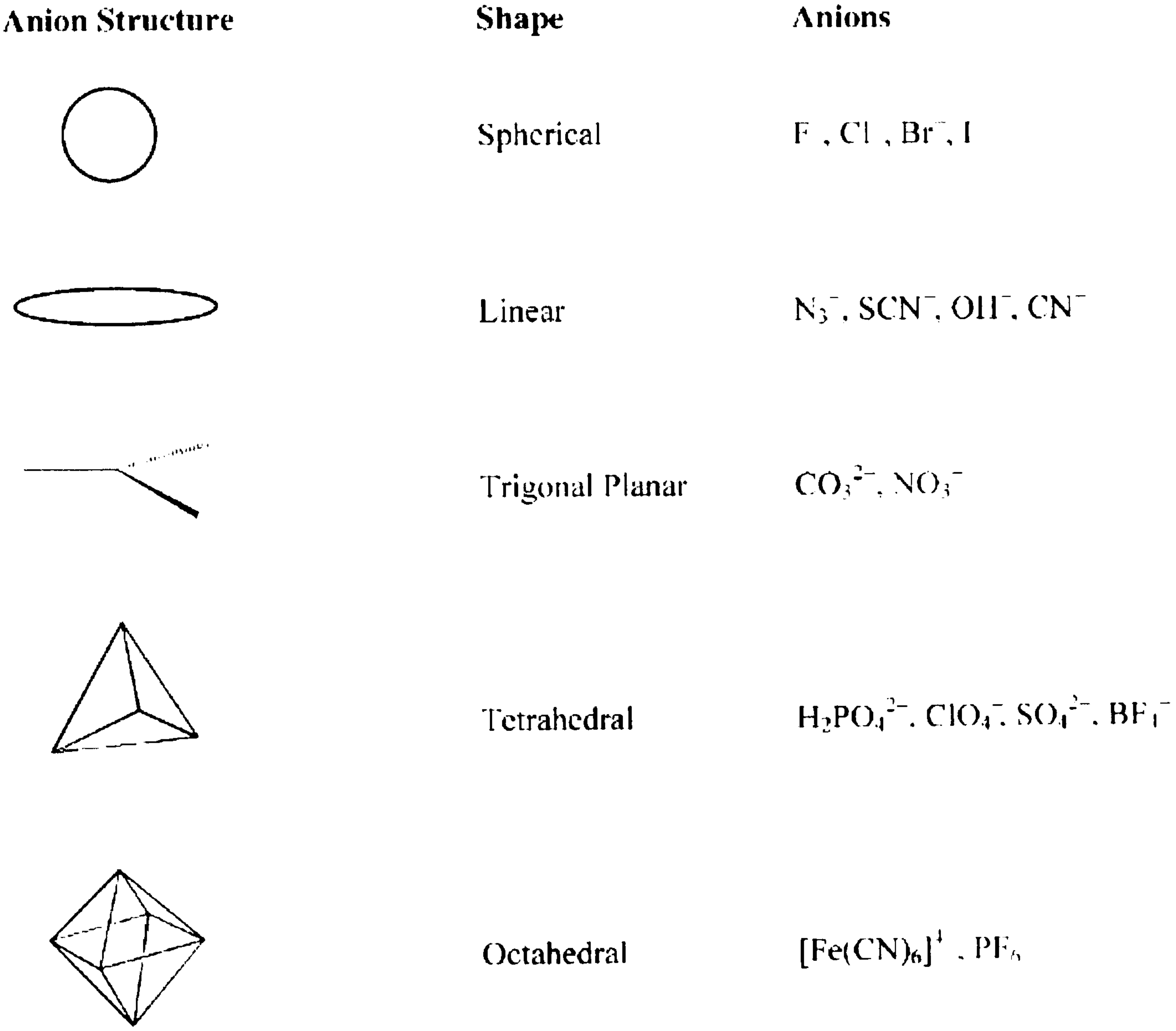


Figure 6.9: The different structure of anions. (26)

The first example of a synthetic anion inclusion complex was reported in 1968 by Park and Simmons. (27) They discovered a new type of ion-pairing in which a halide guest could occupy the cavity of an organic cage. These complexes, known as the "halide katapinates" (Fig. 6.10) were the basis for most of the early work on anion complexation. This work mainly consisted of synthesis of a large number of macrocyclic oligoamines (two of which are shown in Fig. 6.11). (28, 29) The designs used ammonium groups to facilitate anion binding.

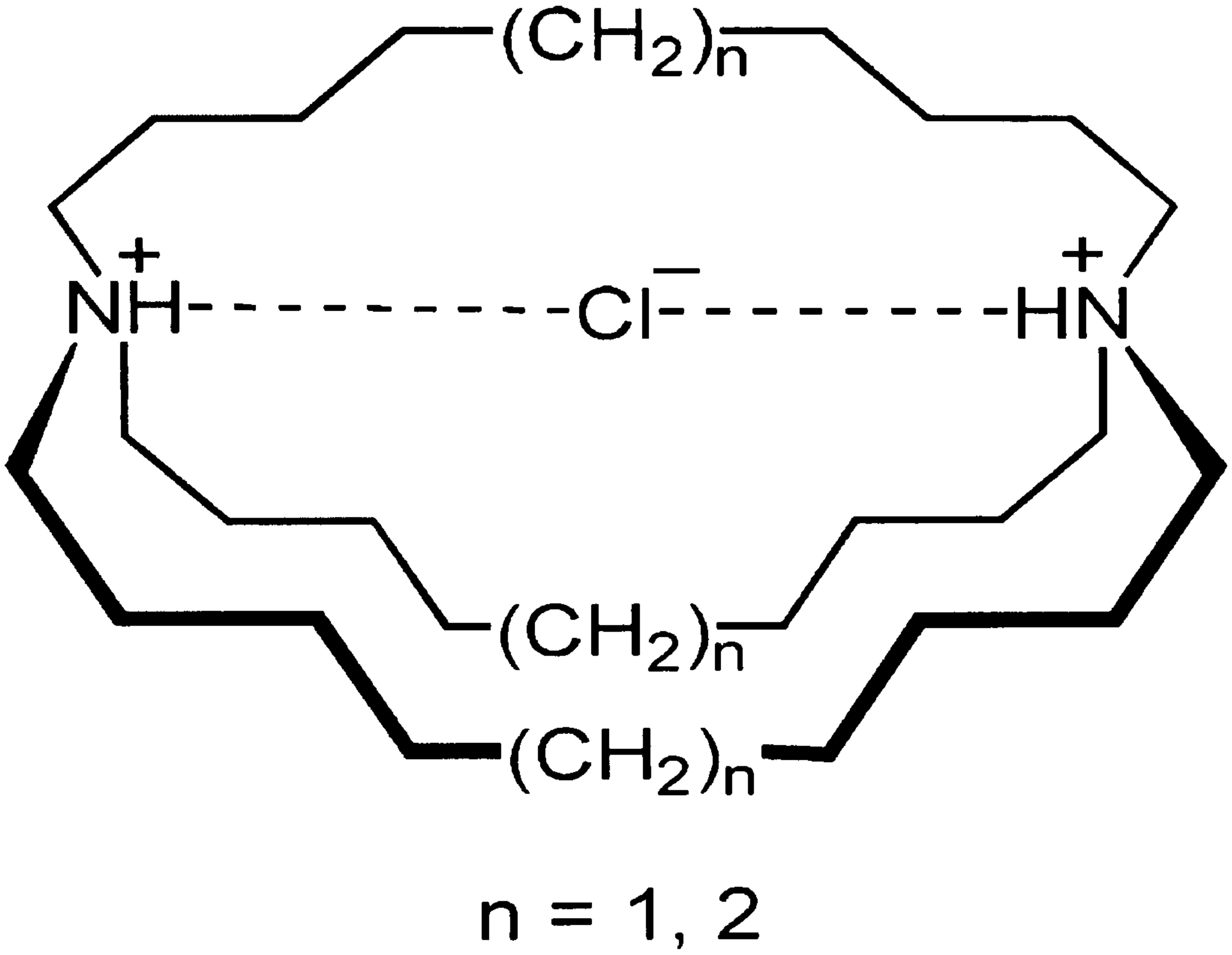
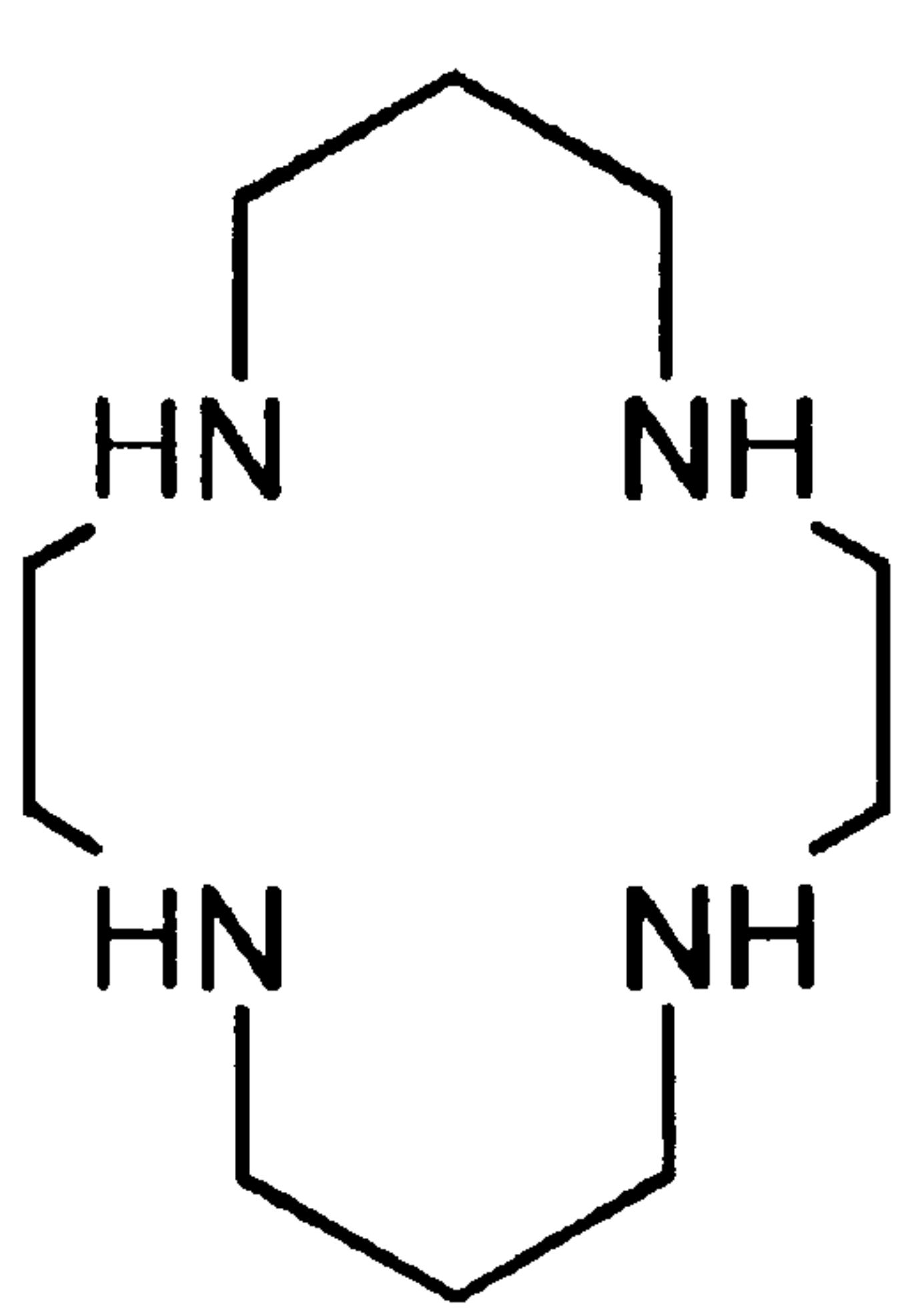


Figure 6.10: Example of chloride katapinates. (27)



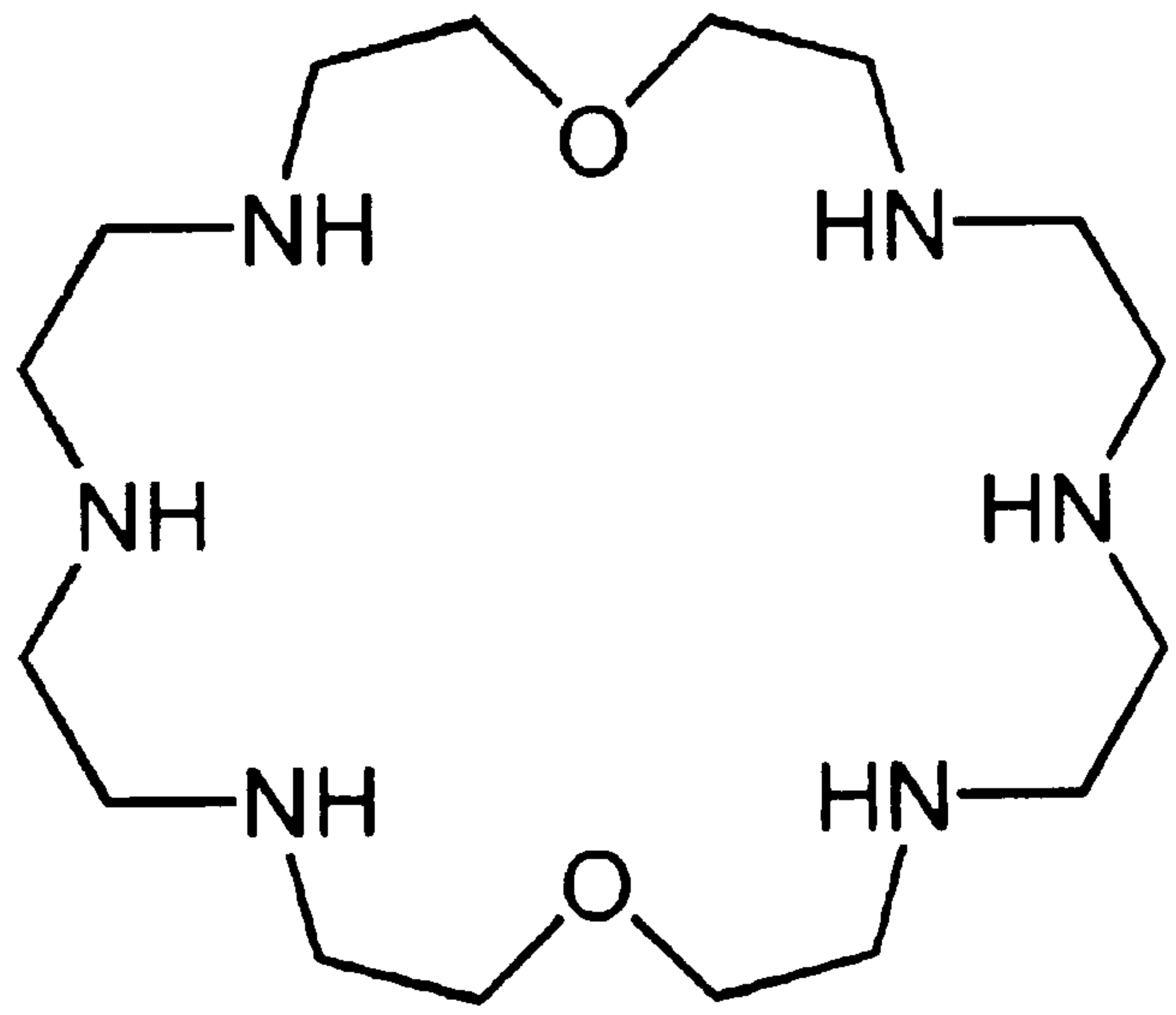


Figure 6.11: Early macrocyclic anion receptors. (28, 29)

Many attempts to bind anions have involved the use of amides because of their ability to function as hydrogen–bond donors to anions. The hydrogen bonding is directional and is therefore very useful when designing receptors of anions of specific shapes and geometries. The first purely amide-based anion receptor was developed in 1986 by Pascal *et al.* (30) and it was found to bind fluoride anions in deuterated DMSO (Fig. 6.12).

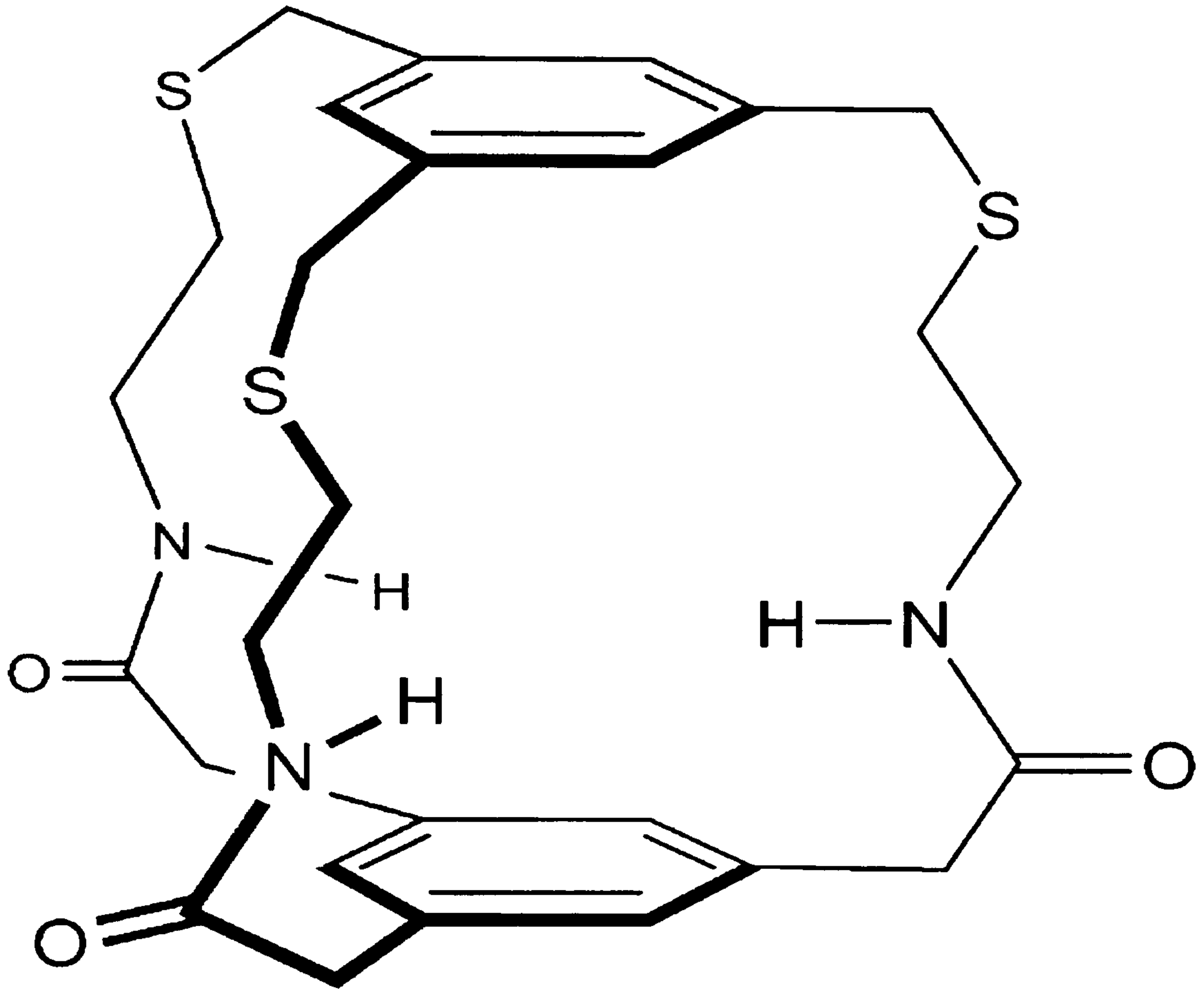


Figure 6.12: The first purely amide-based anion receptor developed by Pascal *et al.* (30)

In 1993, Reinhoudt and co-workers developed the design possibilities further by synthesizing a variety of acyclic tripodal anion receptors containing amide groups. (31) The ligands were all C_3 symmetric and therefore set up to bind tetrahedral anions (Fig. 6.13).

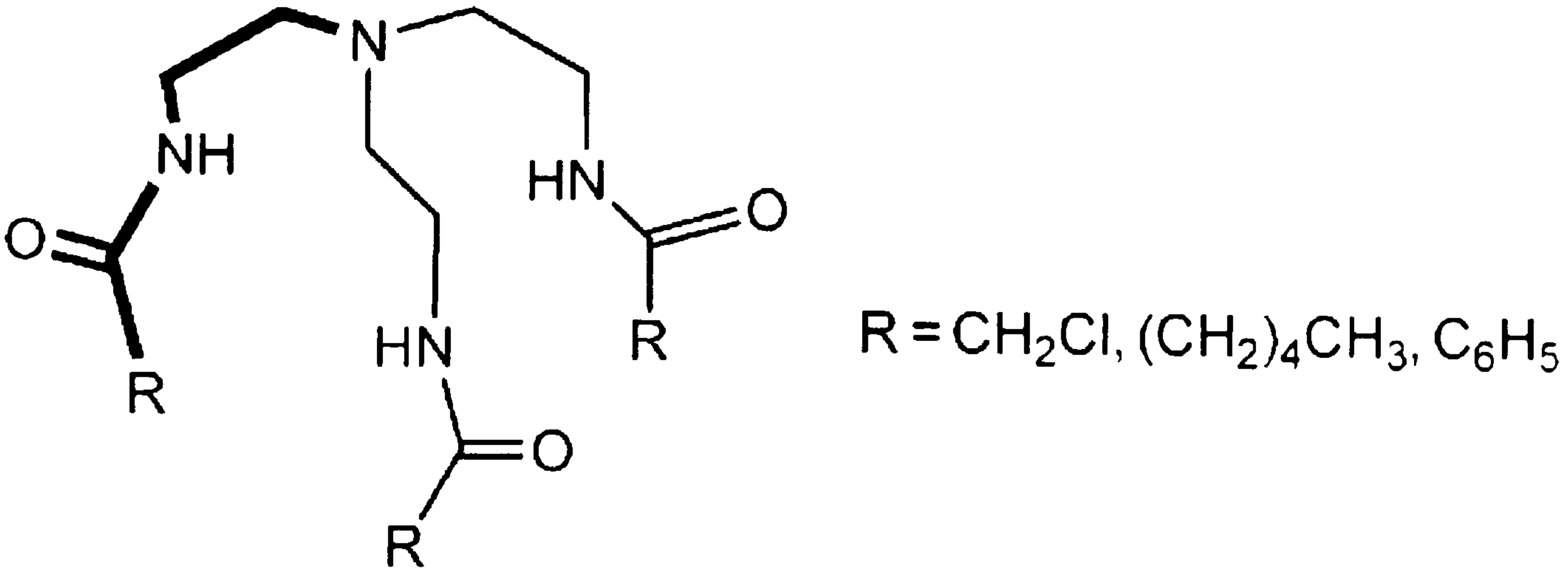


Figure 6.13: Tripodal amide receptors that show selective binding of $H_2PO_4^-$. (31)

6.2 Results and discussion.

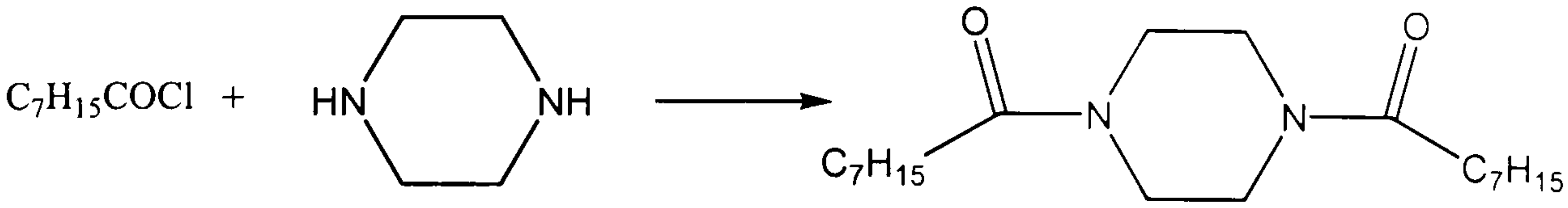
Since Siddall III first studied *N,N'*-dialkylamides as extractants for the separation of actinides in 1961, (32) they were regarded as alternatives to TBP in the reprocessing of nuclear fuel. During the last forty years, many publications have described the remarkable properties of *N,N'*-dialkylamides in the field of solvent extraction. (33) The principal advantages of diamides are: easy synthesis, complete incineration, and high stability with respect to chemical and radiolytical degradation. It has been shown that they are potentially good extractants for actinides, especially for U(VI). However, there are no additional studies of extraction of rare earth elements using these amides.

6.2.1 Ligand synthesis.

The piperazine based amides, L1 and L3, were prepared according to a modified literature procedure. (34) The relevant acid chloride was first prepared by reaction of the parent acid and with thionyl chloride, and then reacted with half an equivalent of piperazine in 1,2-dichloroethane (Scheme 6.1). Following removal of the solvent *in vacuo* the products were recrystallized from diethyl ether (L1) or acetone (L3) and characterized by ^1H, $^{13}C\{^1H\}$NMR, mass spectrometry and elemental analysis.

6.2.1.1 Synthesis of *N,N'*-dioctanoylpiperazine DOPEZ (L1).

$C_7H_{15}COOH + SOCl_2 \rightarrow C_7H_{15}COCl + SO_2 + HCl$



Scheme 6.1: Synthesis of *N,N'*-dioctanoylpiperazine.

The NMR data for the two ligands are given in Tables 6.2 and 6.3, and the spectra for L1 shown in Figs. 6.14 and 6.15.

Table 6.2: ^{1}H and ^{13}C{^{1}H} NMR [$CDCl_3$] assignment of L1.

Chemical Shift (δ, ppm)	Assignment
^{1}H	
3.74 (s, 4H)	C$\underline{H}_2$ of $C_4H_8N_2$
3.65 (s, 4H)	C$\underline{H}_2$ of $C_4H_8N_2$
2.46 (t, 4H, ^{3}J = 4.7 Hz)	C$\underline{H}_2$ of C_7H_{15}
1.76 (t, 4H, ^{3}J = 7.2 Hz)	C$\underline{H}_2$ of C_7H_{15}
1.43-1.41 (m, 16H)	C$\underline{H}_2$ of C_7H_{15}
1.01 (s, 6H)	C$\underline{H}_3$ of C_7H_{15}
^{13}C{^{1}H}	
172.7	C=O
45.8	$\underline{C}H_2$ of $C_4H_8N_2$
41.9	$\underline{C}H_2$ of $C_4H_8N_2$
33.7	$\underline{C}H_2$ of C_7H_{15}
32.1	$\underline{C}H_2$ of C_7H_{15}
31.3	$\underline{C}H_2$ of C_7H_{15}
29.8	$\underline{C}H_2$ of C_7H_{15}
25.6	$\underline{C}H_2$ of C_7H_{15}
23.0	$\underline{C}H_2$ of C_7H_{15}
14.4	$\underline{C}H_3$ of C_7H_{15}

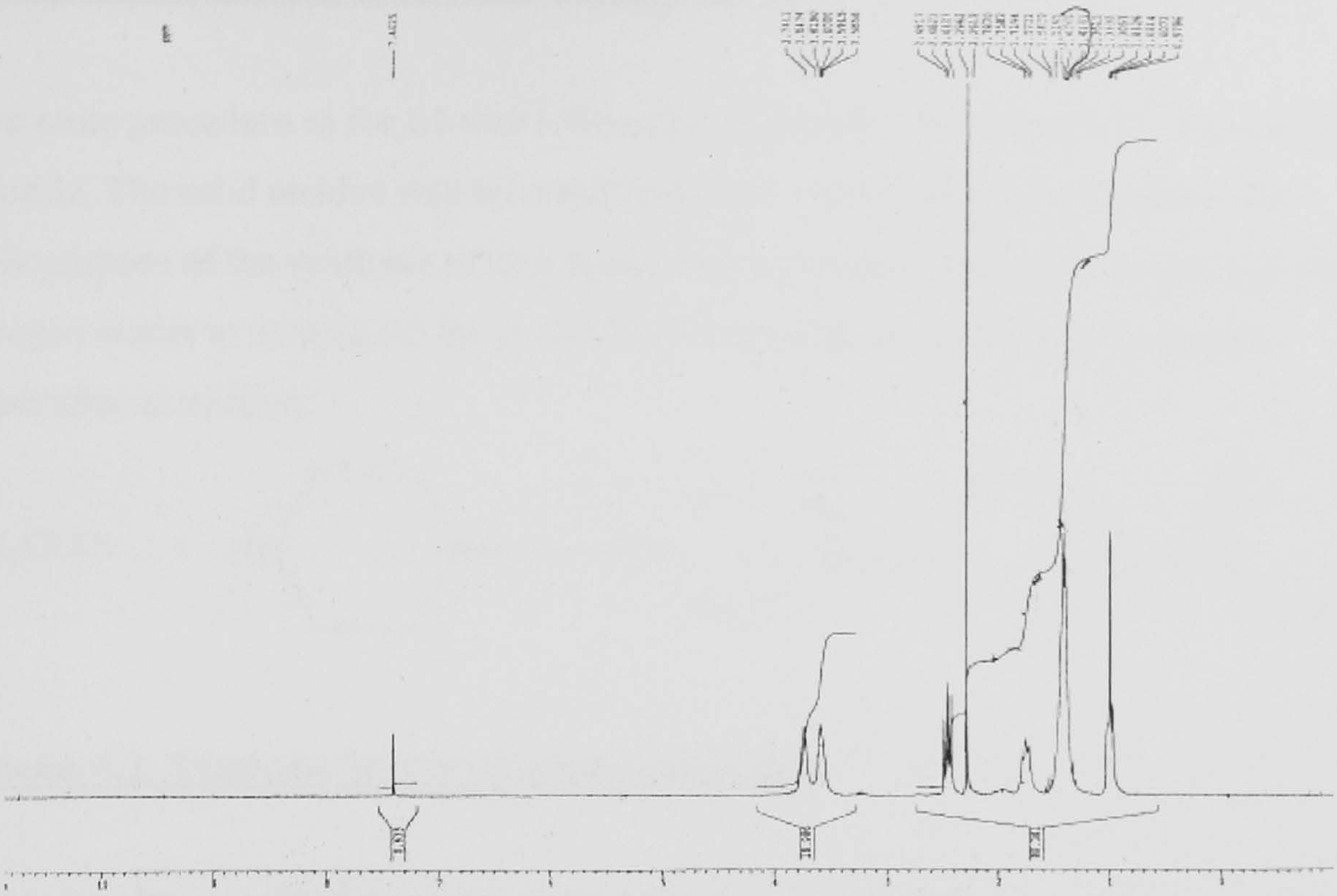


Figure 6.14: ^{1}H NMR [CDCl$_3$] spectrum of L1 (300K).

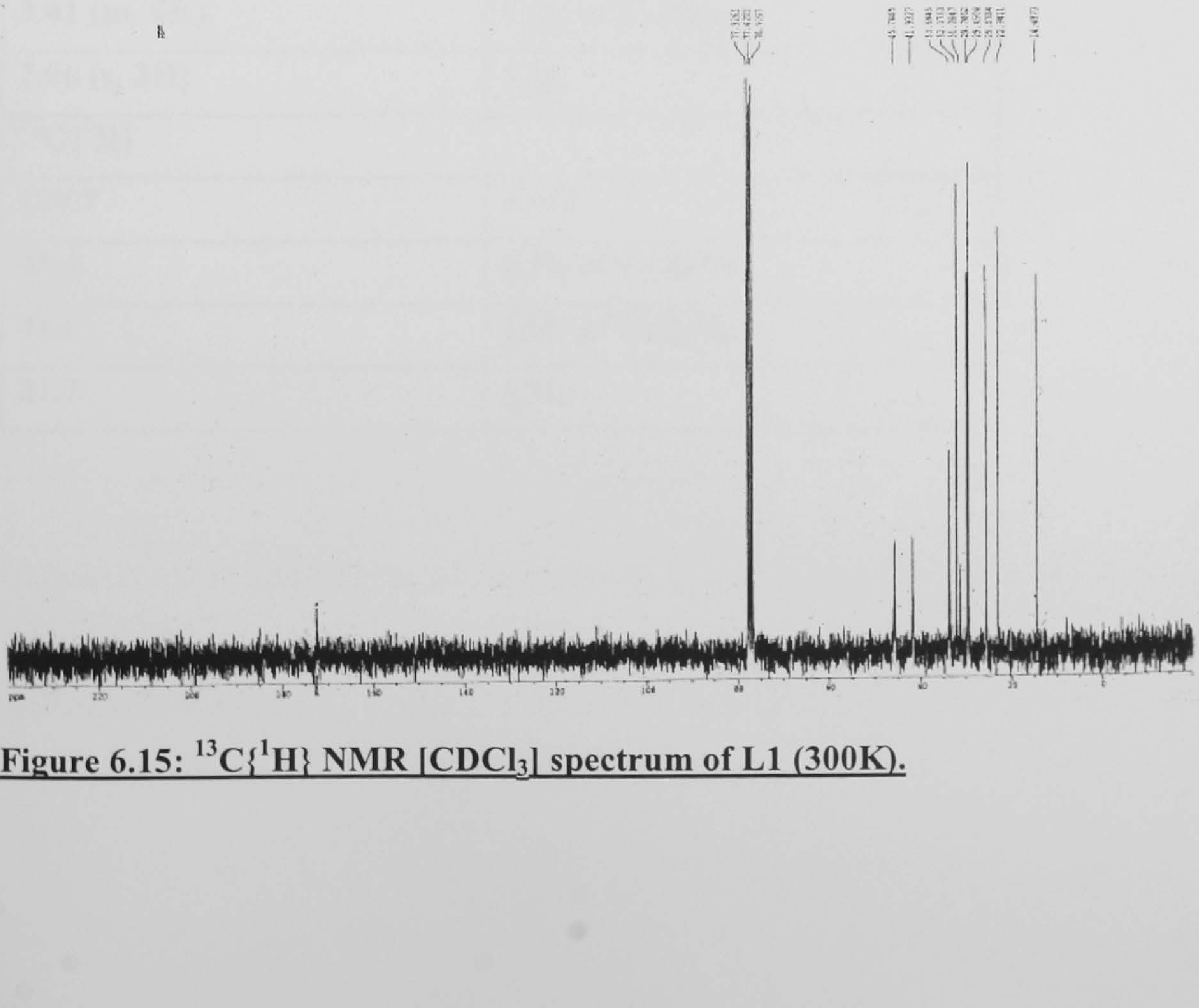
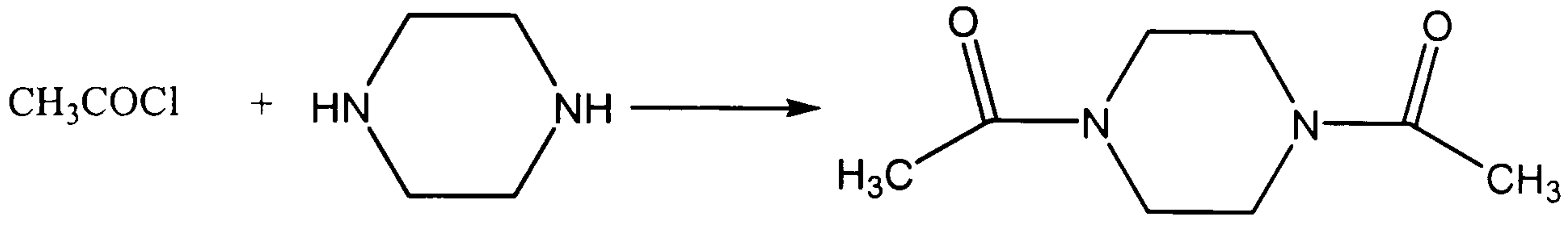


Figure 6.15: ^{13}C{^{1}H} NMR [CDCl$_3$] spectrum of L1 (300K).

6.2.1.2 Synthesis of *N,N'*-diacetylpiperazine (L3).

The same procedure as for L1 was followed using acetyl chloride instead of octanoyl chloride. The solid residue was recrystallized from a small amount of acetone. The main purpose of the synthesis of this ligand was to create a small carbon chain on the nitrogen atoms to investigate the possibility for separating metal from the organic phase after extraction.



Scheme 6.2: Synthesis of *N,N'*-diactetylpiperazine.

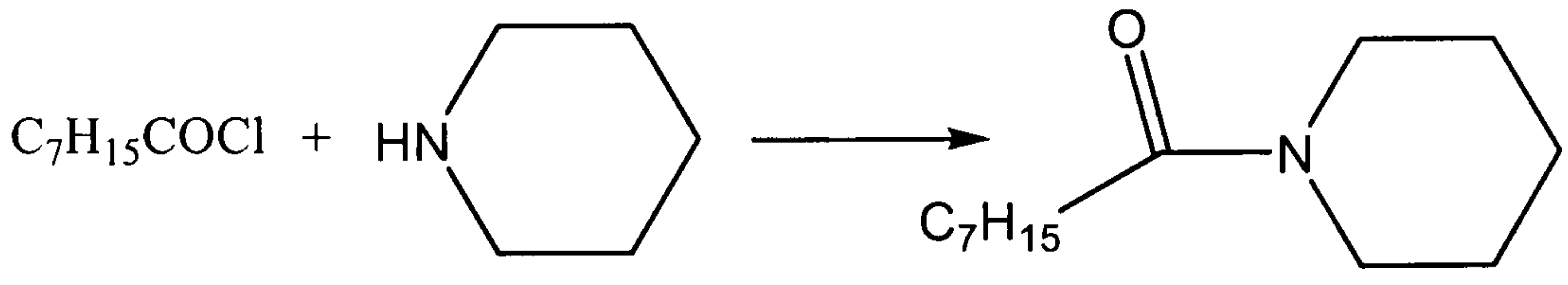
Table 6.3: ^{1}H and ^{13}C{^{1}H} NMR [CDCl$_3$] assignment of L3.

Chemical Shift (δ, ppm)	**Assignment**
^{1}H	
3.56 (m, 4H)	**C$\underline{H}_2$ of $C_4H_8N_2$**
3.41 (m, 4H)	**C$\underline{H}_2$ of $C_4H_8N_2$**
2.06 (s, 3H)	**C$\underline{H}_3$**
^{13}C{^{1}H}	
169.7	**C=O**
46.4	**$\underline{C}H_2$ of $C_4H_8N_2$**
41.6	**$\underline{C}H_2$ of $C_4H_8N_2$**
21.7	**$\underline{C}H_3$**

6.2.1.3 Synthesis of *N*-octanoylpiperidine (L2), Amides of Cyclic Amines.

N,N'-disubstituted amides have been found to be efficient extractants for uranium(VI) from nitric acid media. (35-37) *N*-Octanoylpiperidine is a new member of this family of extractants, which are obtained by using piperidine and its derivatives as cyclic secondary amines. They are resistant to hydrolysis and radiolysis, their degradation products are easily washed away; they can be burned thoroughly and will not result in any solid waste. However there are no studies about the extraction performance of these ligands for rare earth elements. Firstly, the acid chloride was prepared by heating the parent acid in thionyl chloride under reflux for 5 hours. The excess reagent was removed *in vacuo*. The product was used without further purification. These amides were prepared by acylation of cyclic amines (piperidine) with long-chain acid halides in a two-phase system of $CHCl_3$ and H_2O: K_2CO_3. (38) The product was characterised using ^1H, $^{13}C\{^1H\}$NMR, mass spectrometry and elemental analysis. The NMR data for the ligand is given in Table 6.4 and the spectra presented in Figs. 6.16 and 6.17.

$$C_7H_{15}COOH + SOCl_2 \rightarrow C_7H_{15}COCl + SO_2 + HCl$$



Scheme 6.3: Synthesis of *N*-octanoylpiperidine.

Table 6.4: ^{1}H and $^{13}C\{^{1}H\}$ NMR [$CDCl_3$] assignment of L2.

Chemical Shift (δ, ppm)	**Assignment**
^{1}H	
3.55 (t, 2H, ^{3}J = 5.6 Hz)	$C\underline{H}_2$ of $C_5H_{10}N$
3.40 (t, 2H, ^{3}J = 5.4 Hz)	$C\underline{H}_2$ of $C_5H_{10}N$
2.31 (t, 2H, ^{3}J = 7.4 Hz)	$C\underline{H}_2$ of CH_2-C=O
1.67-1.53 (m, 8H)	$C\underline{H}_2$
1.32-1.28 (m, 8H)	$C\underline{H}_2$
0.88 (s, 3H)	$C\underline{H}_3$ of C_7H_{15}
$^{13}C\{^{1}H\}$	
171.8	C=O
47.1	$\underline{C}H_2$ of $C_5H_{10}N$
42.9	$\underline{C}H_2$ of $C_5H_{10}N$
33.8	$\underline{C}H_2$
32.1	$\underline{C}H_2$
29.8	$\underline{C}H_2$
29.4	$\underline{C}H_2$
26.9	$\underline{C}H_2$
26.0	$\underline{C}H_2$
25.8	$\underline{C}H_2$
24.9	$\underline{C}H_2$
22.9	$\underline{C}H_2$
14.4	$\underline{C}H_3$ of C_5H_{10}

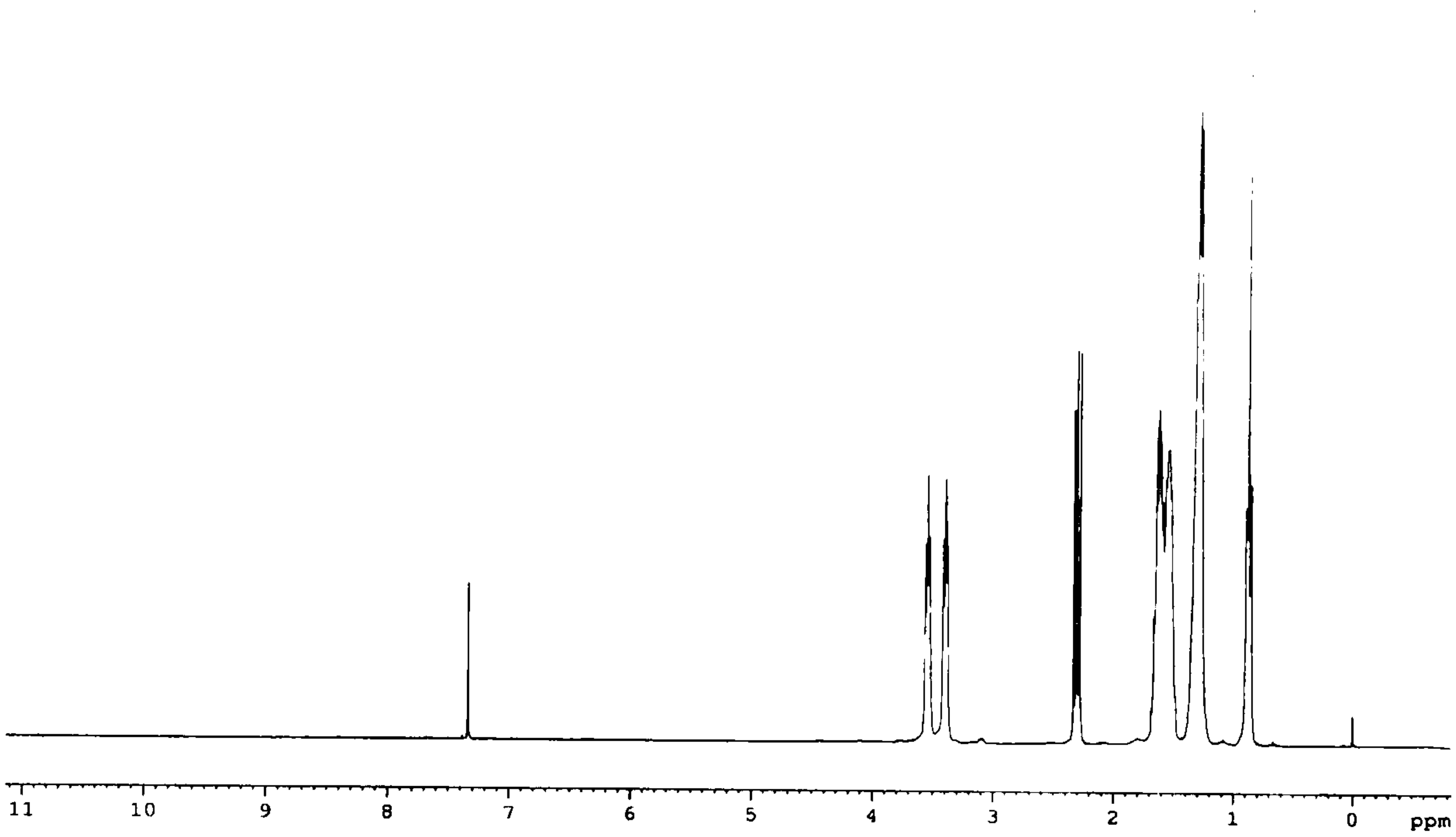


Figure 6.16: ^{1}H NMR [CDCl$_3$] spectrum of L2 (300K).

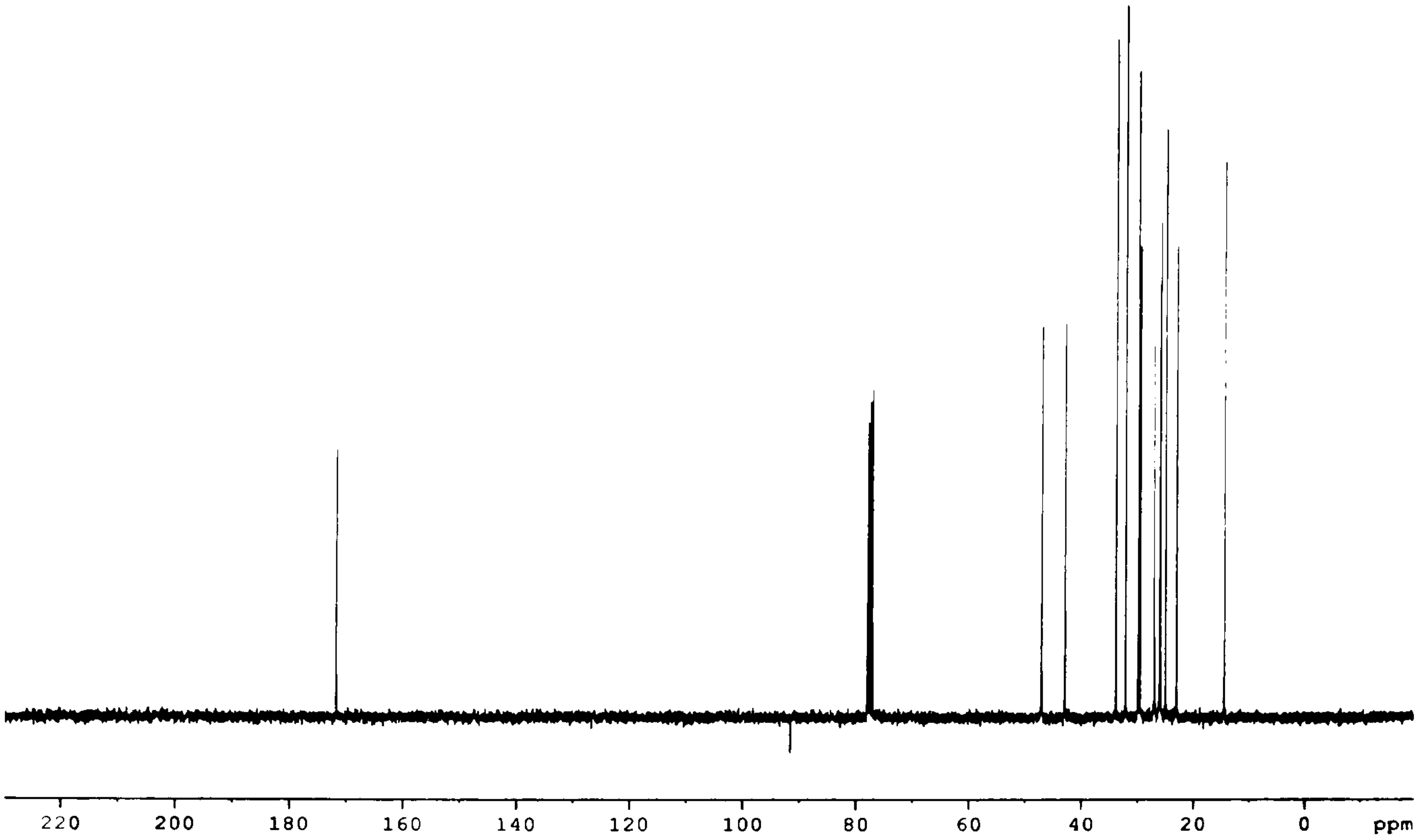
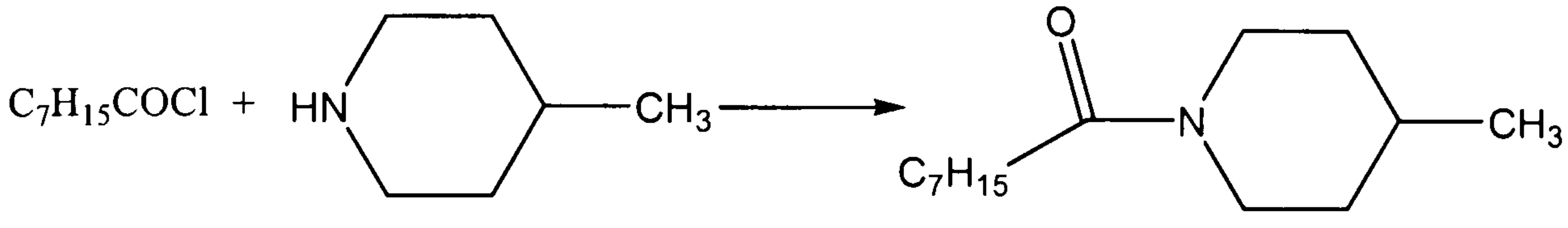


Figure 6.17: ^{13}C{^{1}H} NMR [CDCl$_3$] spectrum of L2 (300K).

6.2.1.4 Synthesis of *N*-octanoyl-4-methylpiperdine (L4).

The same procedure as L2 was followed using 4-methyl piperdine instead of piperdine. The product was characterised using ^{1}H, ^{13}C{^{1}H} NMR, mass spectrometry and elemental analysis. The NMR data for the ligand is given in Table 6.5 and the spectra presented in Figs. 6.18 and 6.19.



Scheme 6.4: Synthesis of *N*-octanoyl-4-methylpiperidine.

Table 6.5: ^{1}H and ^{13}C{^{1}H} NMR [CDCl$_3$] assignment of L4.

Chemical Shift (δ, ppm)	Assignment
^{1}H	
4.64-4.57 (m, 1H)	$\underline{H}$C-N of C_5N ring
3.88-3.80 (m, 1H)	$\underline{H}$C-N of C_5N ring
3.00 (pseudo t of d, 1H, $J_1 = 12.6$ Hz, $J_2 = 2.5$ Hz)	$\underline{H}$C-N of C_5N ring
2.54 (pseudo t of d, 1H, $J_1 = 12.8$ Hz, $J_2 = 2.5$ Hz)	$\underline{H}$C-N of C_5N ring
2.33 (t, 2H, $^{3}J = 7.6$ Hz)	$C\underline{H}_2$ of C_6H_{13}-$CH_2C{=}O$
1.73-1.55 (m, 5H)	Aliphatic C$\underline{H}$
1.37-1.23 (m, 8H)	Aliphatic C$\underline{H}$
1.18-1.02 (m, 2H)	Aliphatic C$\underline{H}$
1.00-0.94 (m, 3H)	$C\underline{H}_3$
0.92-0.88 (m, 3H)	$C\underline{H}_3$
^{13}C{^{1}H}	
169.9	C=O
44.4	$\underline{C}$N of C_5N
40.3	$\underline{C}$N of C_5N
33.1	Aliphatic $\underline{C}$
32.2	Aliphatic $\underline{C}$
31.9	Aliphatic $\underline{C}$
30.1	Aliphatic $\underline{C}$
29.5	Aliphatic $\underline{C}$
27.9	Aliphatic $\underline{C}$
27.5	Aliphatic $\underline{C}$
32.9	Aliphatic $\underline{C}$
21.0	Aliphatic $\underline{C}$
20.1	Aliphatic $\underline{C}$
12.5	$\underline{C}H_3$ of C_7H_{15}

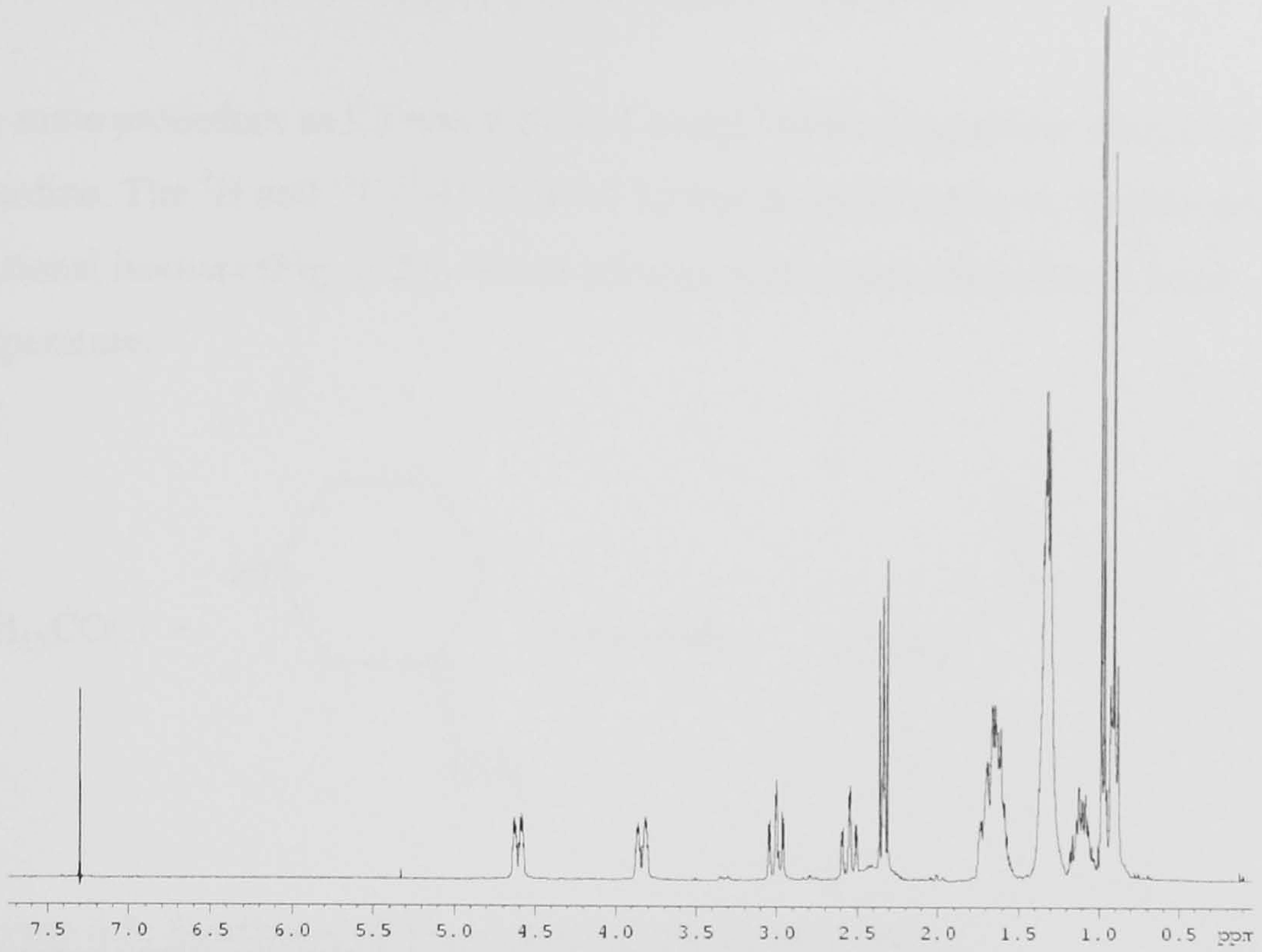


Figure 6.18: ^{1}H NMR [CDCl$_3$] spectrum of L4 (300K).

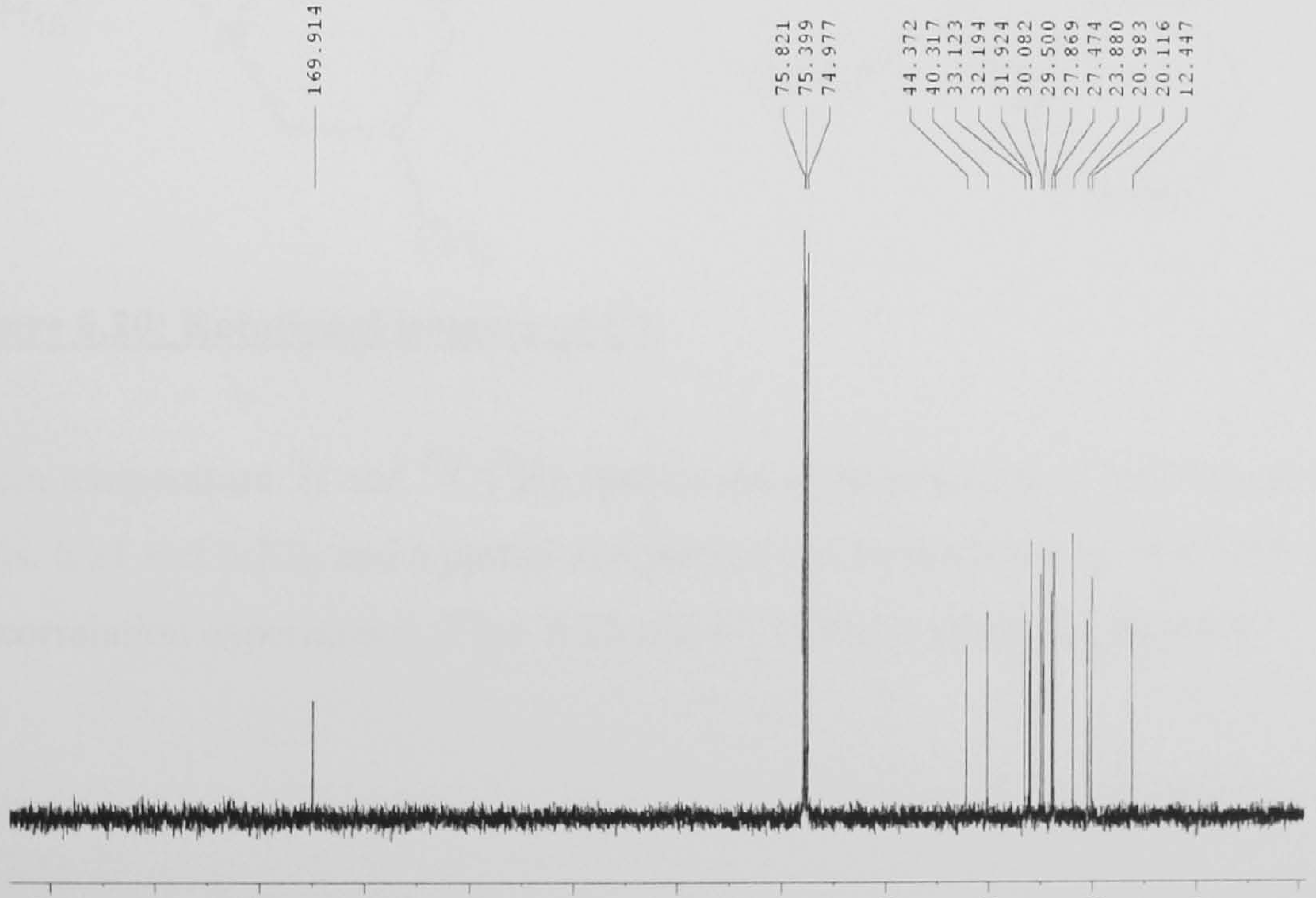
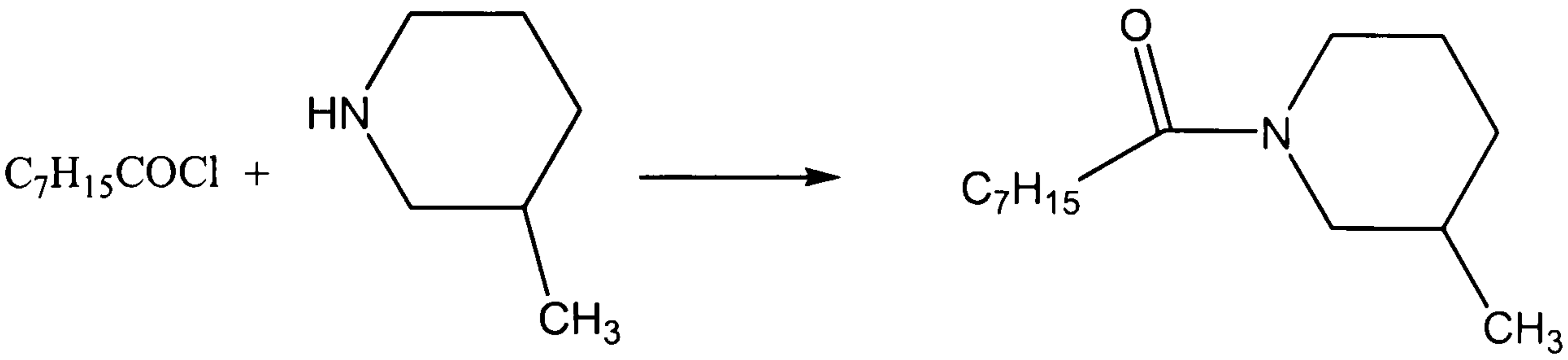


Figure 6.19: ^{13}C{^{1}H} NMR [CDCl$_3$] spectrum of L4 (300K).

6.2.1.5 Synthesis of *N*-octanoyl-3-methylpiperdine (L5).

The same procedure as L2 was followed using 3-methyl piperdine instead of piperdine. The ^1H and $^{13}C\{^1H\}$NMR of L5 are complicated by the presence of two rotational isomers (Fig. 6.20), which undergo slow interconversion at room temperature.



Scheme 6.5: Synthesis of *N*-octanoyl-3-methylpiperidine.

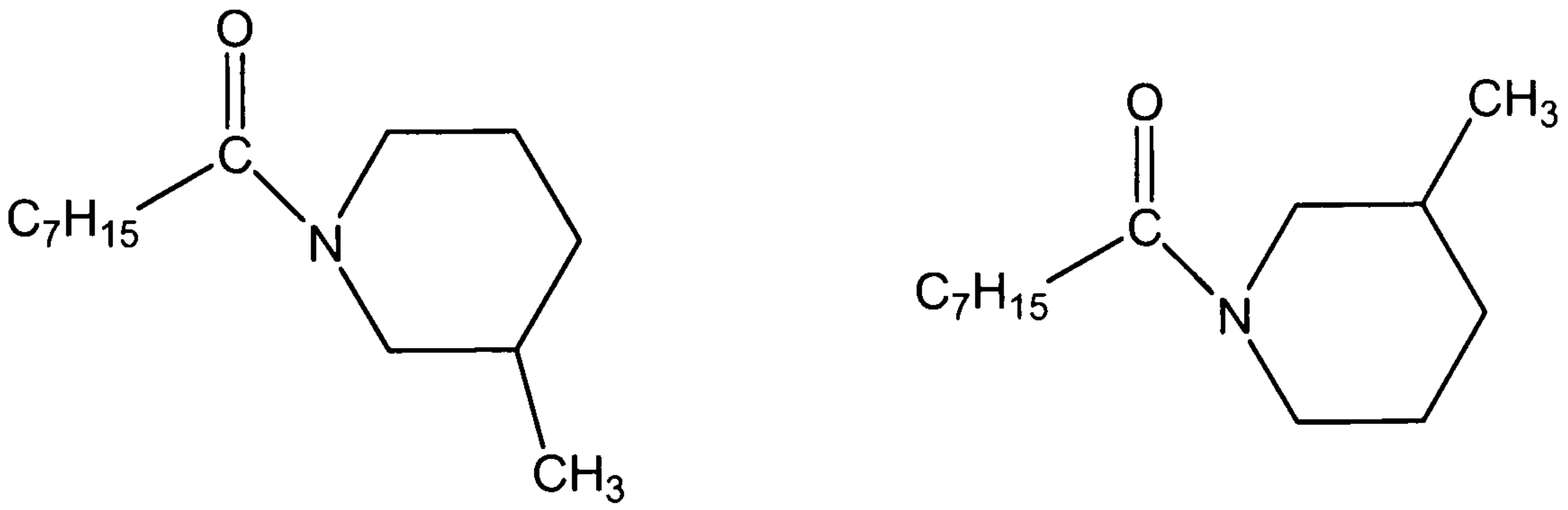


Figure 6.20: Rotational isomers of L5.

Room temperature ^1H and $^{13}C\{^1H\}$ spectra show the presence of both isomers. (Figs. 6.21 and 6.22), and a partial assignment can be made using ^1H COSY and ^{13}C-^1H correlation experiments (Figs. 6.23 and 6.24) and is given in Table 6.6.

Table 6.6: ^1H and $^{13}C\{^1H\}$ NMR [$CDCl_3$] assignment of L5.

Chemical Shift (δ, ppm)	Assignment
^1H	
4.19 (d, 2H, ^2J = 12.6 Hz)	(A) $C\underline{H}N$ of C_5N
3.73-3.66 (m, 2H)	(B) $C\underline{H}N$ of C_5N
2.91-2.89 (m, 1H)	(B) $C\underline{H}N$ of C_5N
~ 2.62 (m, 1H)	(B) $C\underline{H}N$ of C_5N
~ 2.49 (m, 1H)	(A) $C\underline{H}N$ of C_5N
2.26-0.78 (integeral)	Unable to assign and differentiate between the isomers
$^{13}C\{^1H\}$	
53.6	$\underline{C}H_2N$ of C_5H ring (B)
49.4	$\underline{C}H_2N$ of C_5H ring (A)
46.6	$\underline{C}H_2N$ of C_5H ring (B)
42.5	$\underline{C}H_2N$ of C_5H ring (A)
33.9, 33.7, 33.5, 33.4, 32.2, 32.1, 31.6, 31.3, 29.8, 29.5, 26.4, 26.0, 25.9, 25.8, 25.2, 23.0, 19.9, 19.4, 19.3, 14.4	Unable to differentiate between isomers

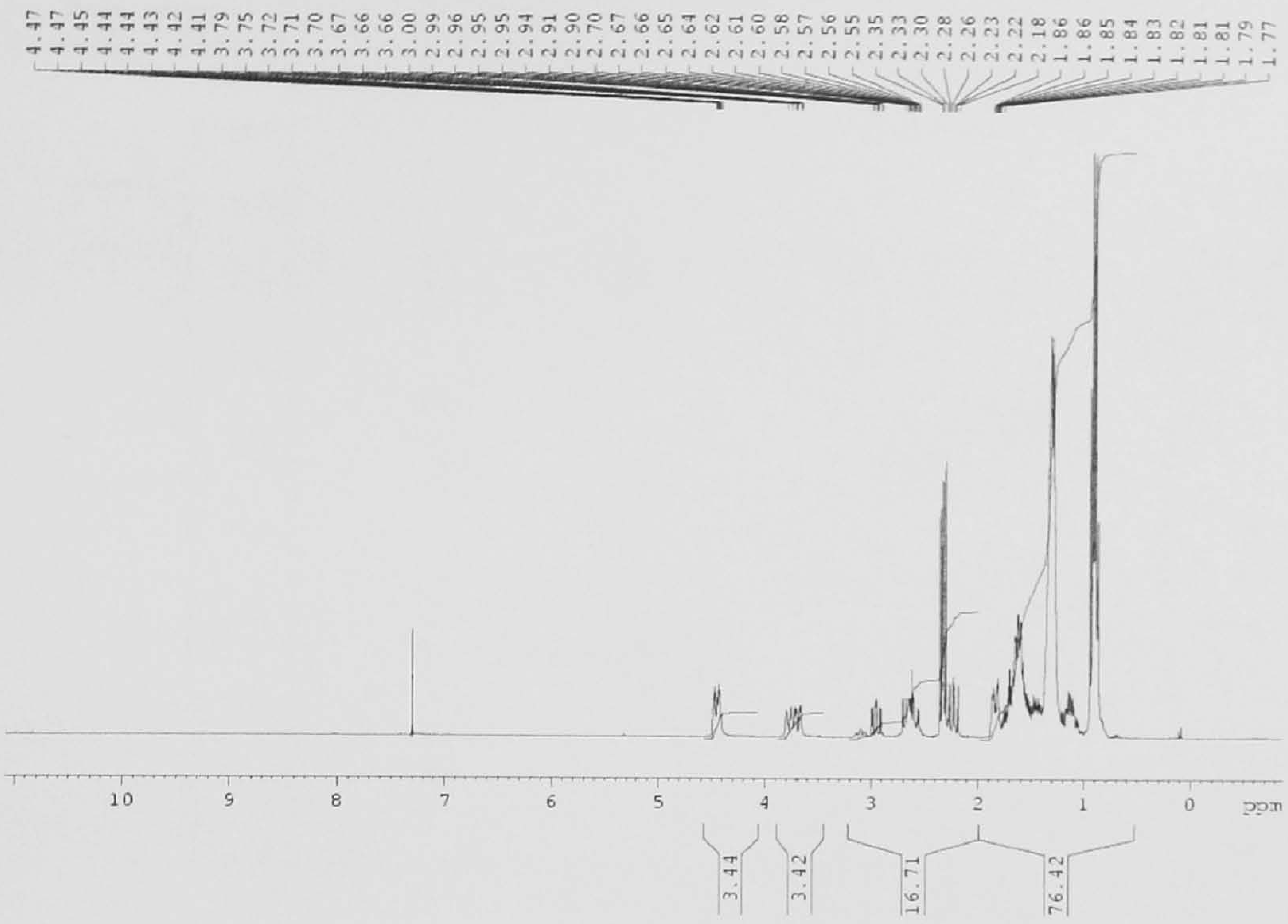


Figure 6.21: ^{1}H NMR [$CDCl_3$] spectrum of L5 (300K).

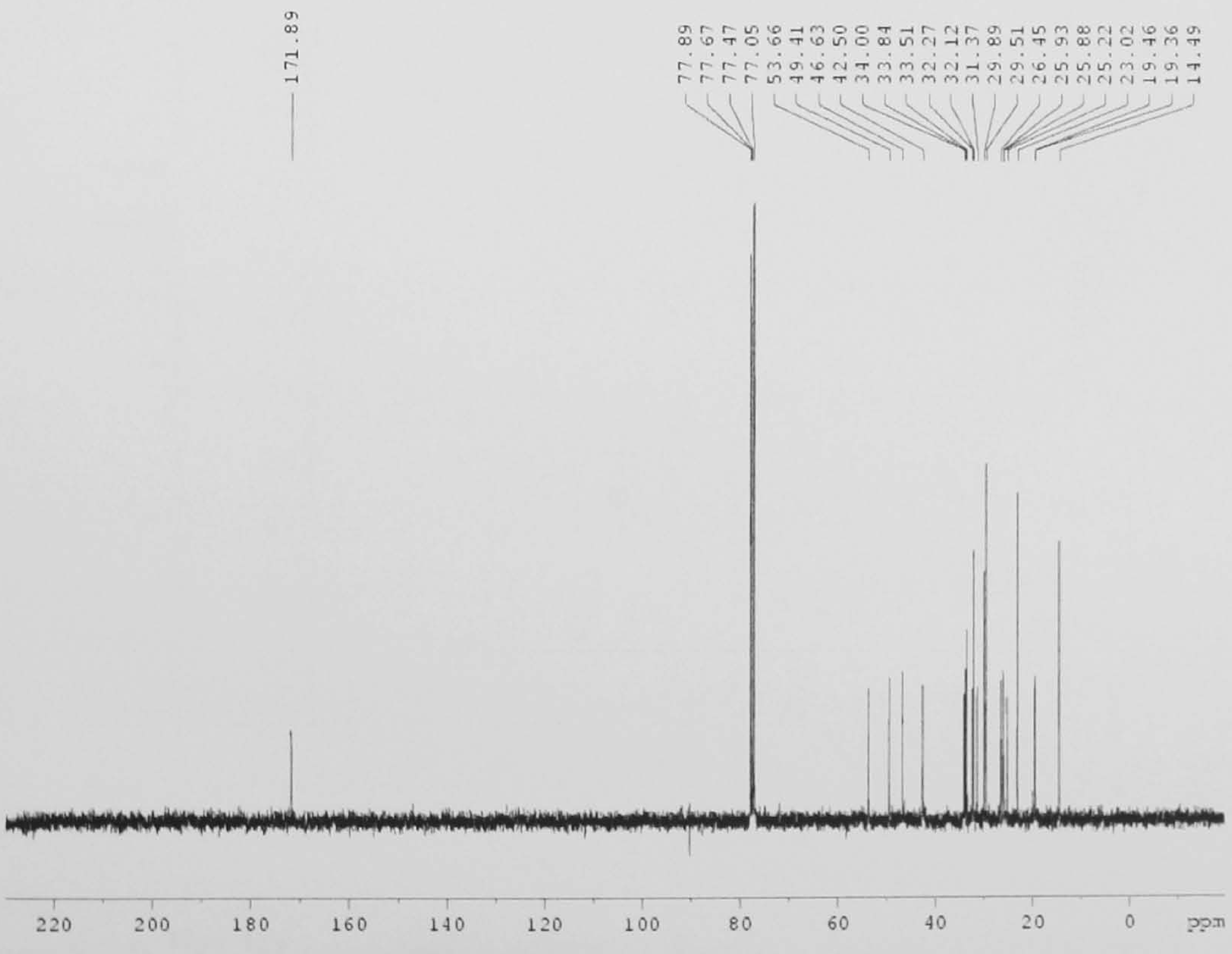


Figure 6.22: $^{13}C\{^{1}H\}$ NMR [$CDCl_3$] spectrum of L5 (300K).

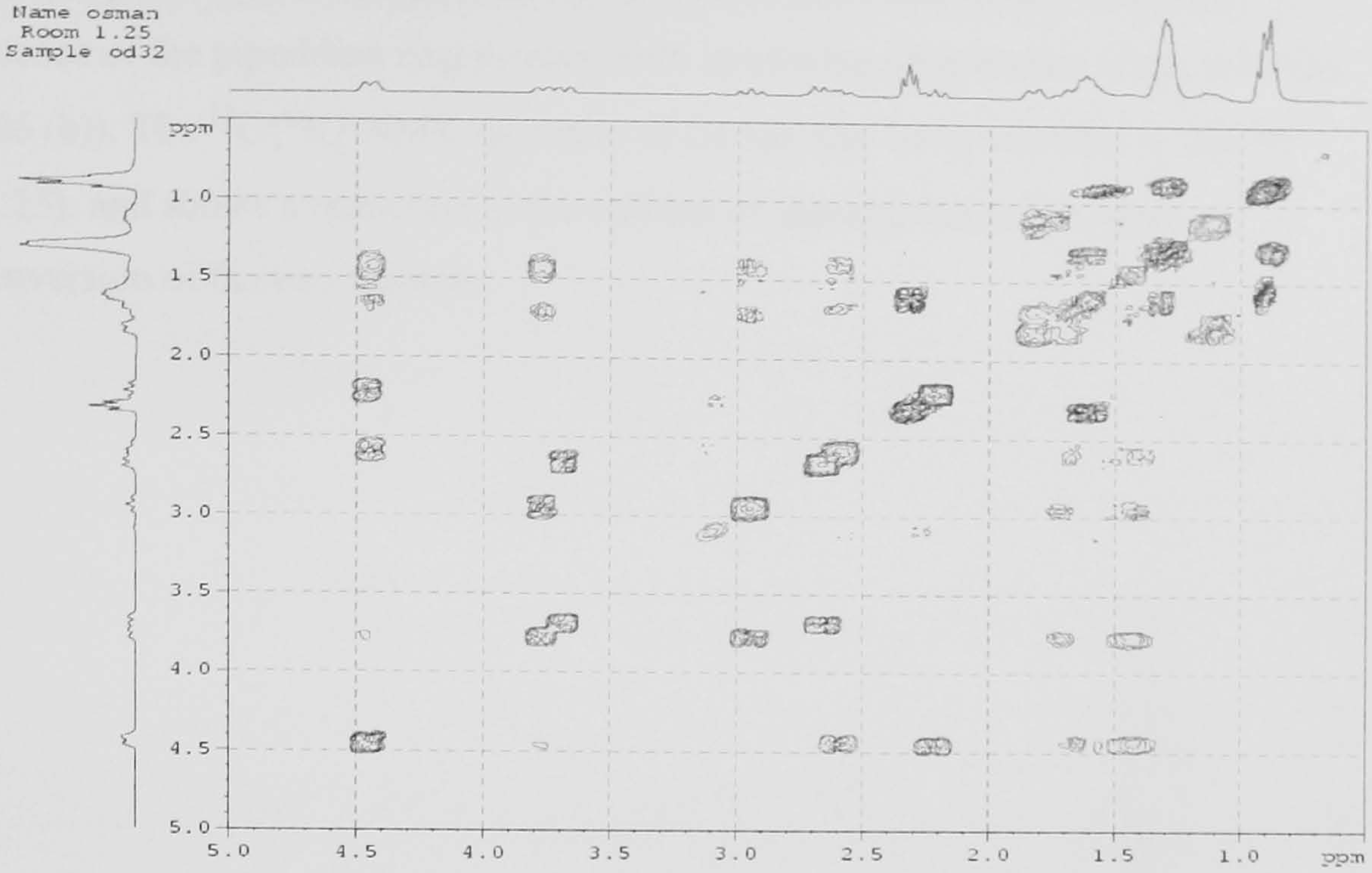


Figure 6.23: ^{1}H COSY NMR [CDCl$_3$] spectrum of L5 (300K).

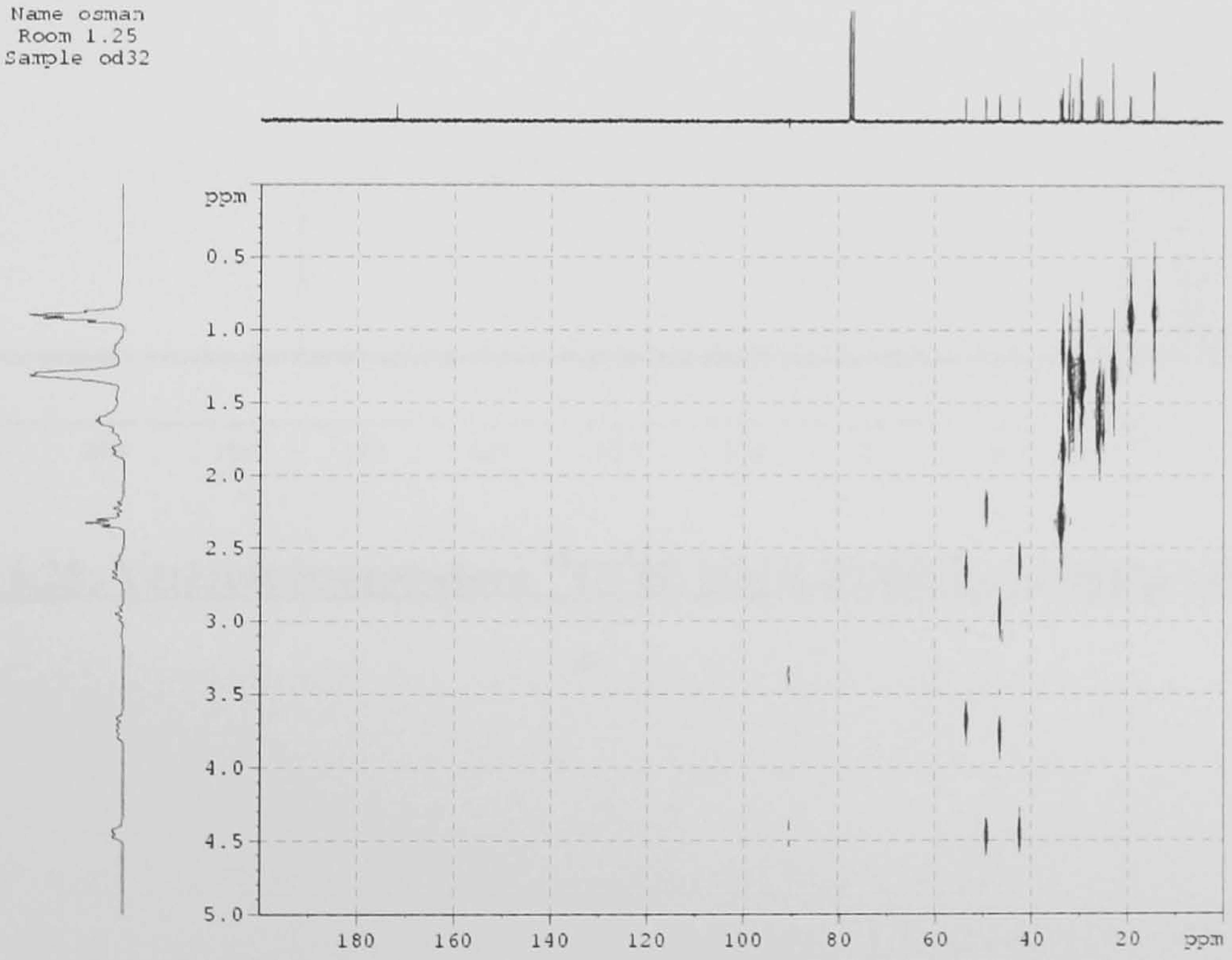


Figure 6.24: ^{13}C-^{1}H correlation NMR [CDCl$_3$] spectrum of L5 (300K).

Variable temperature NMR experiments were undertaken, and clearly show the coalescence of the piperidine ring protons with increasing temperature (Figs. 6.26 (a) and 6.26 (b)). The $^{13}C\{^1H\}$ NMR spectrum of L5 has also been recorded at 100 °C (Fig. 6.25), and shows a reduction in the number of signals, due to the rapid interconversion of the two isomers.

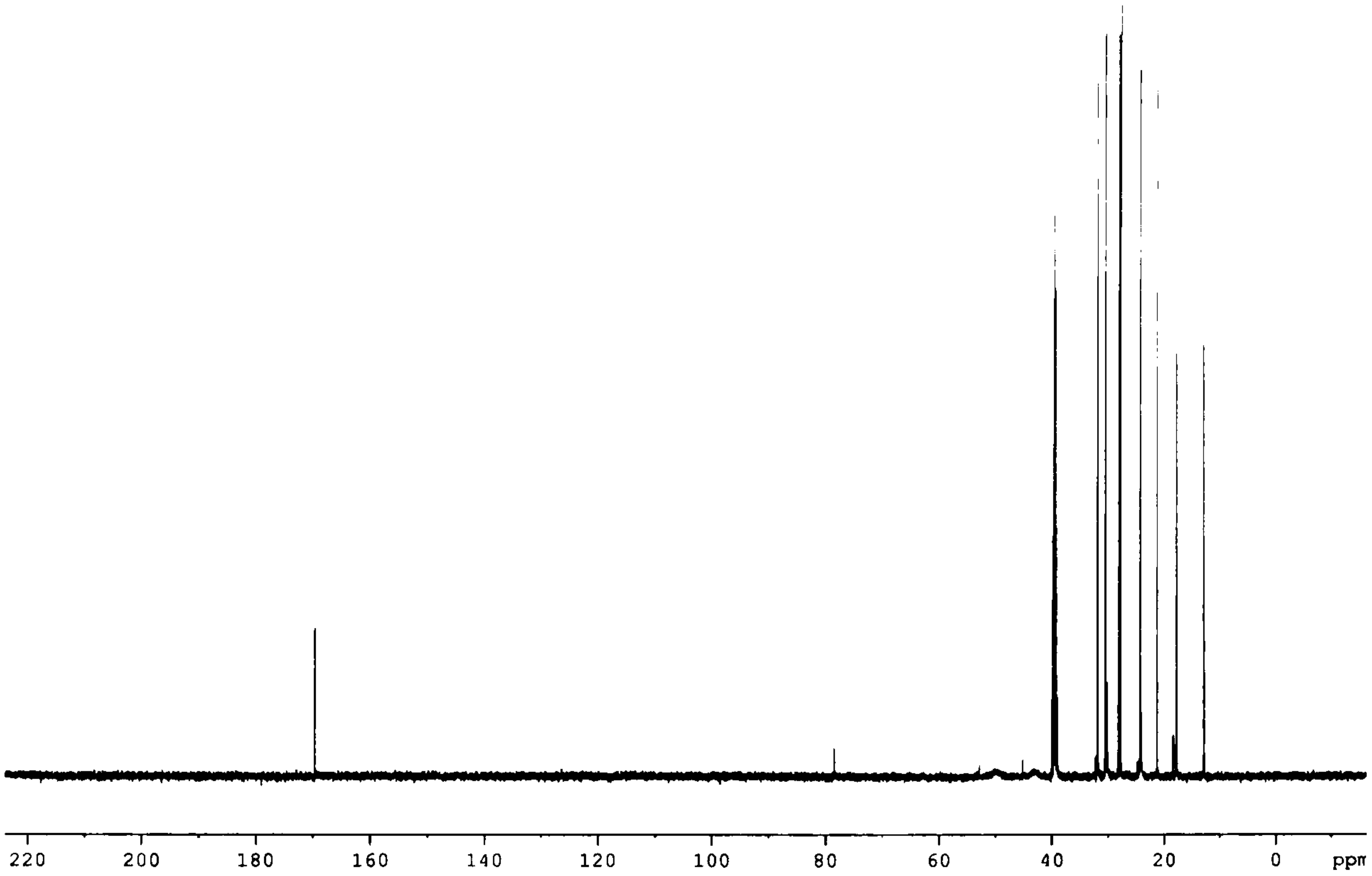


Figure 6.25: Variable temperature $^{13}C\{^1H\}$ NMR [DMSO] spectrum of L5.

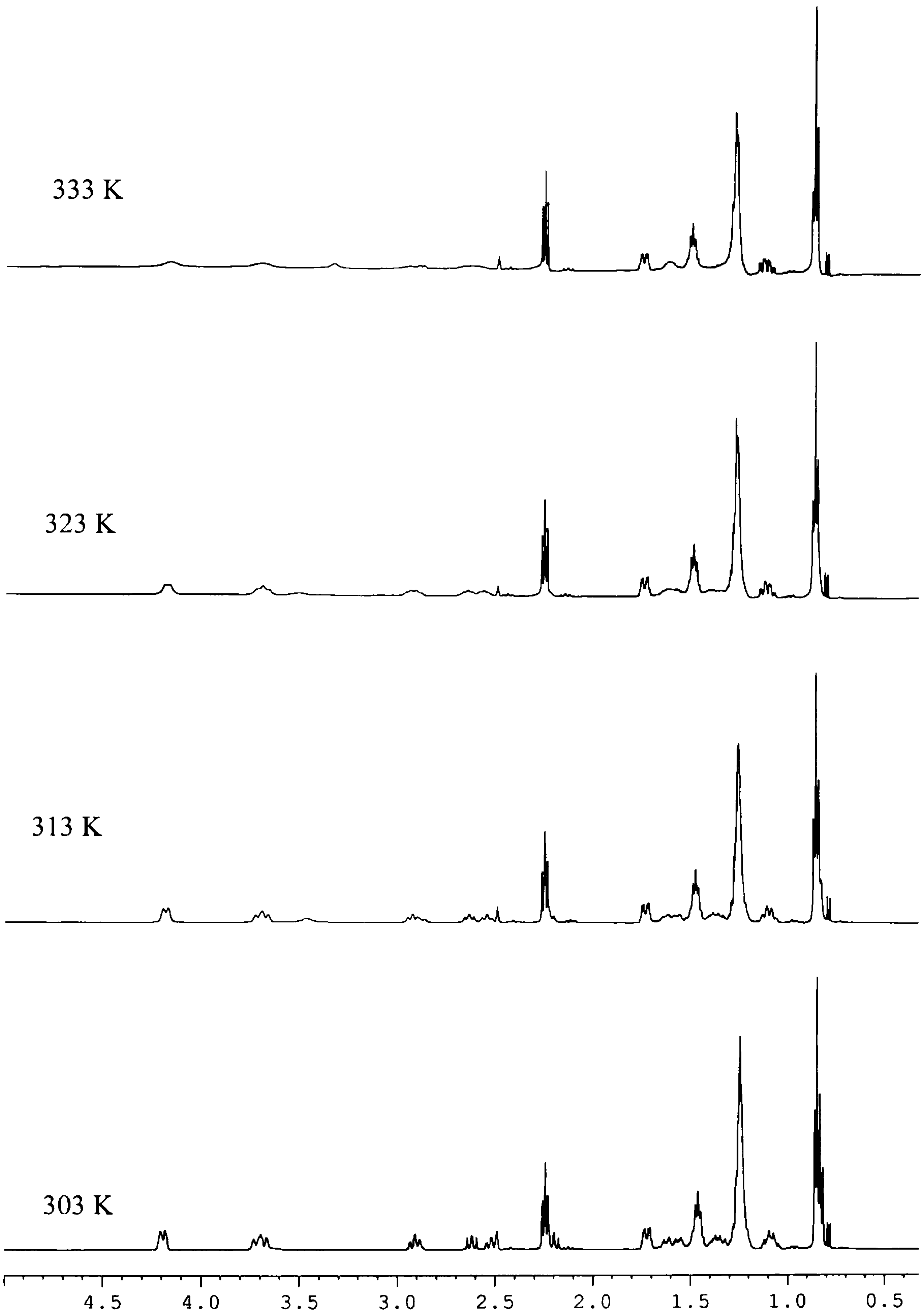


Figure 6.26 (a): Variable temperature ^{1}H NMR [DMSO] spectrum of L5.

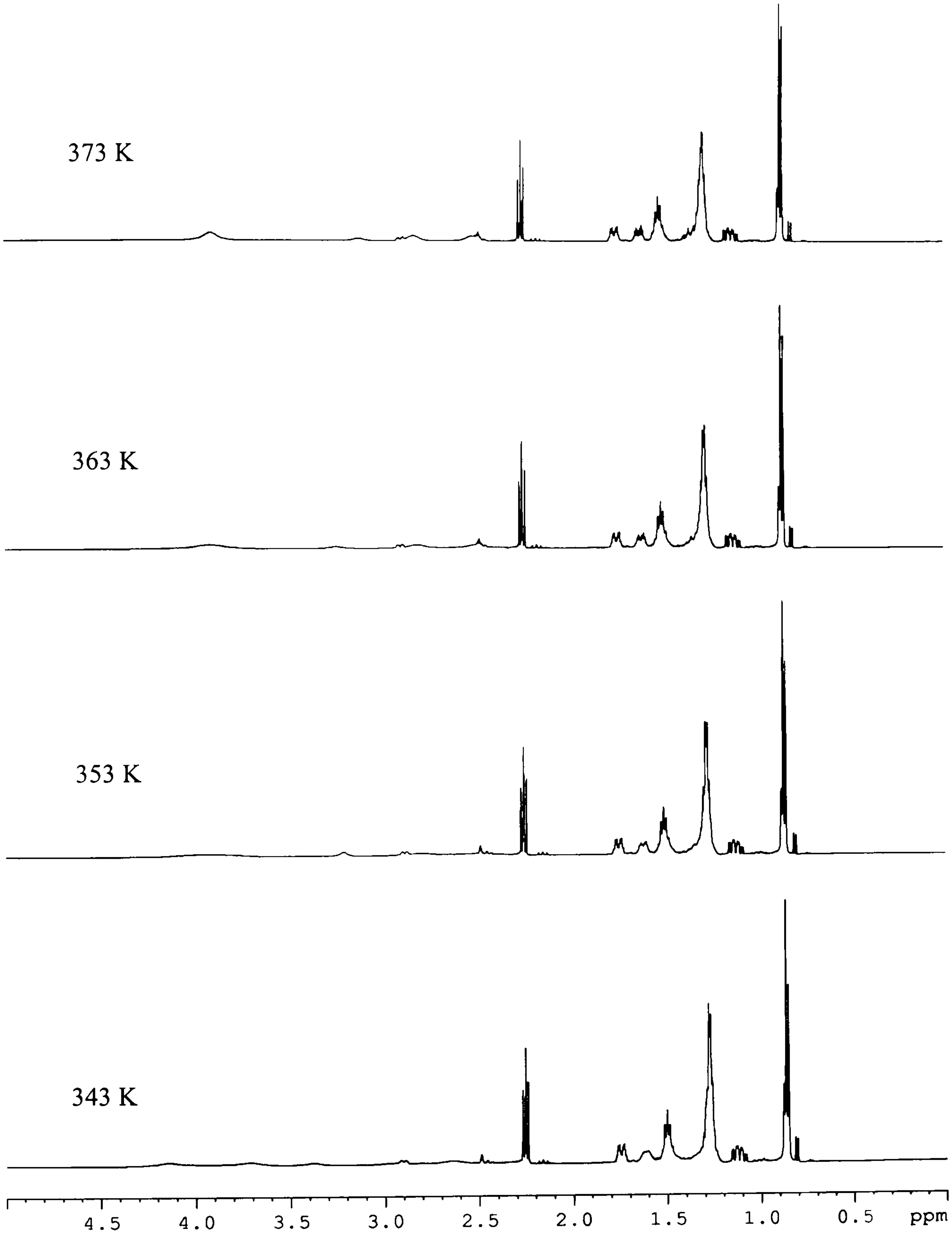
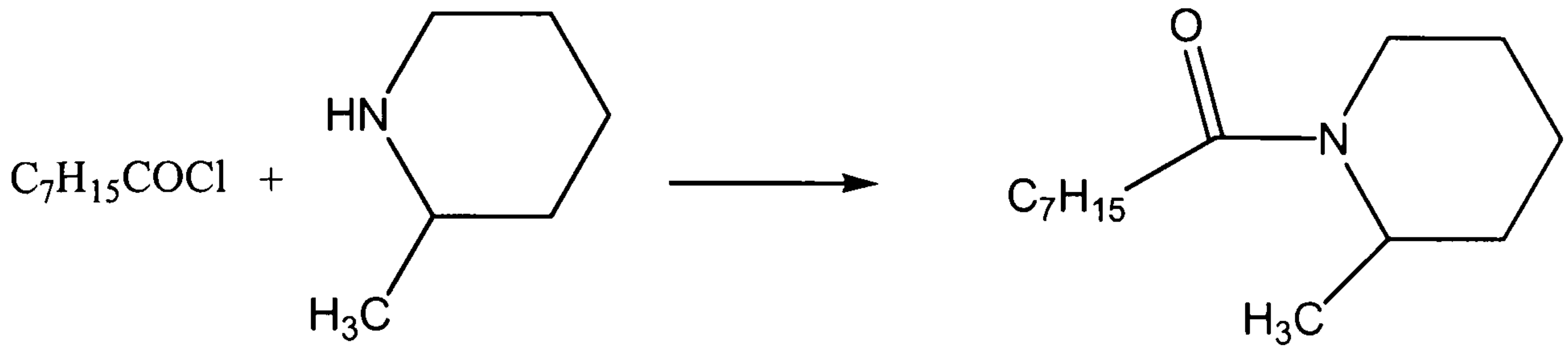


Figure 6.26(b): Variable temperature ^{1}H NMR [DMSO] spectrum of L5.

6.2.1.6 Attempted synthesis of *N*-octanoyl-2-methylpiperidine (L6).

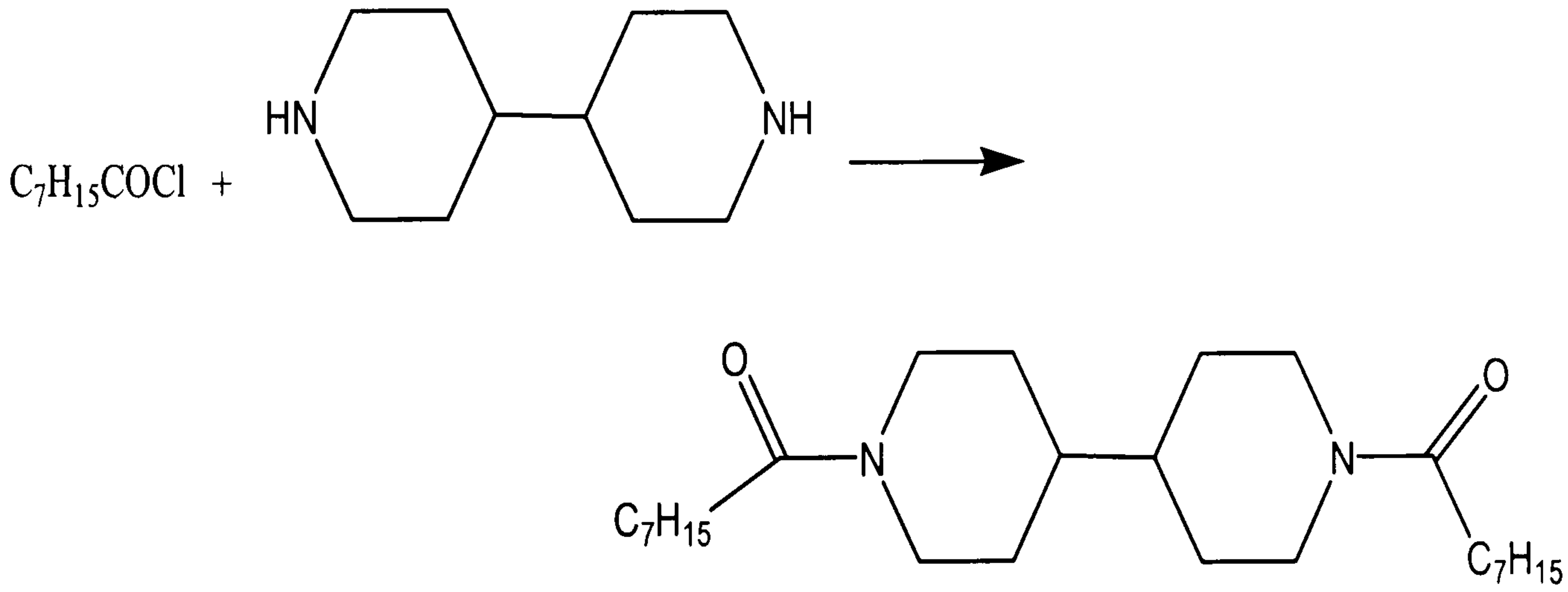
The synthesis of the *ortho* methylated of L2 derivative was attempted but was unsuccessful, analysis of the reaction showed no sign of the desired product. This is probably due to steric effects from the *ortho* methyl group.



Scheme 6.6: Synthesis of *N*-octanoyl-2-methylpiperidine.

6.2.1.7 Attempted synthesis of *N,N'*-dioctanoyl4,4-bipiperidyl (L7).

Following on from piperazine based ligands the synthesis of bipiperidyl-based amides by the same route was attempted. Starting materials and reaction conditions were varied, but yields and purities were poor.



Scheme 6.7: Synthesis of *N,N'*-dioctanoyl4,4-bipiperidyl.

6.2.2 Extraction equilbrium experiments.

Experiments using the ligands L1-L5 to identify their efficiency on the distribution coefficient and the extraction of rare earth elements were carried out due to the promise shown by amides in the extraction of thorium and uranium.

6.2.2.1 Effect of DOPEZ (L1) concentration on the distribution coefficient of yttrium from sulfate medium.

To 4 ml of the sulfate liquor (yttrium initial concentration 5.22 x 10^{-3} Mol.dm^{-3}), 4 ml of a solution of DOPEZ dissolved in carbon tetrachloride was added with concentration ranging from 0.01 to 0.1M, and the solution shaken for 10 minutes at room temperature to attain equilibrium state. The optimum value of a 0.02M solution of DOPEZ in CCl_4 was chosen from the data reported in Table 6.7 and presented in Fig. 6.27.

Table 6.7: Effect of DOPEZ concentration on the distribution coefficient of yttrium from sulfuric acid medium.

[DOPEZ]/M	Percent extraction	Distribution coefficient
0.01	86.50	6.40
0.02	87.00	6.70
0.04	85.80	6.04
0.05	85.60	5.94
0.10	85.30	5.80

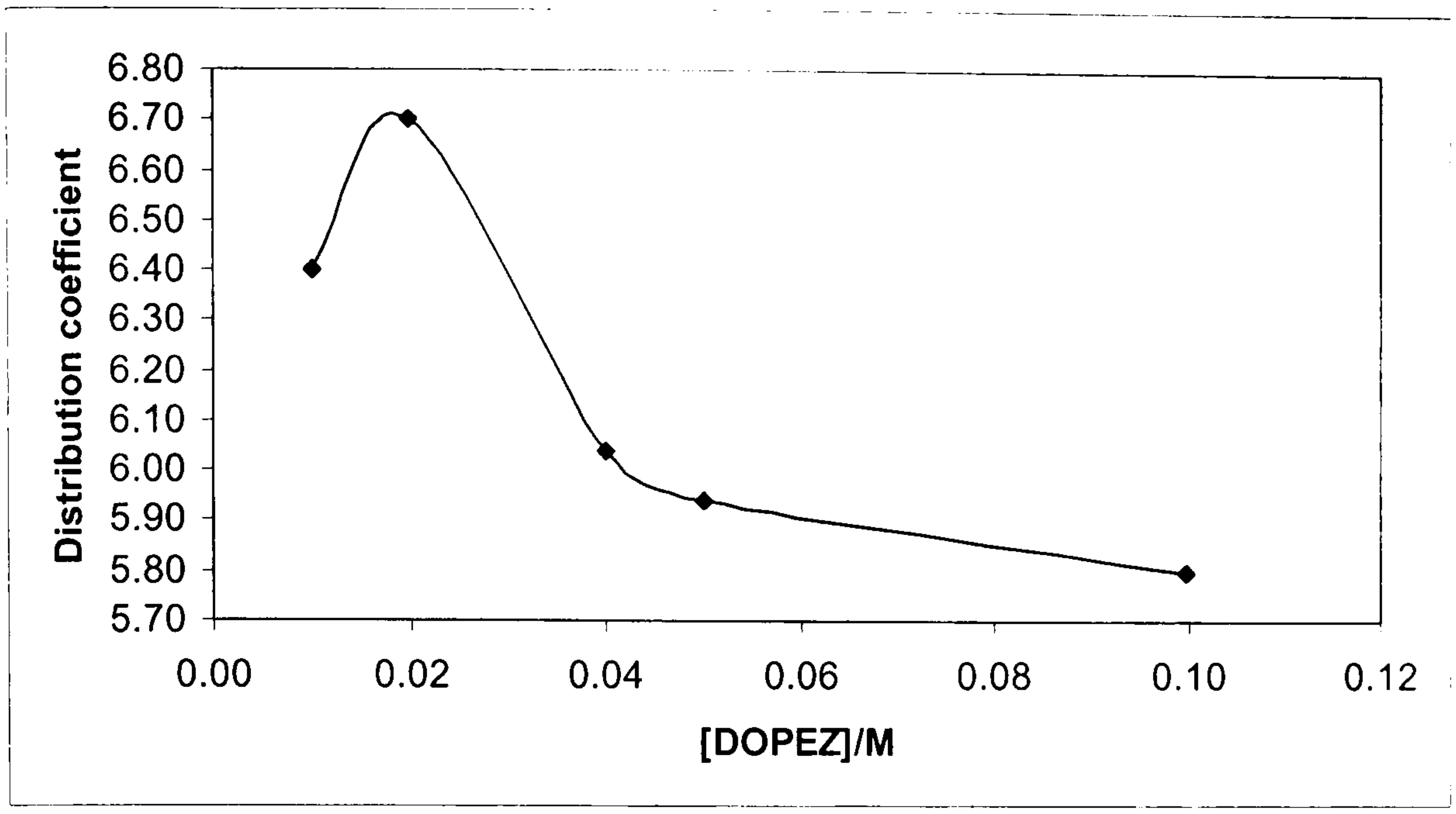


Figure 6.27: The effect of DOPEZ concentration on the distribution coefficient of yttrium from sulfuric acid medium.

6.2.2.2 Effect of DOPEZ concentration on the distribution coefficient of cerium(III) from sulfate medium.

To 4 ml of the sulfate liquor (cerium(III) initial concentration 5.22 x 10^{-3} Mol.dm^{-3}), 4 ml of a solution of DOPEZ dissolved in carbon tetrachloride was added with concentration ranging from 0.01 to 0.1M, and the solution shaken for 10 minutes at room temperature to attain equilibrium state. The optimum value of a 0.04M solution of DOPEZ in CCl_4 was chosen from the data reported in Table 6.8 and presented in Fig. 6.28, which is slightly higher than that of yttrium and can be used to separate cerium(III) from yttrium using different concentration of DOPEZ.

Table 6.8: Effect of DOPEZ concentration on the distribution coefficient of cerium(III) from sulfuric acid medium.

[DOPEZ]/M	Percent extraction	Distribution coefficient
0.01	84.90	5.62
0.02	86.30	6.29
0.04	88.00	7.33
0.05	86.80	6.57
0.10	86.25	6.27

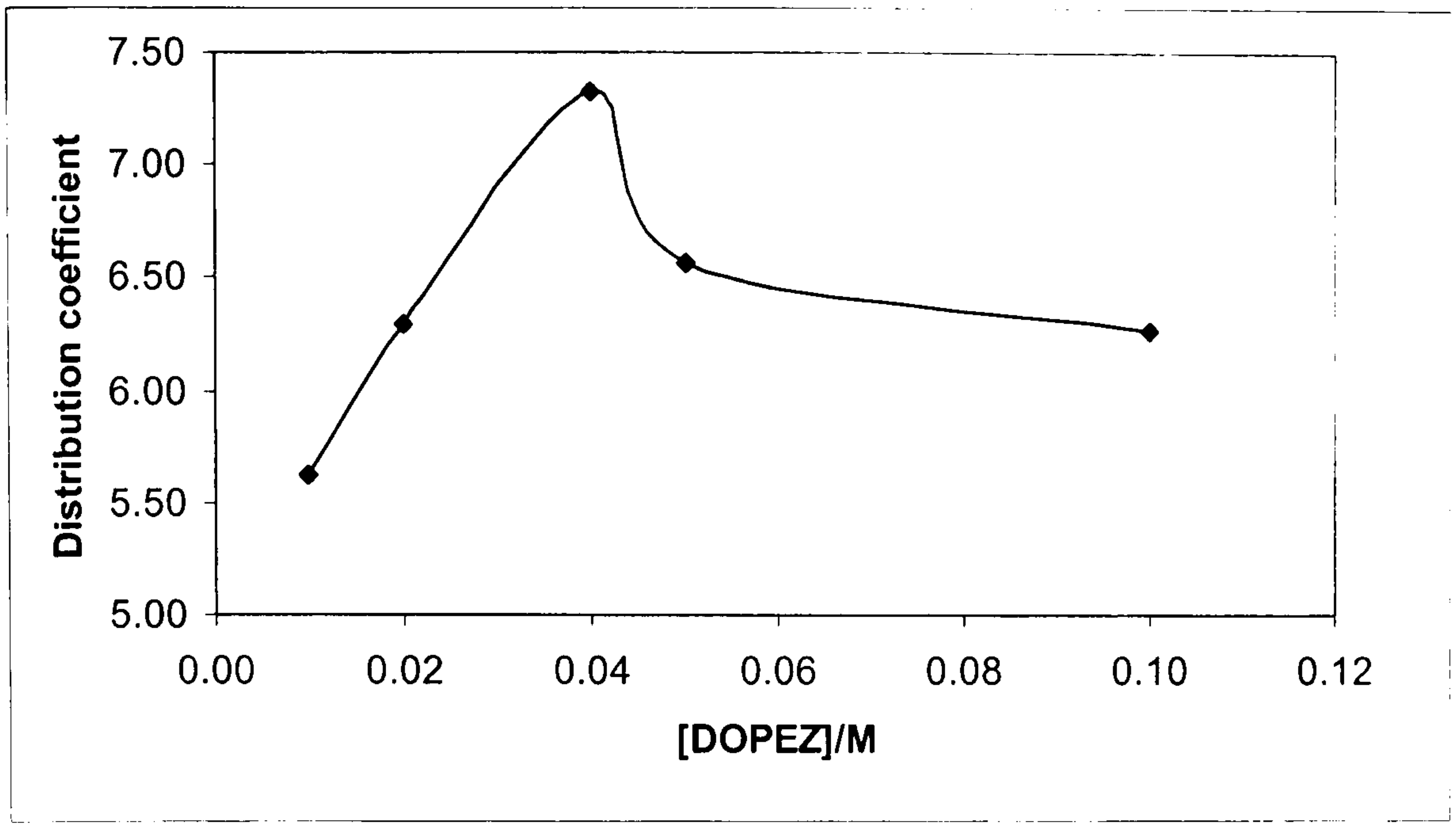


Figure 6.28: Effect of DOPEZ concentration on the distribution coefficient of cerium(III) from sulfuric acid medium.

6.2.2.3 Effect of DOPEZ concentration on the distribution coefficient of lanthanum from sulfate medium.

To 4 ml of the sulfate liquor (lanthanum initial concentration 5.22 x 10^{-3} Mol.dm^{-3}), 4 ml of a solution of DOPEZ dissolved in carbon tetrachloride was added with a concentration ranging from 0.01 to 0.1M, and the solution shaken for 10 minutes at room temperature to attain equilibrium state. The optimum value of a 0.05M solution of DOPEZ in CCl_4 was chosen from the data reported in Table 6.9 and presented in Fig. 6.29, the similarity of this optimum concentration of DOPEZ to that for cerium(III) can be attributed to that both lanthanum and cerium(III) have slightly different ionic radii (light rare earths). However, extractions using different concentrations of DOPEZ might be used to separate lanthanum from yttrium and cerium(III).

Table 6.9: Effect of DOPEZ concentration on the distribution coefficient of lanthanum from sulfuric acid medium.

[DOPEZ]/M	Percent extraction	Distribution coefficient
0.01	57.00	1.33
0.02	60.40	1.53
0.04	67.32	2.06
0.05	74.40	2.91
0.10	74.80	2.96

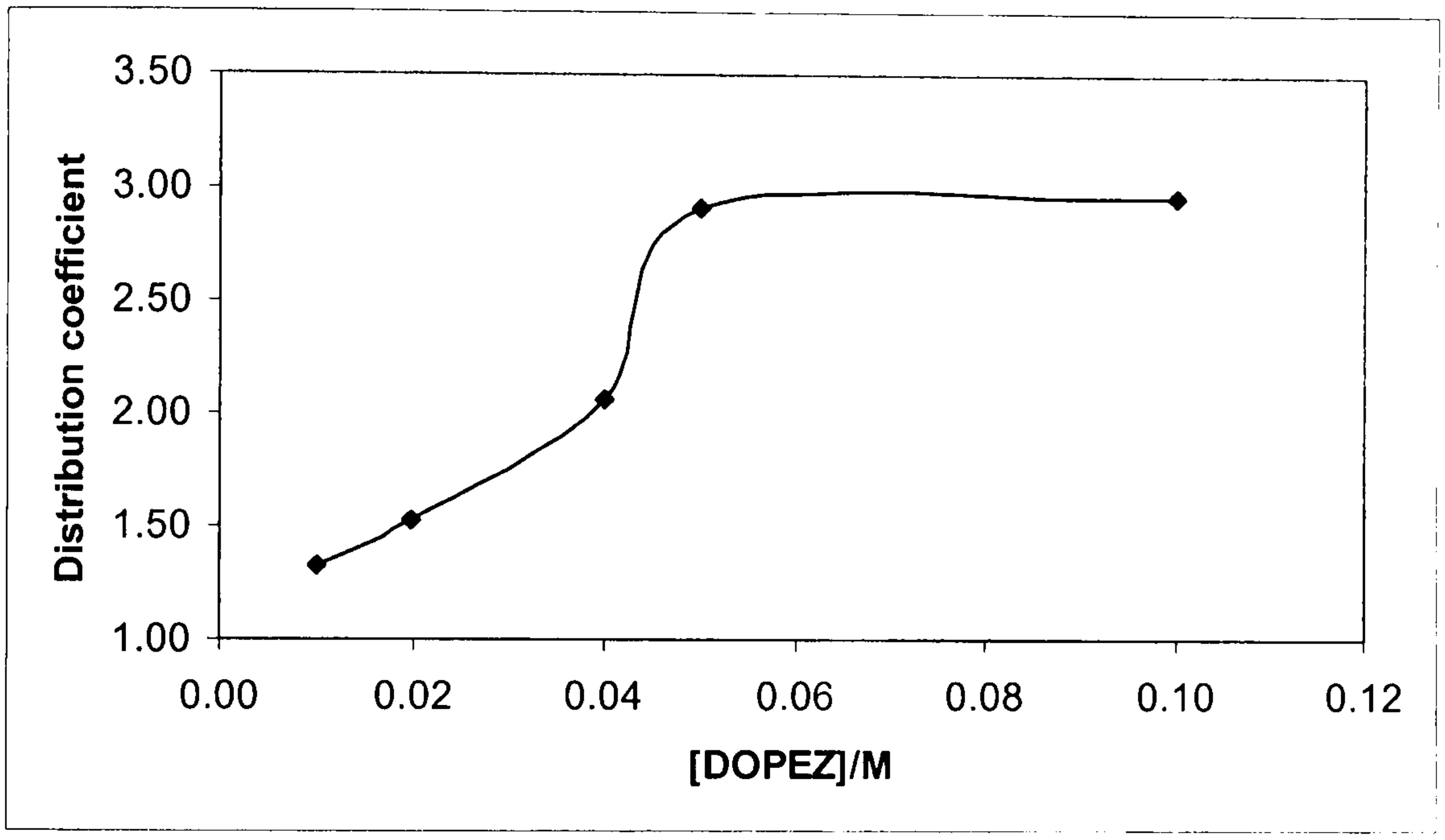


Figure 6.29: The effect of DOPEZ concentration on the distribution coefficient of lanthanum from sulfuric acid.

6.2.2.4 Effect of sulfuric acid concentration on the distribution coefficient of yttrium.

Fig. 6.30 shows the effect of different concentrations of H_2SO_4 on the distribution coefficients of yttrium in the two phases. The distribution coefficient of yttrium increases as the concentration of H_2SO_4 increases from 0.1-2M, The reason for this high-concentration increase may be that sulfuric acid reacts with water from the hydration sphere which makes the yttrium more available and easily extracted by this ligand. Other factors in this experiment were fixed at 1:1 v/v organic to aqueous phase ratio, 0.02M DOPEZ in carbon tetrachloride, mixing time 10 minutes and the experiments were carried out at room temperature. The results obtained are presented in Table 6.10 and reported in Fig. 6.30.

Table 6.10: Variation of yttrium distribution coefficient with concentration of sulfuric acid solution.

$[H_2SO_4]$/M	Percent extraction	Distribution coefficient
0.1	79.65	3.90
0.5	87.00	6.70
1.0	87.85	7.23
1.5	88.95	8.05
2.0	89.95	8.95

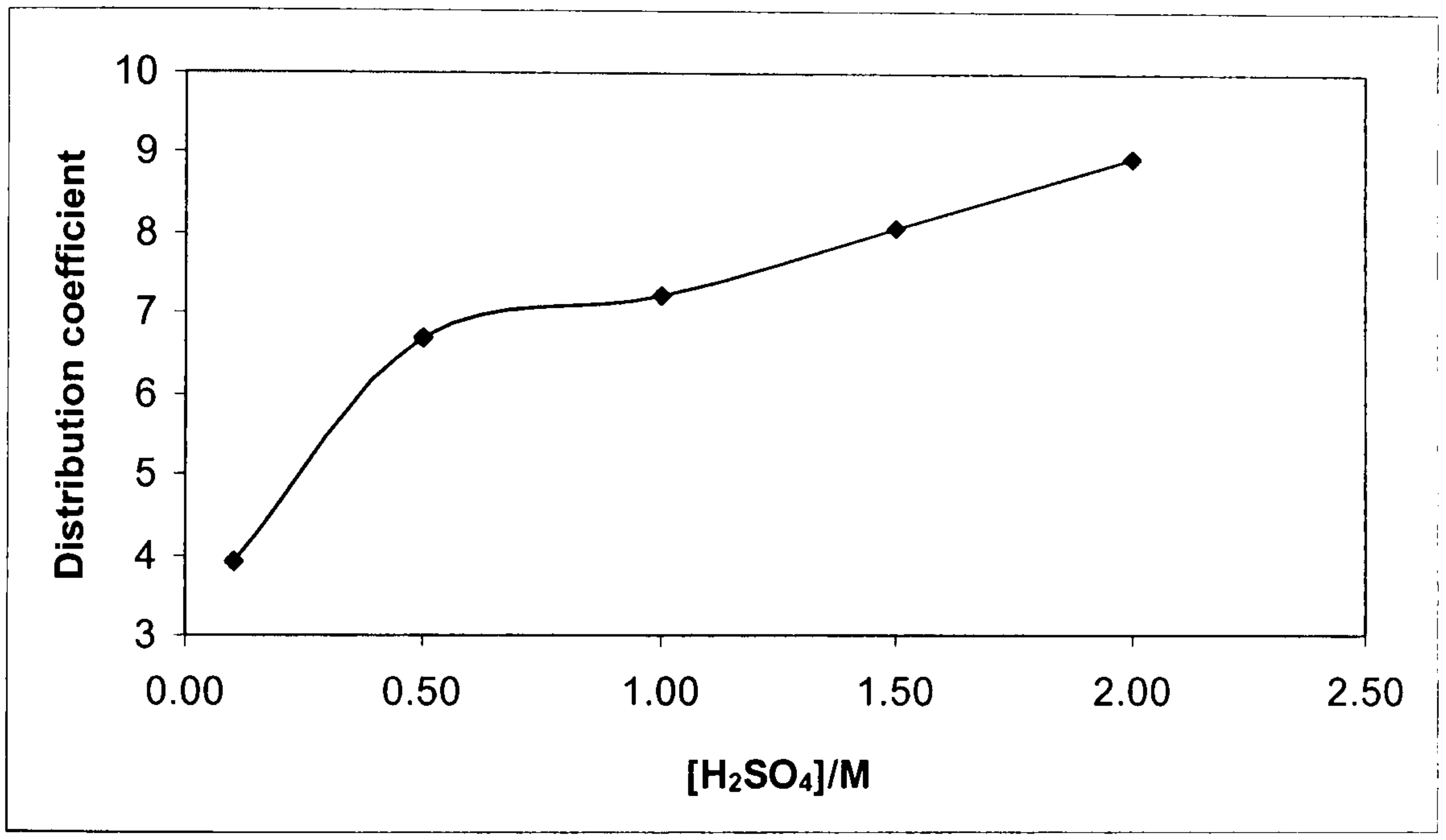


Figure 6.30: The effect of sulfuric acid concentration on the distribution coefficient of yttrium.

6.2.2.5 Effect of sulfuric acid concentration on the distribution coefficient of cerium(III).

The effect of sulfuric acid concentration on the distribution coefficient of cerium(III) is shown in Fig. 6.31. By increasing the concentration of H_2SO_4 the distribution coefficient of cerium(III) decreases gradually at higher acidity. This is because DOPEZ can also co-extract H_2SO_4 from aqueous solution, so at higher acidity the concentration of free extractant decrease which leads to a decrease in the extraction and distribution coefficient of cerium(III). The phenomenon is similar to that occurring with other amide extractants. (39-41)

Table 6.11: Variation of cerium(III) distribution coefficient with the concentration of sulfuric acid solution.

$[H_2SO_4]$/M	Percent extraction	Distribution coefficient
0.1	88.13	7.45
0.5	88.00	7.33
1.0	74.55	2.92
1.5	55.75	1.25
2.0	52.00	1.08

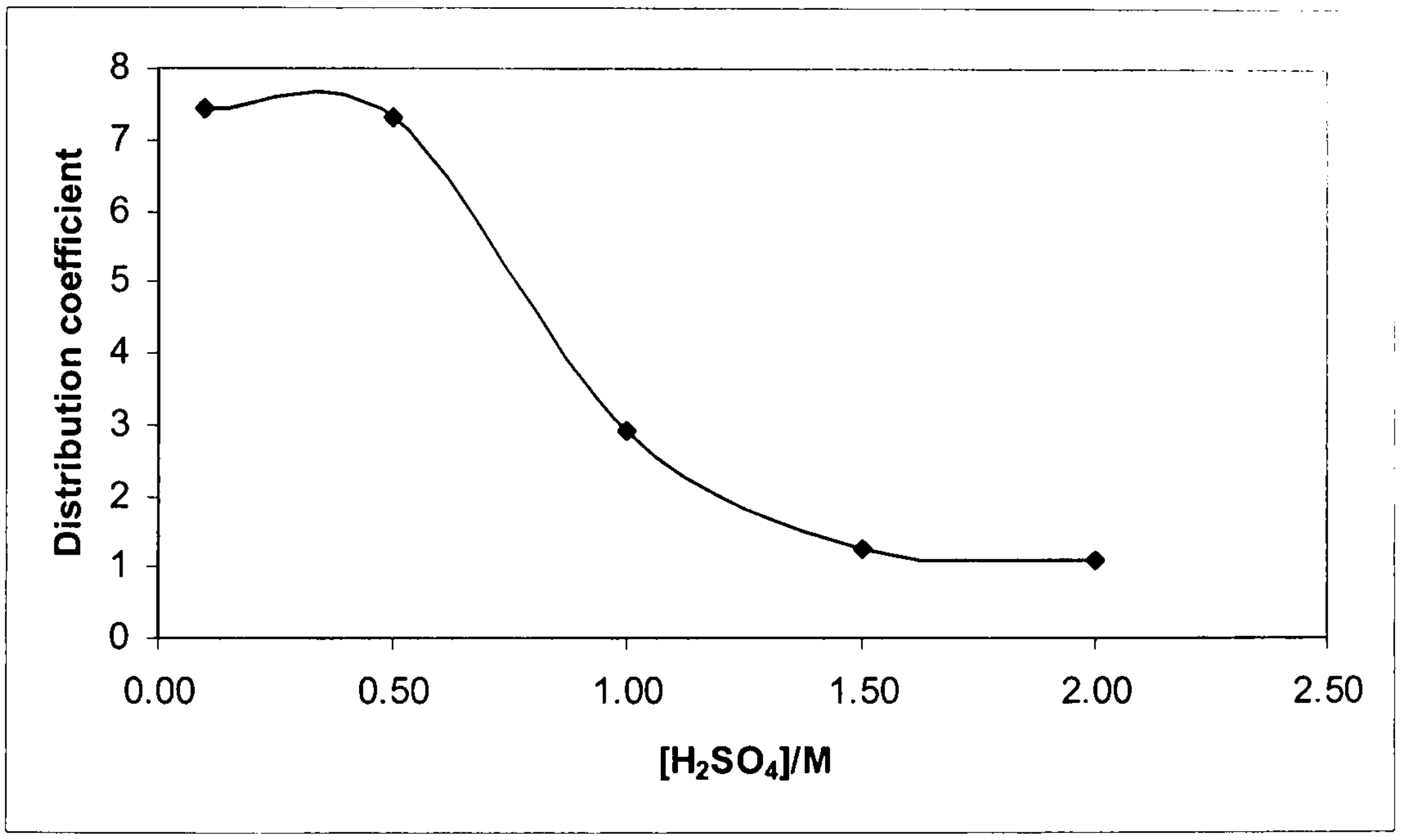


Figure 6.31: The effect of sulfuric acid concentration on the distribution coefficient of cerium(III).

6.2.2.6 Effect of sulfuric acid concentration on the distribution coefficient of lanthanum.

The effect of sulfuric acid concentration on the distribution coefficient of lanthanum is shown in Fig. 6.32 and reported in Table 6.12. By increasing the concentration of H_2SO_4 the distribution coefficient of lanthanum sharply decreases at higher acidity, which is similar to the behaviour of cerium(III) and the reason for this decrease was explained in section 6.2.2.5. However, increasing the aqueous phase acidity (sulfuric acid concentration) the distribution coefficient of yttrium increases which was opposite of lanthanum and cerium(III). This difference might be helpful in separating yttrium from both lanthanum and cerium(III).

Table 6.12: Variation of lanthanum distribution coefficient with the concentration of sulfuric acid solution.

[H_2SO_4]/M	Percent extraction	Distribution coefficient
0.1	74.60	2.94
0.5	74.40	2.91
1.0	54.84	1.21
1.5	30.68	0.44
2.0	20.00	0.25

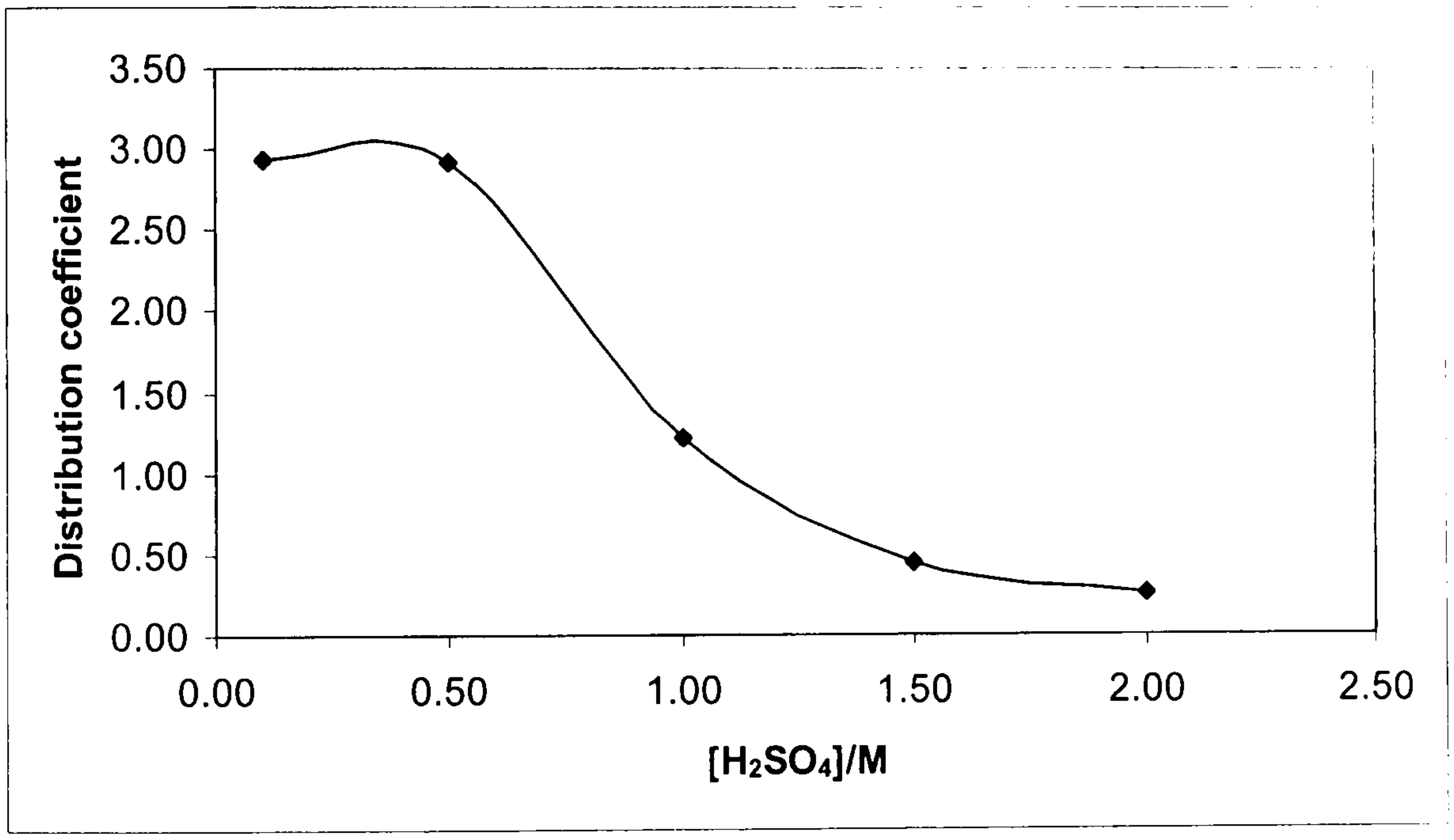


Figure 6.32: The effect of sulfuric acid concentration on the distribution coefficient of lanthanum.

6.2.2.7 Effect of diluent on the distribution coefficient of yttrium by DOPEZ.

The distribution coefficient of yttrium has been studied using different organic diluents, namely benzene (1), toluene (2), carbon tetrachloride (3), chloroform (4), and 1,2-dichloroethane (5). The other factors were fixed at the values at which maximum distribution coefficient occurred i. e. 1:1 (v/v) organic to aqueous phase ratio, room temperature, 0.02M DOPEZ in all diluents, contact time 10 minutes. Results are presented in Table 6.13. It is obvious that although benzene and toluene have dielectric constants of the same order of magnitude as that of CCl_4, they both came below CCl_4 with regards to the efficiency of distribution coefficient of yttrium. This is probably due to the lower solubility of the extracted species in these diluents as compared with CCl_4. This is probably a function of the different intermolecular diluent: diluent, and solvent: diluent, interactions that occur in aromatic, and non-aromatic, diluents. It is clear from Table 6.13 and Fig. 6.33 that CCl_4 is the best diluent.

Table 6.13: Effect of different diluents on the distribution coefficient of yttrium.

Diluents	Percent extraction	Distribution coefficient
Benzene	83.90	5.20
Toluene	83.20	4.95
Carbon tetrachloride	87.00	6.70
Chloroform	82.50	4.71
1,2-dichloroethane	83.00	4.88

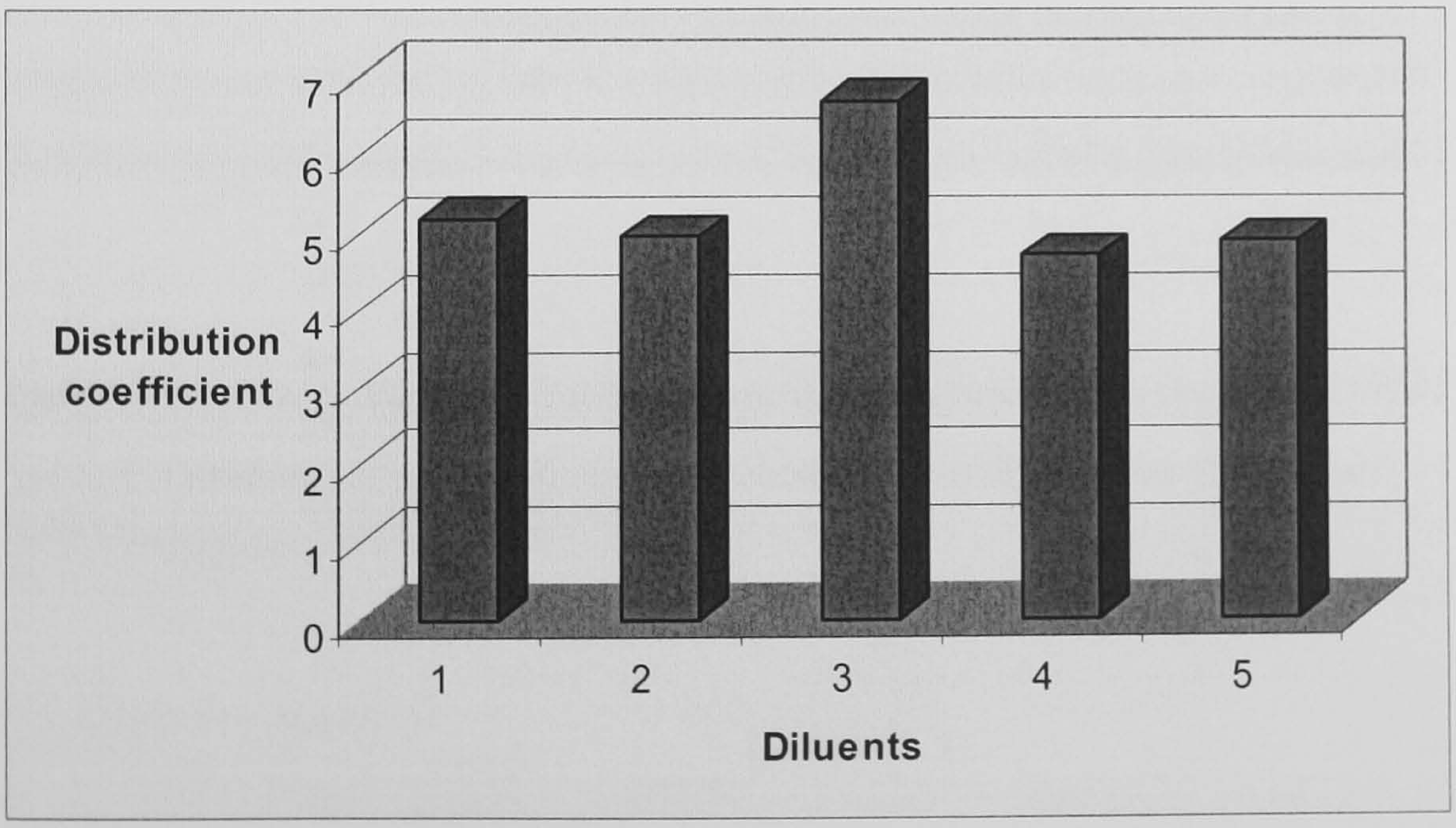


Figure 6.33: Effect of different diluents on the distribution coefficient of yttrium.

6.2.2.8 Effect of diluent on the distribution coefficient of cerium(III) by DOPEZ.

The distribution coefficient of cerium(III) has been studied using different organic diluents, namely, benzene (**1**), toluene (**2**), carbon tetrachloride (**3**), chloroform (**4**), and 1,2-dichloroethane (**5**). The other factors were fixed at the values at which maximum distribution coefficient occurred i.e. 1:1 (v/v) organic to aqueous phase ratio, room temperature, 0.04M DOPEZ in all diluents, contact time 10 minutes. Results are presented in Table 6.14. It is obvious that from Table 6.14 and Fig. 6.34 that CCl_4 is the best diluent that is similar to that obtained in the case of yttrium.

Table 6.14: Effect of different diluents on the distribution coefficient of cerium(III).

Diluents	Percent extraction	Distribution coefficient
Benzene	81.50	4.41
Toluene	79.40	3.85
Carbon tetrachloride	88.00	7.33
Chloroform	70.15	2.35
1,2-dichloroethane	74.55	2.93

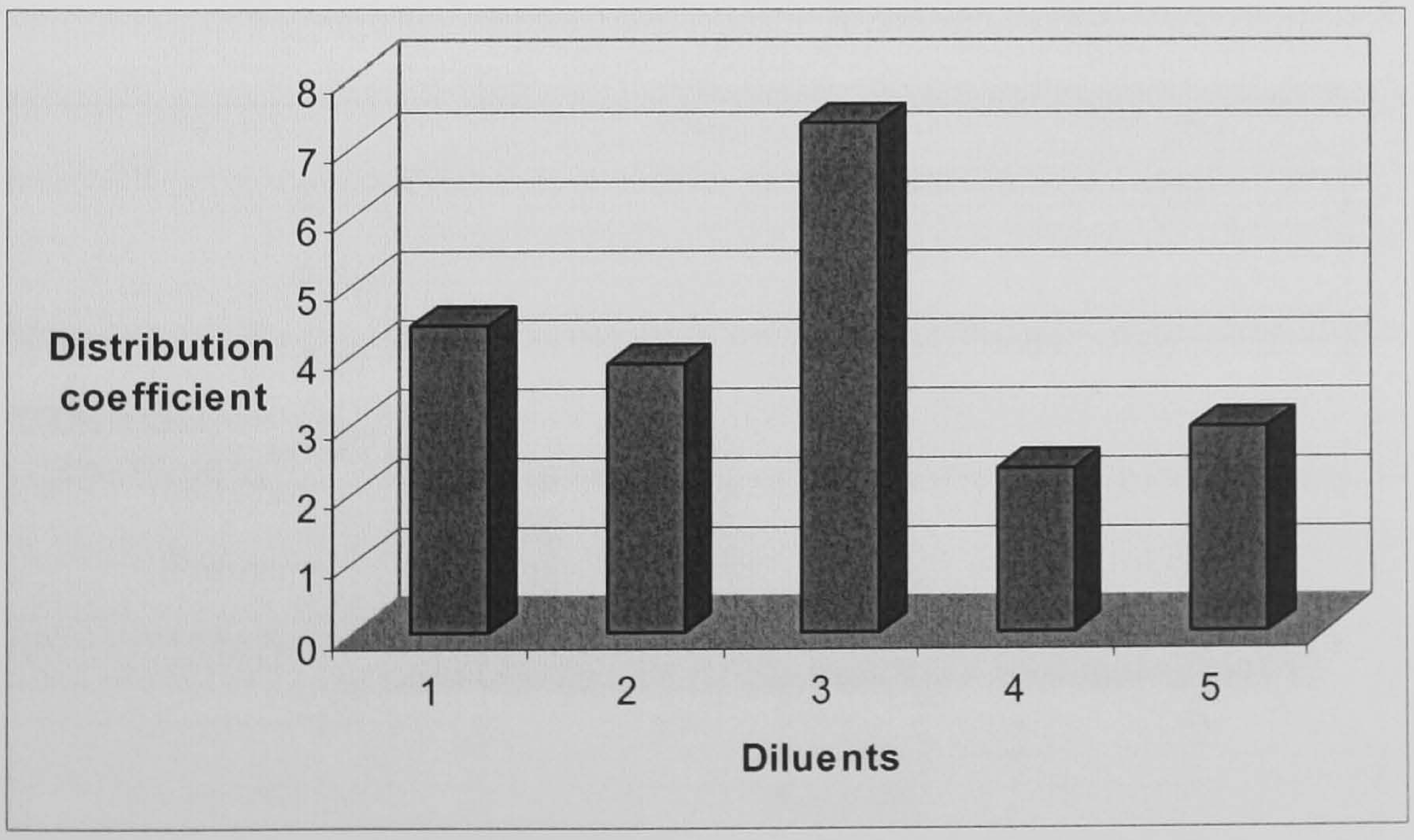


Figure 6.34: Effect of different diluents on the distribution coefficient of cerium(III).

6.2.2.9 Effect of diluent on the distribution coefficient of lanthanum by DOPEZ.

The distribution coefficient of lanthanum has been studied using different organic diluents namely, benzene (**1**), toluene (**2**), carbon tetrachloride (**3**), chloroform (**4**), and 1,2-dichloroethane (**5**). The other factors were fixed at the values at which maximum distribution coefficient occurred i. e. 1:1 (v/v) organic to aqueous phase ratio, room temperature, 0.05M DOPEZ in all diluents, contact time 10 minutes. Results are presented in Table 6.15. It is noticed that this is identical to the previous section. It is clear from Table 6.15 and Fig. 6.35 that CCl_4 is the best diluent. So, the diluents effect does not offer any help in separating these elements using DOPEZ.

Table 6.15: Effect of different diluents on the distribution coefficient of lanthanum.

Diluents	Percent extraction	Distribution coefficient
Benzene	47.12	0.89
Toluene	57.84	1.37
Carbon tetrachloride	74.40	2.91
Chloroform	52.24	1.09
1,2 dichloroethane	57.20	1.34

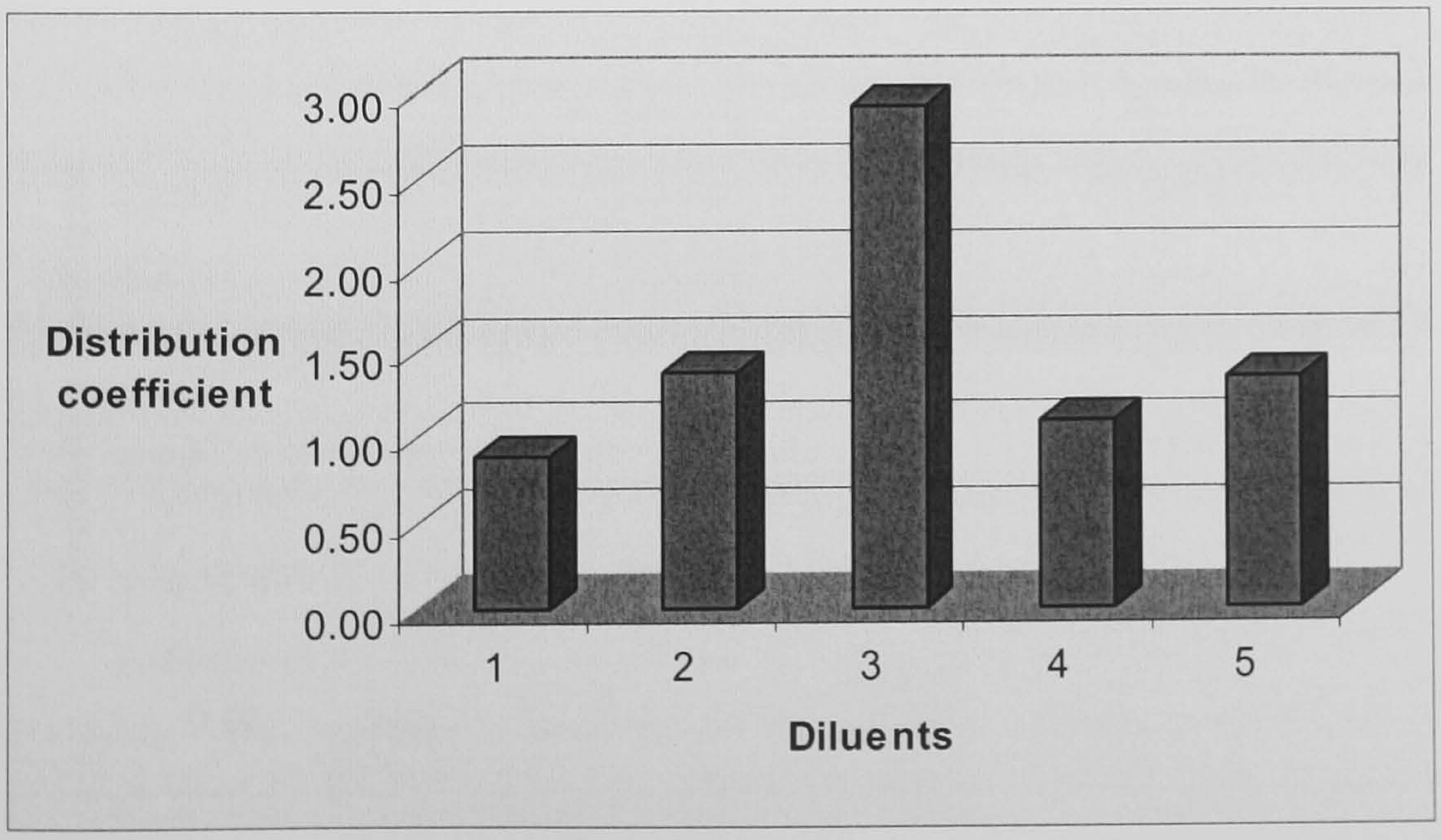


Figure 6.35: Effect of different diluents on the distribution coefficient of lanthanum.

6.2.2.10 Effect of equilibration time on the distribution coefficient of yttrium by DOPEZ.

The effect of contact time on the attainment of an equilibrium state was studied at intervals between 1–30 minutes, while the other factors were kept as mentioned before. The results obtained are given in Table 6.16 and shown in Fig. 6.36. It is obvious that by increasing the contact time from1-10 minutes the distribution coefficient was increased and above 10 minutes slightly decreased, so contact time of 10 minutes is quite adequate for efficient yttrium extraction but it is slower than for the amines studied in this work.

Table 6.16: Effect of equilibration time on the distribution coefficient of yttrium by 0.02M DOPEZ/carbon tetrachloride.

Time/minutes	Percent extraction	Distribution coefficient
1	84.00	5.25
5	86.50	6.41
10	87.00	6.70
20	86.75	6.55
30	86.55	6.43

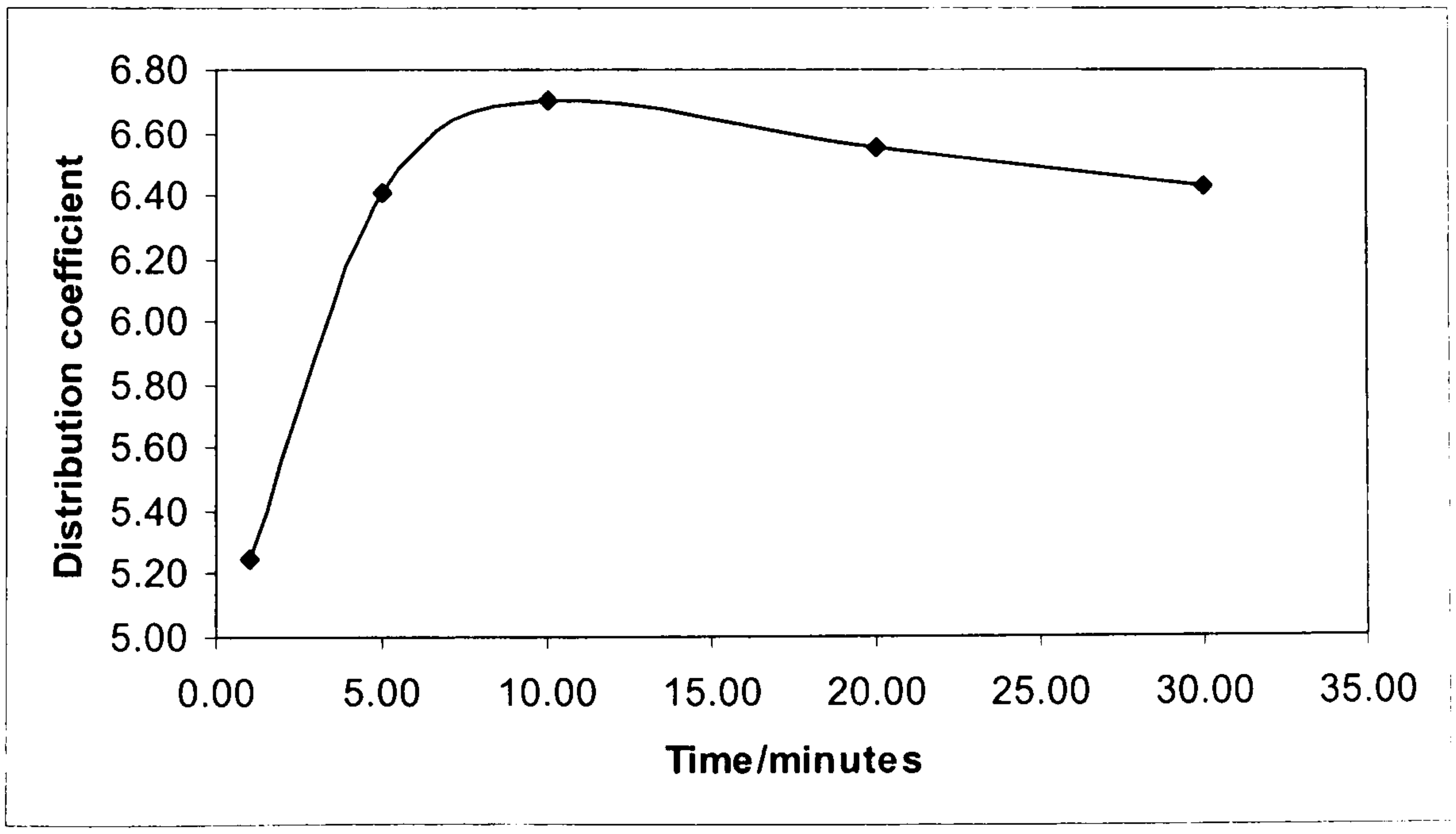


Figure 6.36: The effect of equilibration time on the distribution coefficient of yttrium by 0.02M DOPEZ/carbon tetrachloride.

6.2.2.11 Effect of equilibration time on the distribution coefficient of cerium(III) by DOPEZ.

The effect of mixing time on the attainment of an equilibrium state was studied at intervals between 1–30 minutes, while the other factors were kept as mentioned before. The results obtained are given in Table 6.17 and shown in Fig. 6.37. It is noticed that by increasing the contact time the distribution coefficient increased to the maximum after 10 minutes and began to decrease which was attributed to the entrainment of some ligands droplet into the aqueous phase, then contact time of 10 minutes is quite adequate for efficient cerium(III) extraction.

Table 6.17: Effect of equilibration time on the distribution coefficient of cerium(III) by 0.04M DOPEZ/carbon tetrachloride.

Time/minutes	Percent extraction	Distribution coefficient
1	79.50	3.87
5	80.00	4.00
10	86.00	6.14
20	81.00	4.26
35	80.75	4.19

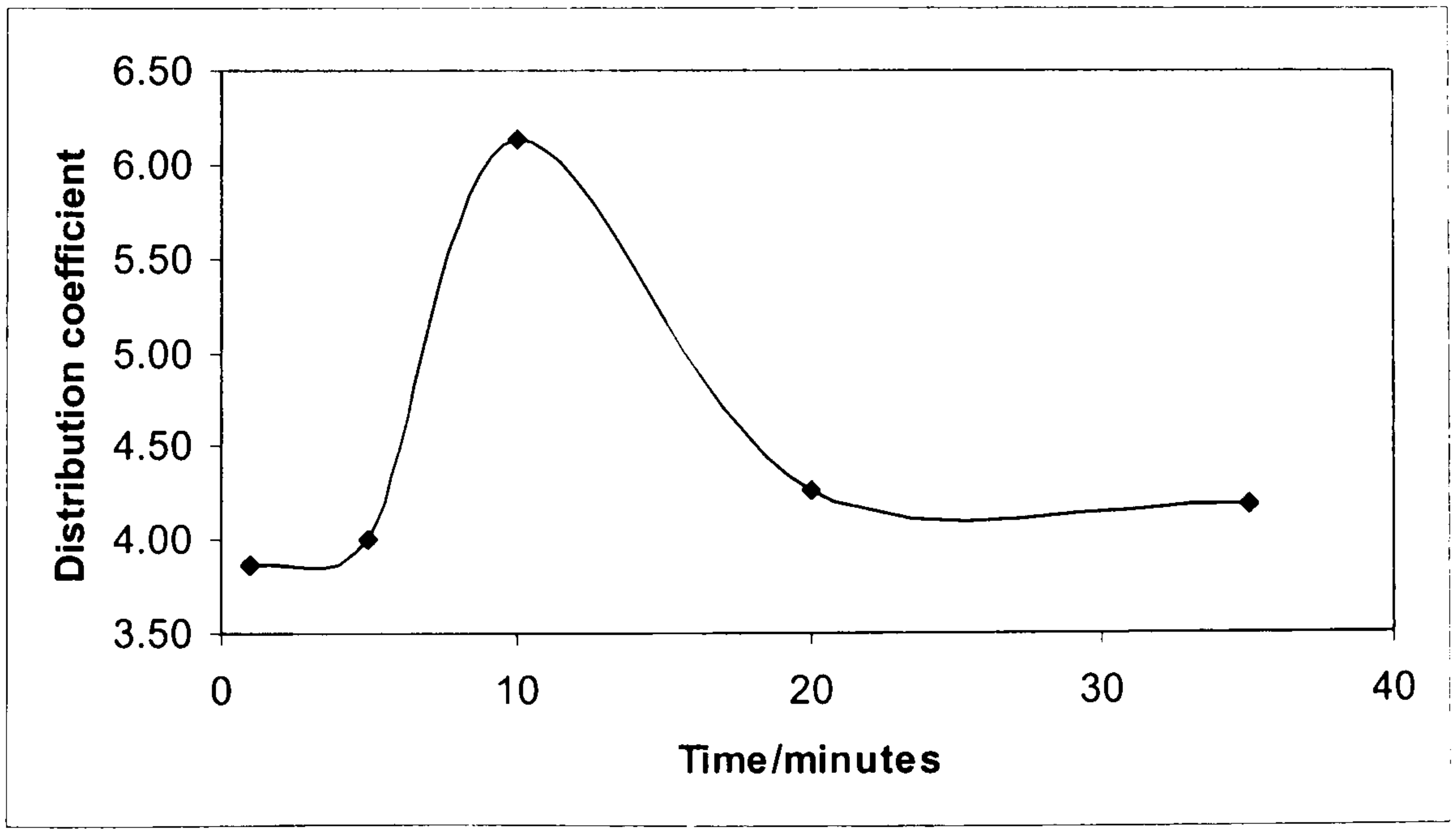


Figure 6.37: The effect of equilibration time on the distribution coefficient of cerium(III) by 0.04M DOPEZ/carbon tetrachloride.

6.2.2.12 Effect of equilibration time on the distribution coefficient of lanthanum by DOPEZ.

The effect of equilibration time on the attainment of an equilibrium state was studied at intervals between 1–35 minutes, while the other factors were kept as mentioned before. The results obtained are given in Table 6.18 and shown in Fig. 6.38. It is obvious that contact time of 10 minutes is quite adequate for efficient lanthanum extraction, which is identical to the previous section.

Table 6.18: Effect of equilibration time on the distribution coefficient of lanthanum by 0.05 M DOPEZ/carbon tetrachloride.

Time/minutes	Percent extraction	Distribution coefficient
1	71.00	2.44
5	72.50	2.64
10	78.00	3.55
20	76.50	3.26
35	75.00	3.00

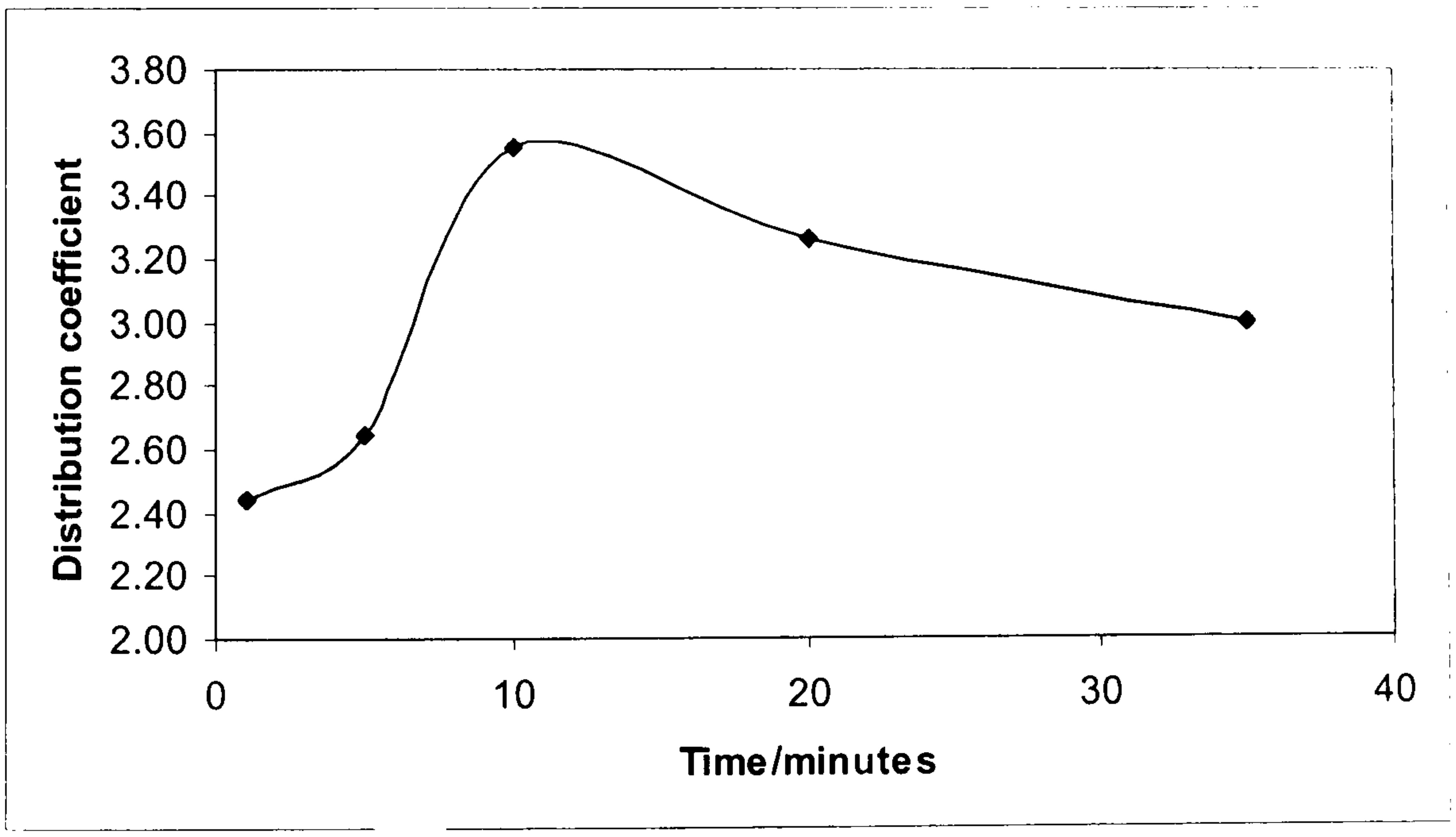


Figure 6.38: The effect of equilibration time on the distribution coefficient of lanthanum by 0.05M DOPEZ/carbon tetrachloride.

6.2.2.13 Effect of pH on the distribution coefficient of yttrium.

The distribution coefficient has been studied by varying the pH values of the sulfate liquor from 0.5 to 2.00, using either sulfuric acid or sodium hydroxide. Other factors were fixed at 1:1 (v/v) organic to aqueous phase ratio, 0.02M DOPEZ in carbon tetrachloride, contact time 10 minutes and the experiments were carried out at room temperature. The results obtained are given in Table 6.19 and shown in Fig. 6.39. It is clear that the pH 0.50 of the sulfate liquor can be taken as an optimum pH value. Fortunately, that is the same pH of the parent sulfate liquor under examination and by increasing pH the yttrium distribution coefficient decreased. This decreasing on distribution coefficient is caused by formation of non-extractable species at higher acidity.

Table 6.19: Variation of distribution coefficient of yttrium with the pH of the sulfate solution.

pH	Yttrium % extraction	Distribution coefficient
0.50	91.80	11.19
0.75	86.70	6.52
1.00	81.60	4.43
1.50	80.50	4.13
2.00	79.25	3.82

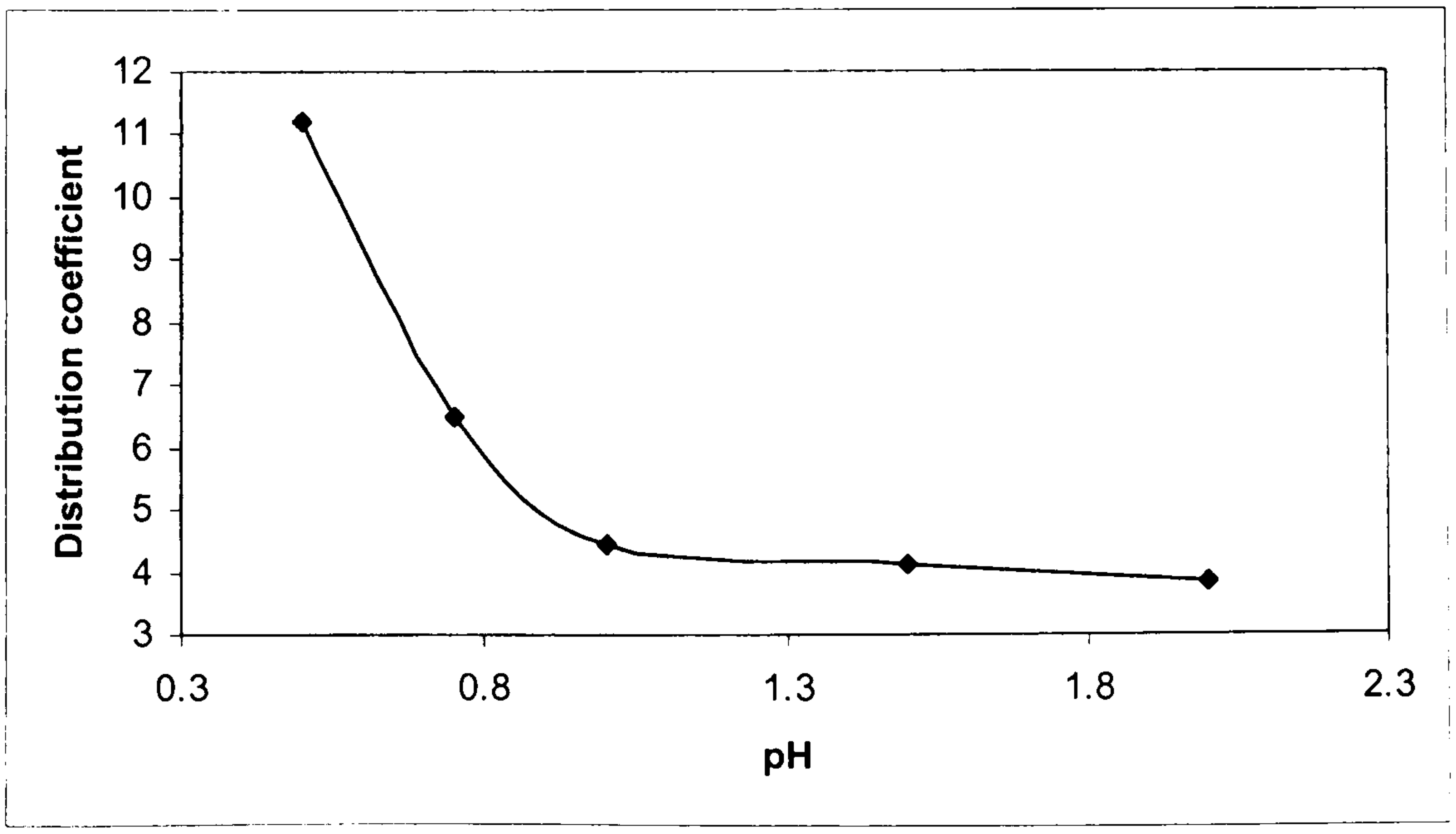


Figure 6.39: The effect of pH on the distribution coefficient of yttrium.

6.2.2.14 Effect of *N*-octanoyl-4-methylpiperidine (L4) concentration on the distribution coefficient of yttrium from sulfate medium.

To 5 ml of the sulfate liquor (yttrium sulfate), 5ml of a solution of N-octanoyl-4-methylpiperidine dissolved in chloroform was added with a concentration ranging from 0.01 to 0.5M, and the solution shaken for 10 minutes at room temperature to attain equilibrium state. By increasing the ligand concentration, the distribution coefficient increased until the concentration reached 0.25M, after which the distribution coefficient began to decrease probably due to viscosity problems (insufficient mixing between the aqueous and organic phases). Also at higher concentrations of the ligand the tendency for dimerization or polymerization increased causing the decrease in the distribution coefficient. The data are reported in Table 6.20 and presented in Fig. 6.40.

Table 6.20: Effect of concentration of (L4) on the distribution coefficient of yttrium from sulfuric acid medium.

Amide/M	Yttrium % extraction	Distribution coefficient
0.01	80.60	4.15
0.02	80.70	4.18
0.04	80.75	4.19
0.05	80.90	4.23
0.10	81.45	4.39
0.25	81.65	4.43
0.50	81.30	4.34

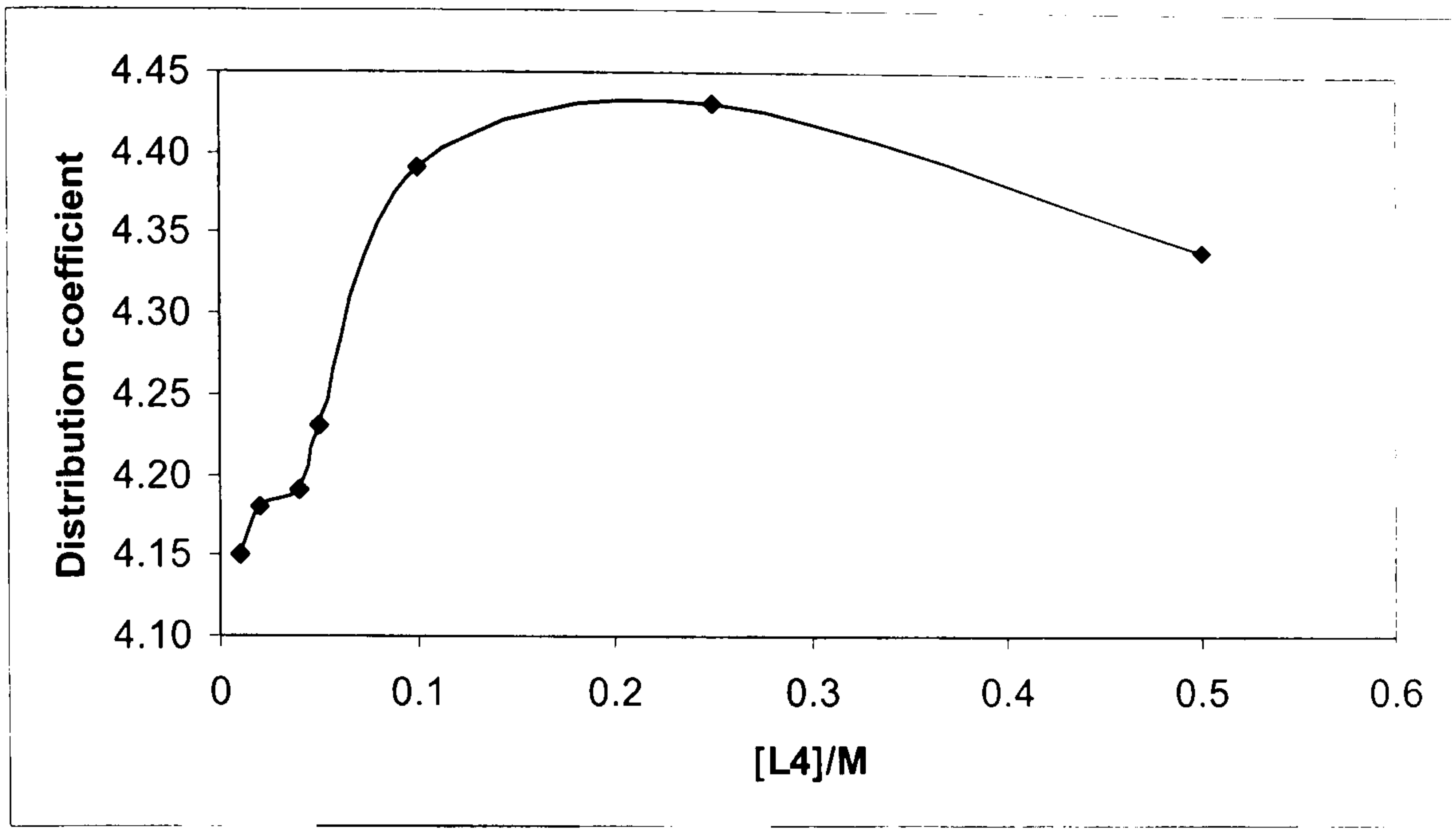


Figure 6.40: The effect of different concentrations of (L4) on the distribution coeffcient of yttrium.

6.2.3 Liquid-liquid extraction loading capacities experiments using different amide ligands L1, L2, L3, and L4.

6.2.3.1 Yttrium loading capacity of different amide ligands L1, L2, L3, and L4.

20 ml of each of the organic phase (0.02M L1, L2, L3, and L4 dissolved in chloroform) and aqueous phase were contacted for 10 minutes until equilibrium was obtained. The phases were allowed to separate and the aqueous phase was removed and analysed. A measured portion of the organic phase was also taken for analysis. Fresh aqueous solution was then added to the remainder of the organic phase to give the same phase ratio as originally used. The phases were again contacted until equilibrium was obtained, and the same procedure adopted as described above. This process was carried out until saturation of the solvent with yttrium was obtained. Care must be taken to keep the same pH value of 0.6 throughout the series of shake-outs. From Figs. 6.41-6.44 yttrium extraction under these conditions needs different extraction stages for nearly completed recovery and the loading capacity for L1 was 2.04 KgM^{-3}, L2 is 1.23 KgM^{-3}, L3 is 1.61 KgM^{-3}, and L4 is 1.62KgM^{-3}.

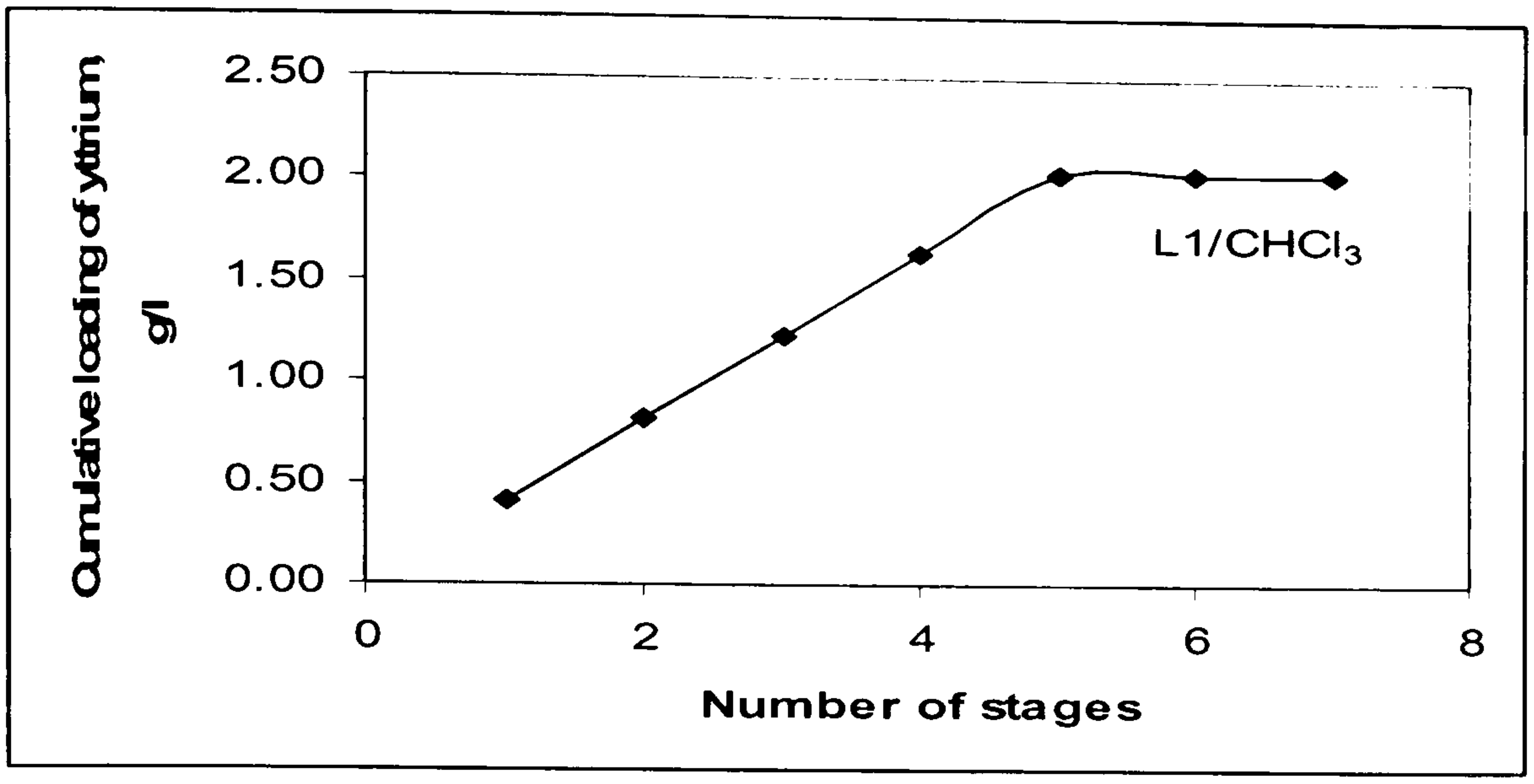


Figure 6.41: The effect of number of stages on the yttrium loading capacity of L1/$CHCl_3$.

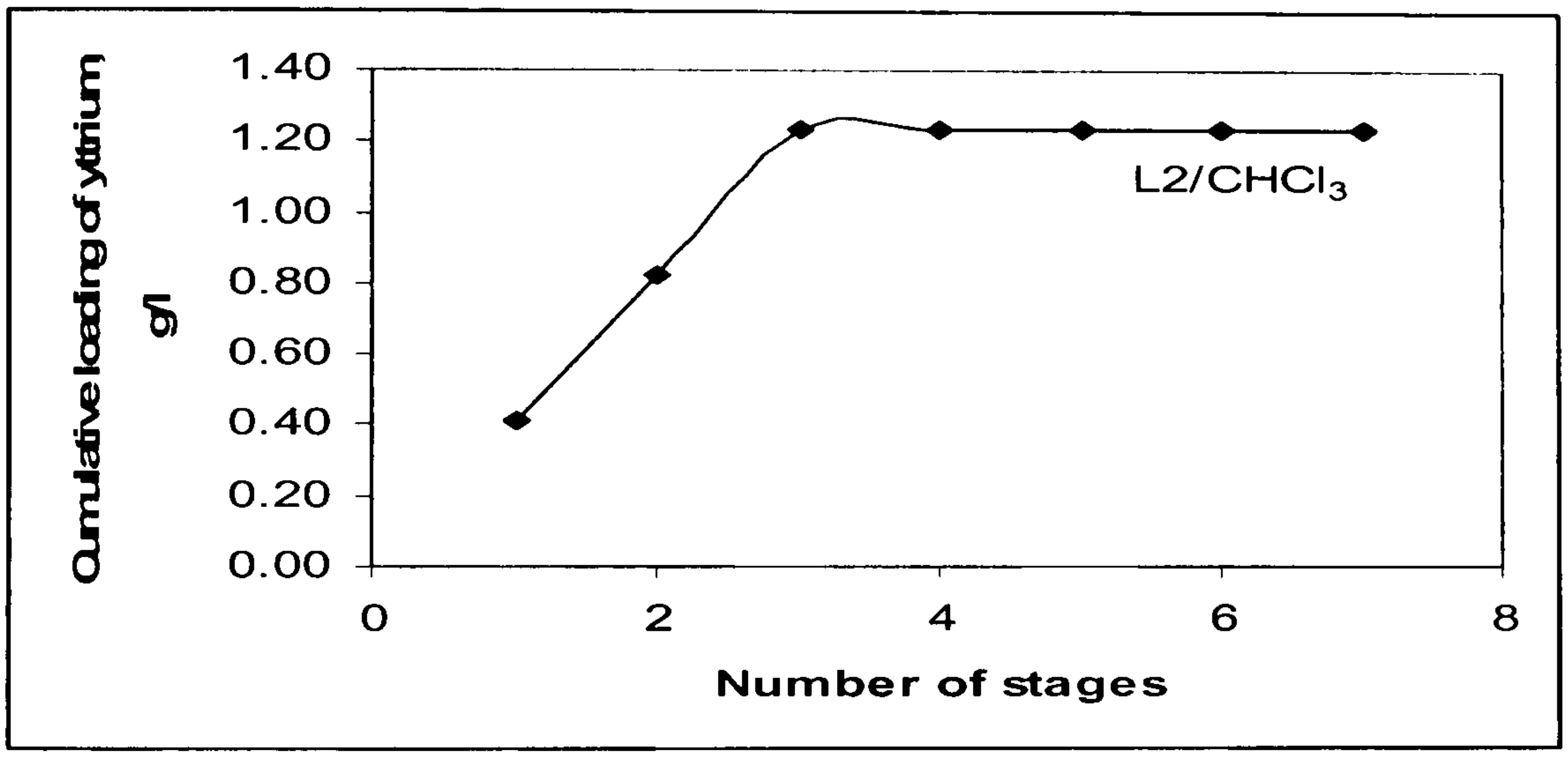


Figure 6.42: The effect of number of stages on the yttrium loading capacity of L2/$CHCl_3$.

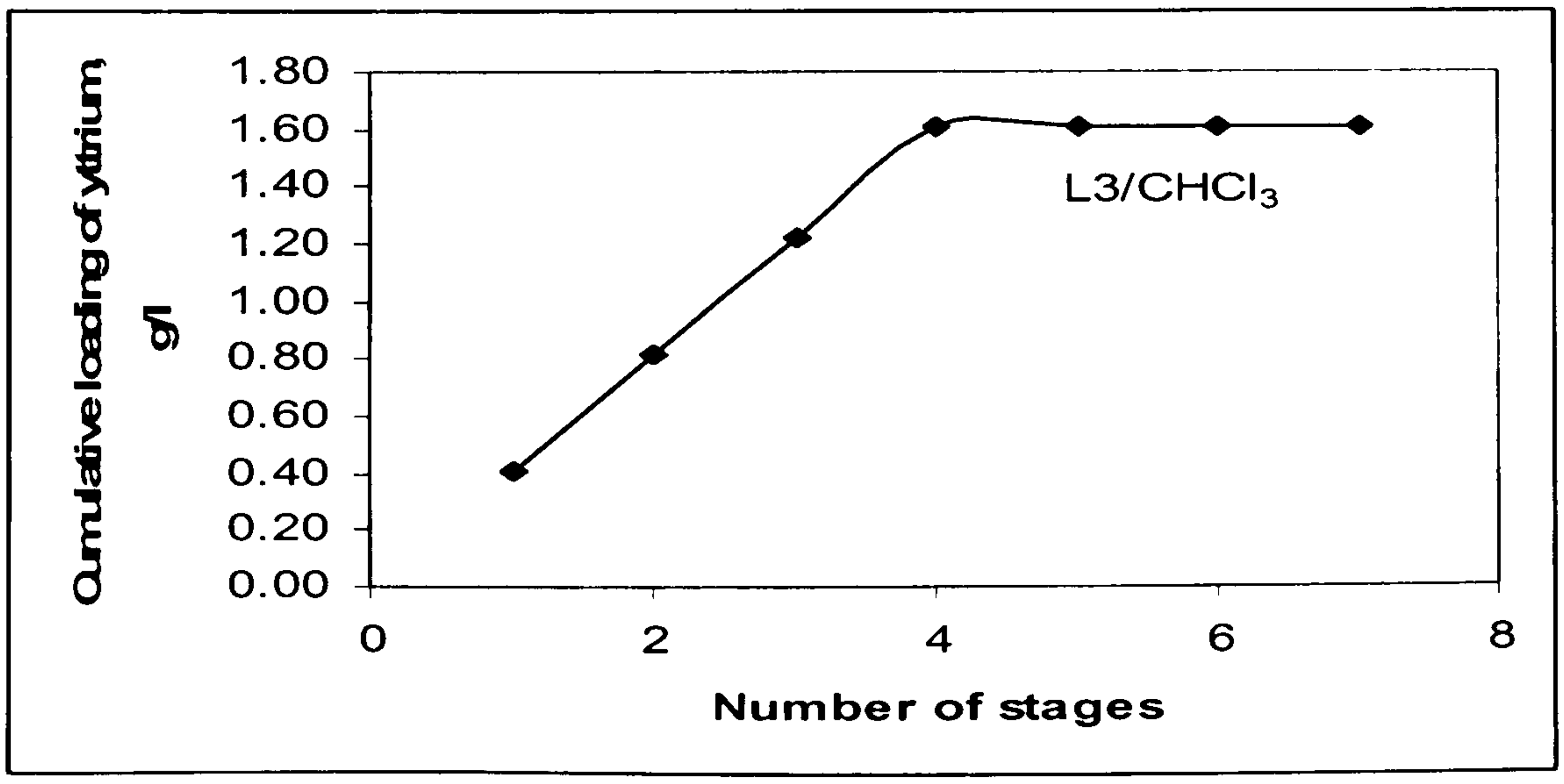


Figure 6.43: The effect of number of stages on the yttrium loading capacity of L3/$CHCl_3$.

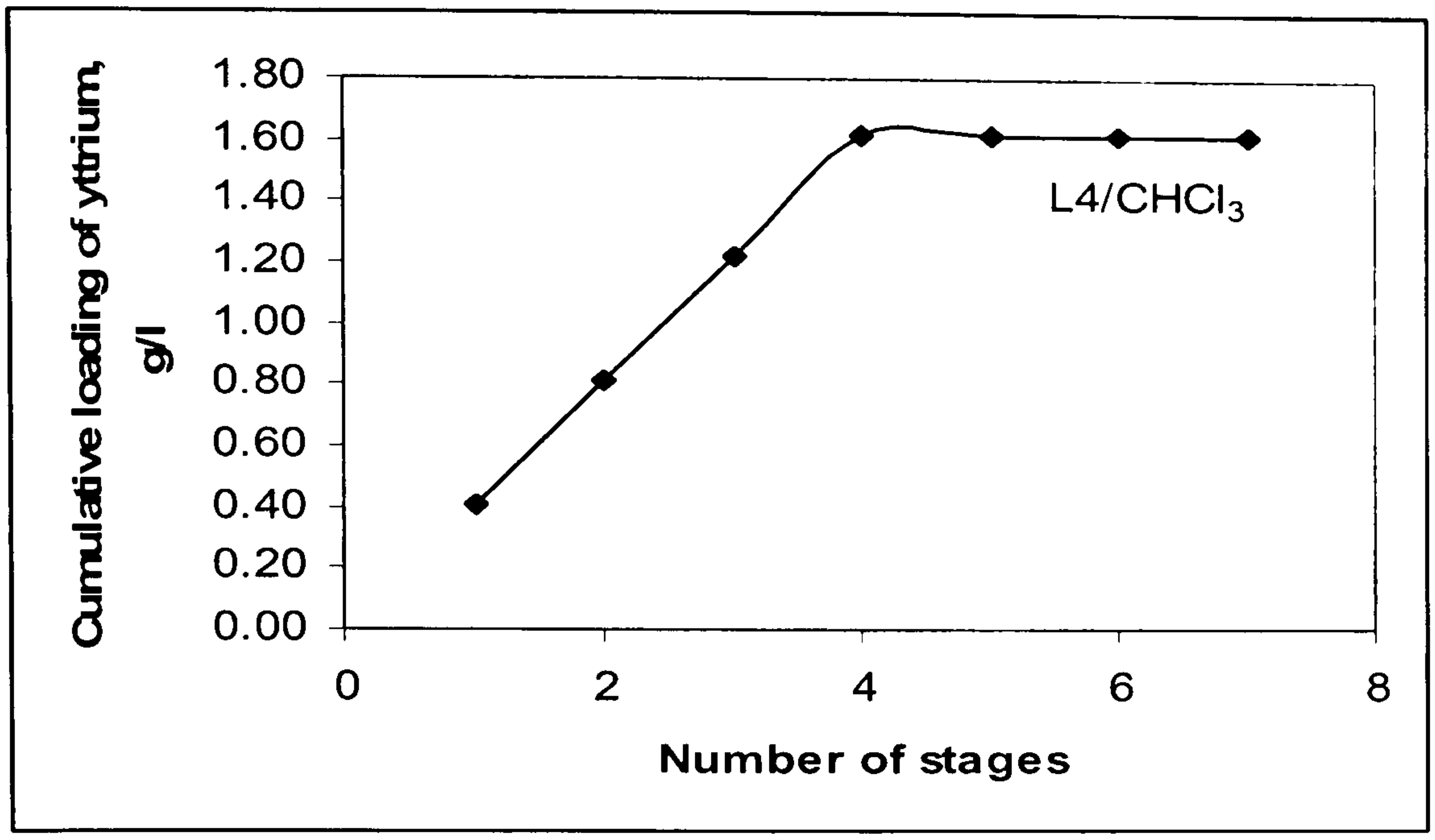


Figure 6.44: The effect of number of stages on the yttrium loading capacity of L4/$CHCl_3$.

6.2.3.2 Cerium(III) loading capacity of different ligands.

20 ml of each of the organic phase (0.04M L1, L2, L3, and L4 in chloroform) and aqueous phase were contacted for 10 minutes until equilibrium was obtained. The phases were allowed to separate and the aqueous phase was removed and analysed. A measured portion of the organic phase was also taken for analysis. Fresh aqueous solution was then added to the remainder of the organic phase to give the same phase ratio as originally used. The phases were again contacted until equilibrium was obtained, and the same procedure adopted as described above. This process was carried out until saturation of the solvent with cerium(III) was obtained. Care must be taken to keep the same pH value of 0.6 throughout the series of shake-outs. From Figs. 6.45-6.48 cerium(III) extraction under these conditions needs different extraction stages for nearly completed recovery and the loading capacity for L1 was 2.44 KgM^{-3}, L2 is 1.72 KgM^{-3}, L3 is 1.73 KgM^{-3}, and L4 is 2.15 KgM^{-3}.

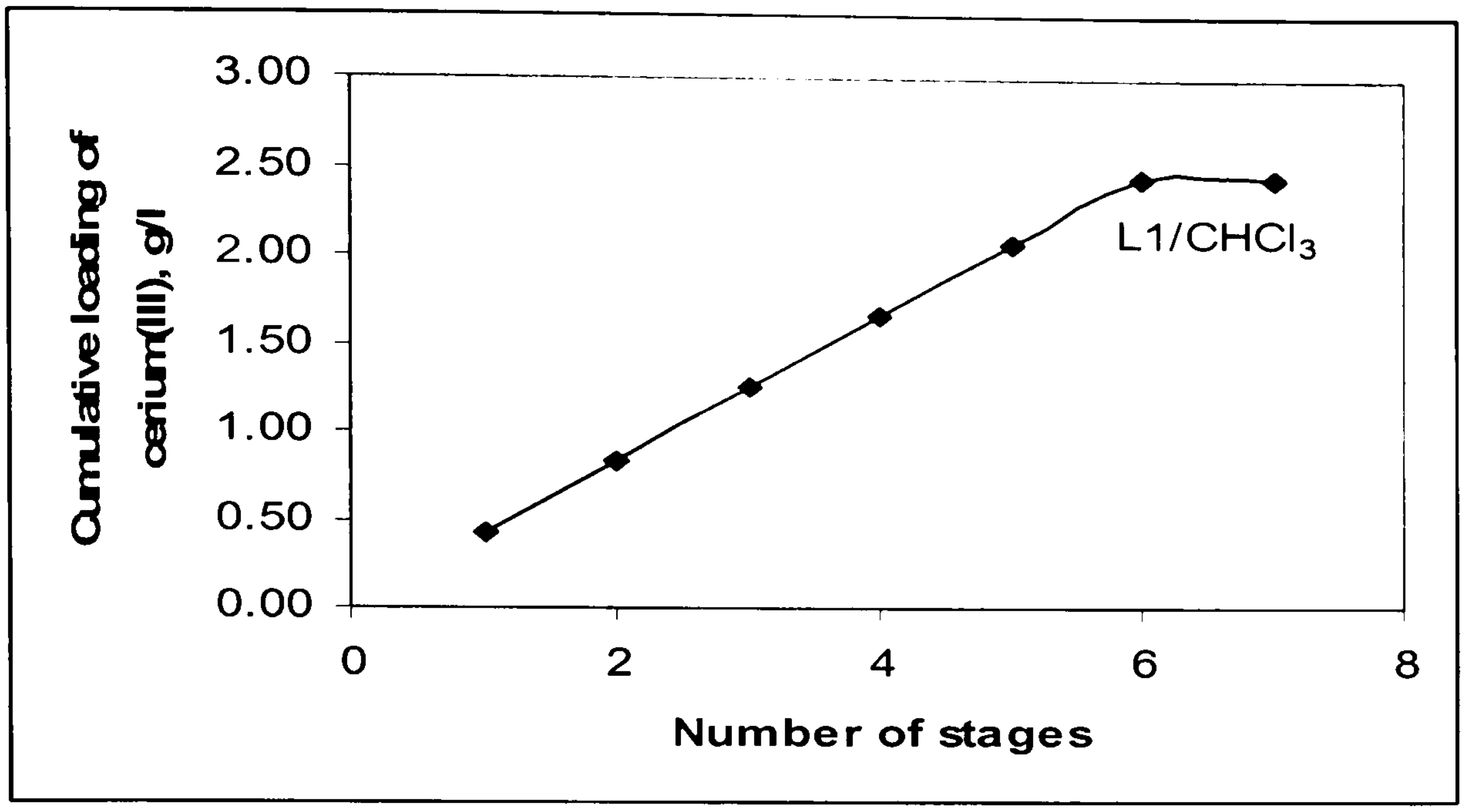


Figure 6.45: The effect of number of stages on the cerium(III) loading capacity of L1/$CHCl_3$.

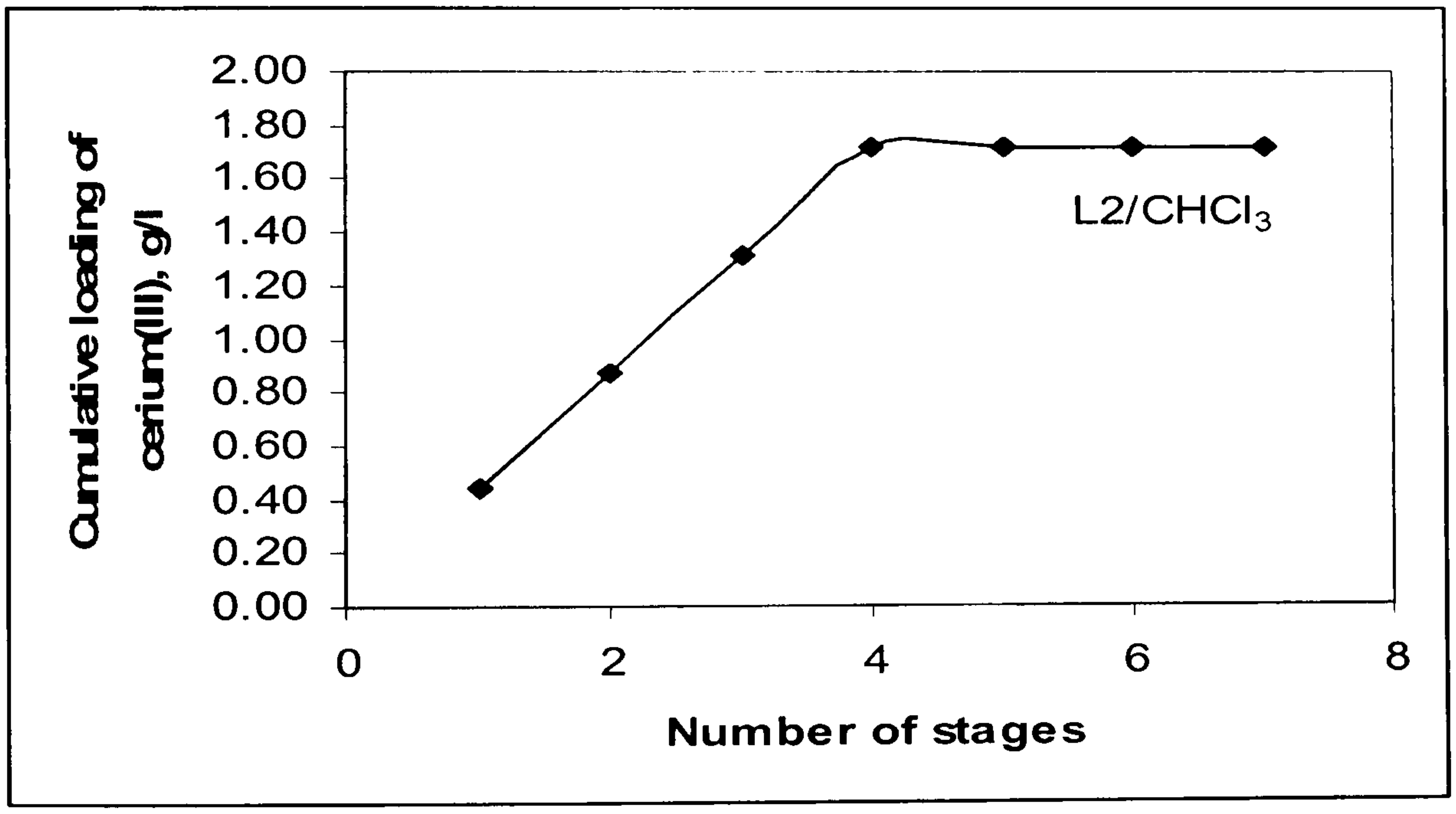


Figure 6.46: The effect of number of stages on the cerium(III) loading capacity of L2/$CHCl_3$.

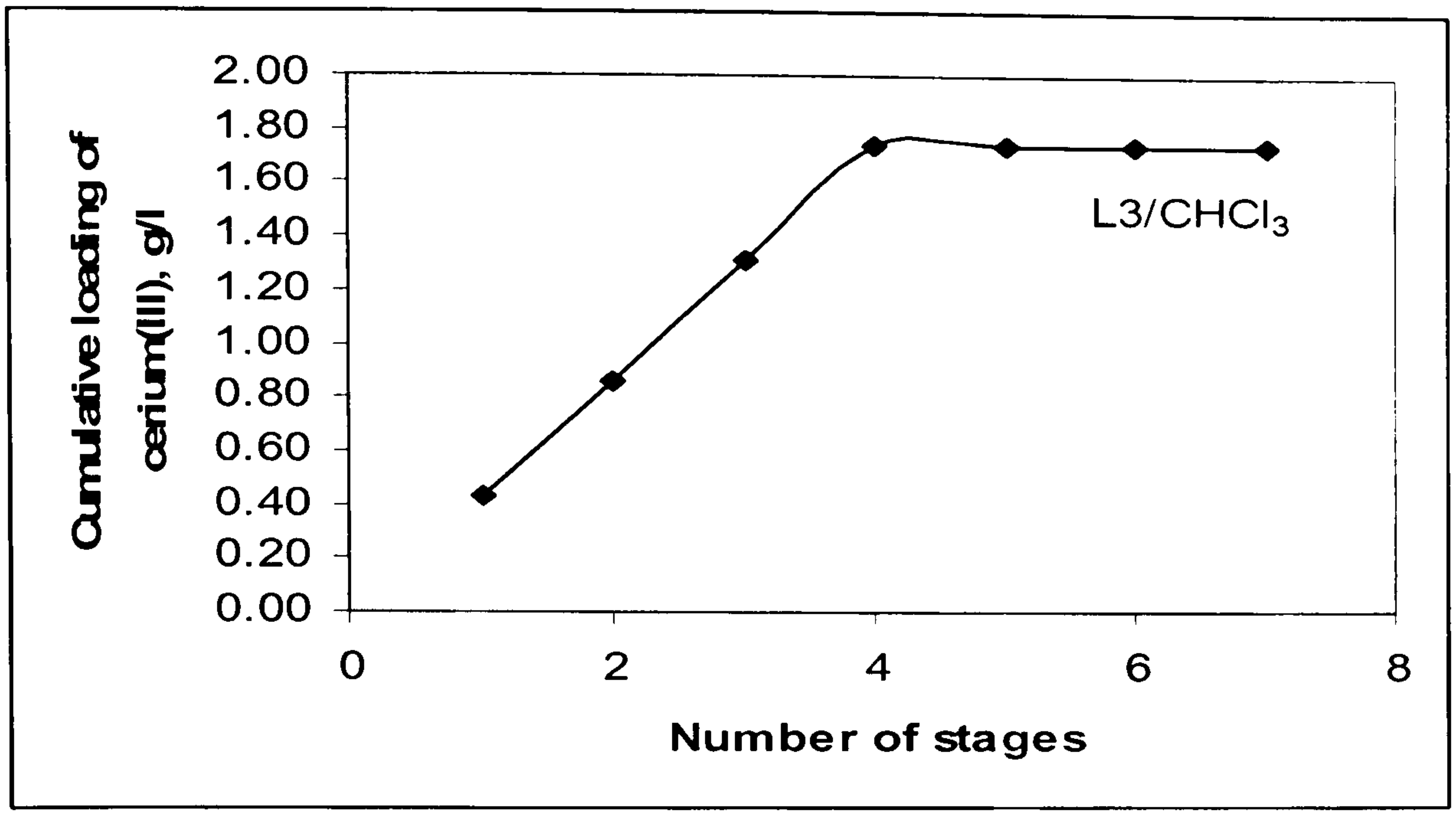


Figure 6.47: The effect of number of stages on the cerium(III) loading capacity of L3/$CHCl_3$.

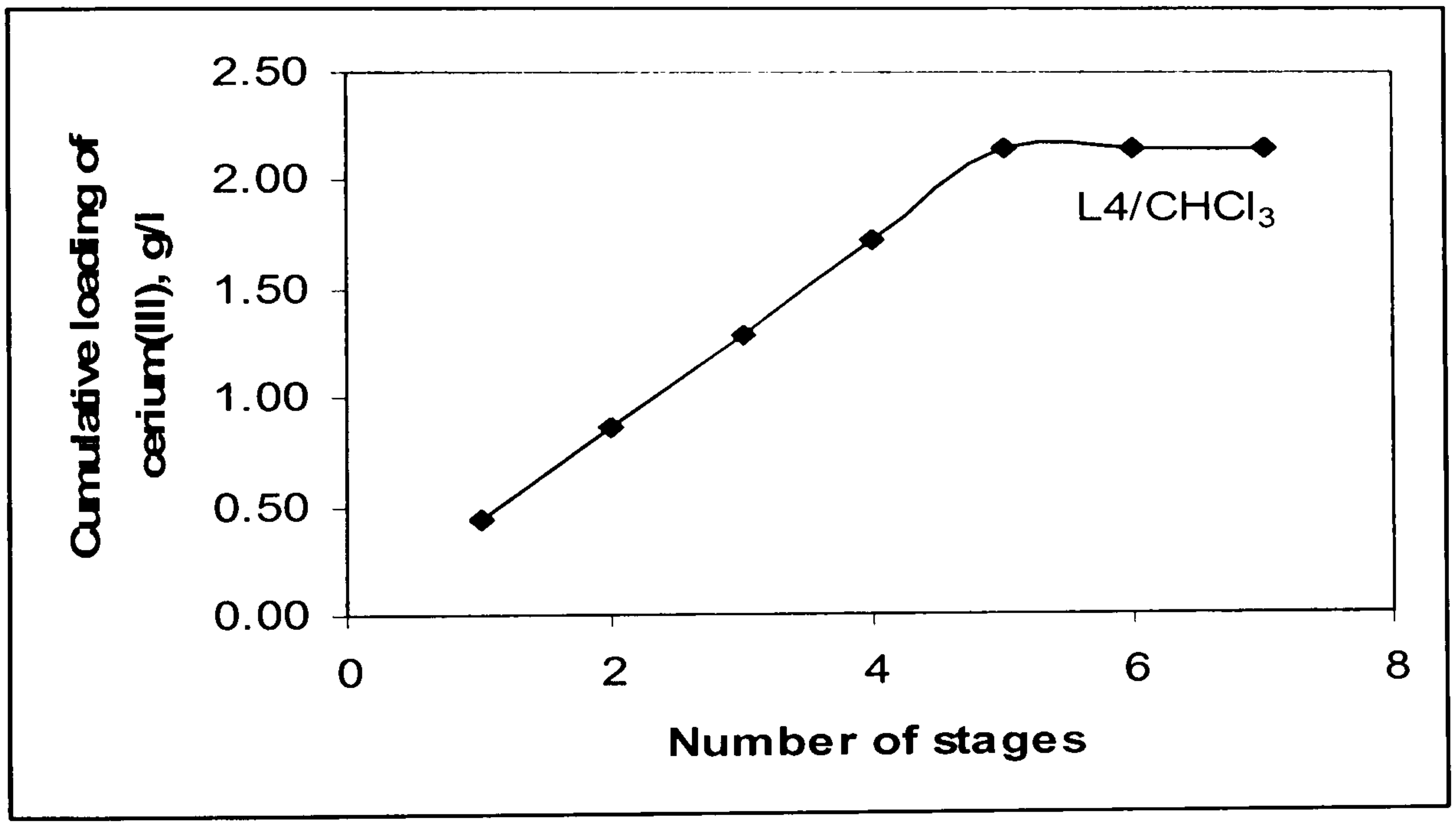


Figure 6.48: The effect of number of stages on the cerium(III) loading capacity of L4/$CHCl_3$.

6.2.4 Comparison between the piperidine ligands on the distribution coefficient of yttrium.

The effect of methyl group in piperidine compounds on the distribution coefficient of yttrium from 0.5M sulfuric acid solutions as a representative for the heavy rare earth elements was investigated. By mixing equal volume of aqueous and organic phase (0.02M ligand dissolved in $CHCl_3$), 1/1 phase ratio, contact time 10 minutes, and the experiments were carried out at room temperature. The results in Table 6.21 and Fig 6.49 show that the extracting power of these amides for Y^{3+} is slightly affected by position of their methyl group.

Table 6.21: Comparison between the piperidine ligands on the distribution coefficient of yttrium.

Ligand	Yttrium % extraction	Distribution coefficient
***N*-octanoic piperidine (L2)**	**88.20**	**7.47**
***p*-methyl *N*-octanoic piperidine (L4)**	**87.00**	**6.69**
***m*-methyl *N*-octanoic piperidine (L5)**	**87.5**	**7.00**

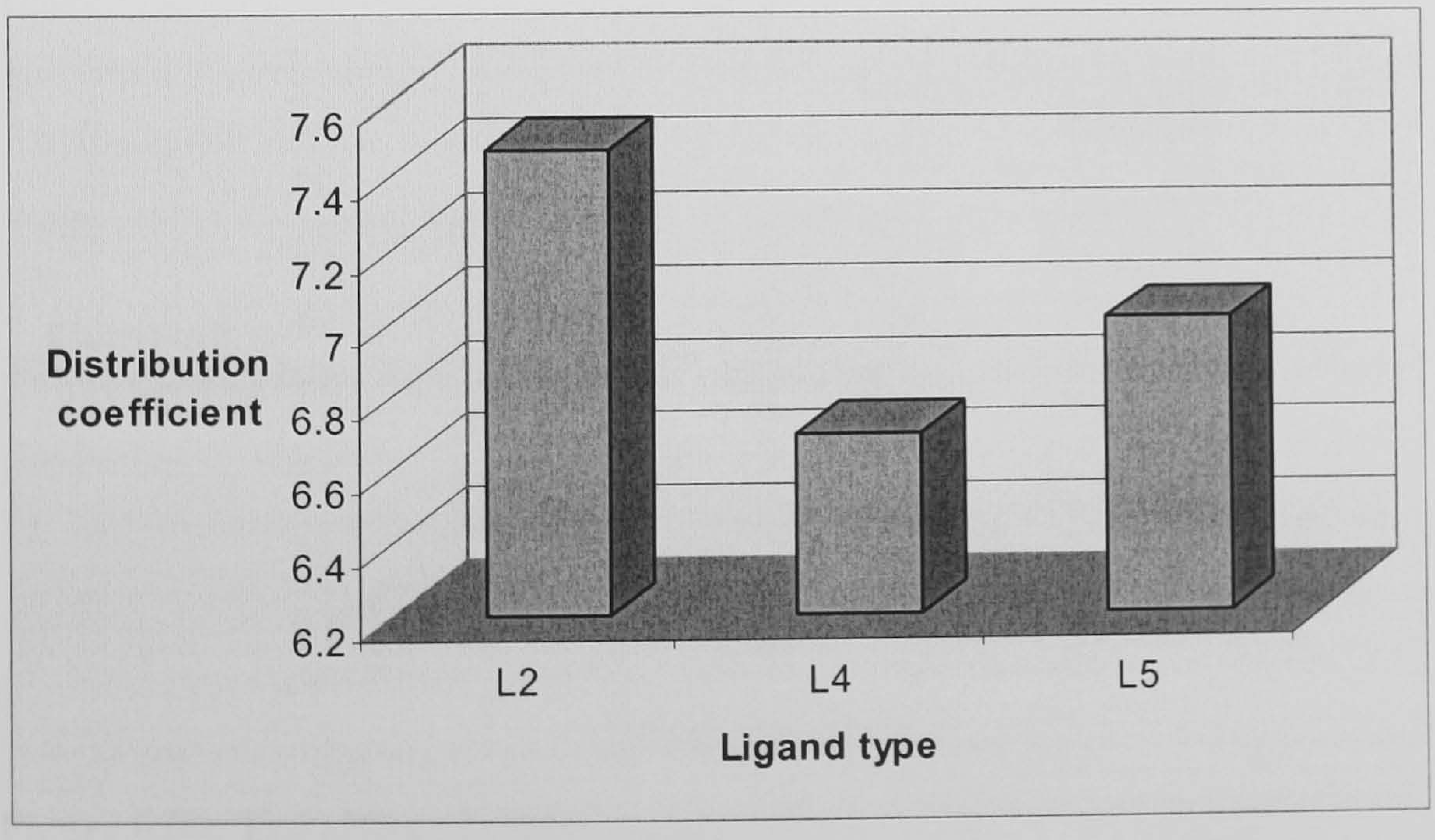


Figure 6.49: The effect of different piperidine ligands on the distribution coefficient of yttrium.

6.2.5 Comparison between the piperidine ligands on the distribution coefficient of cerium(III).

The effect of methyl group in piperidine compounds on the distribution coefficient of Ce(III) as a representative of light rare earth elements was investigated. By mixing equal volume of aqueous and organic phase (0.04M ligand dissolved in $CHCl_3$), 1/1 phase ratio, contact time 10 minutes, and the experiments were carried out at room temperature. The results show that the extracting power of these amides for Ce(III) is also slightly affected by position of methyl group.

Table 6.22: Comparison between the piperidine ligands on the distribution coefficient of cerium(III).

Ligand	Cerium(III) % extraction	Distribution coefficient
N-octanoic piperidine (L2)	86.85	6.60
p-methyl *N*-octanoic piperidine (L4)	82.70	4.78
m-methyl *N*-octanoic piperidine (L5)	86.65	6.49

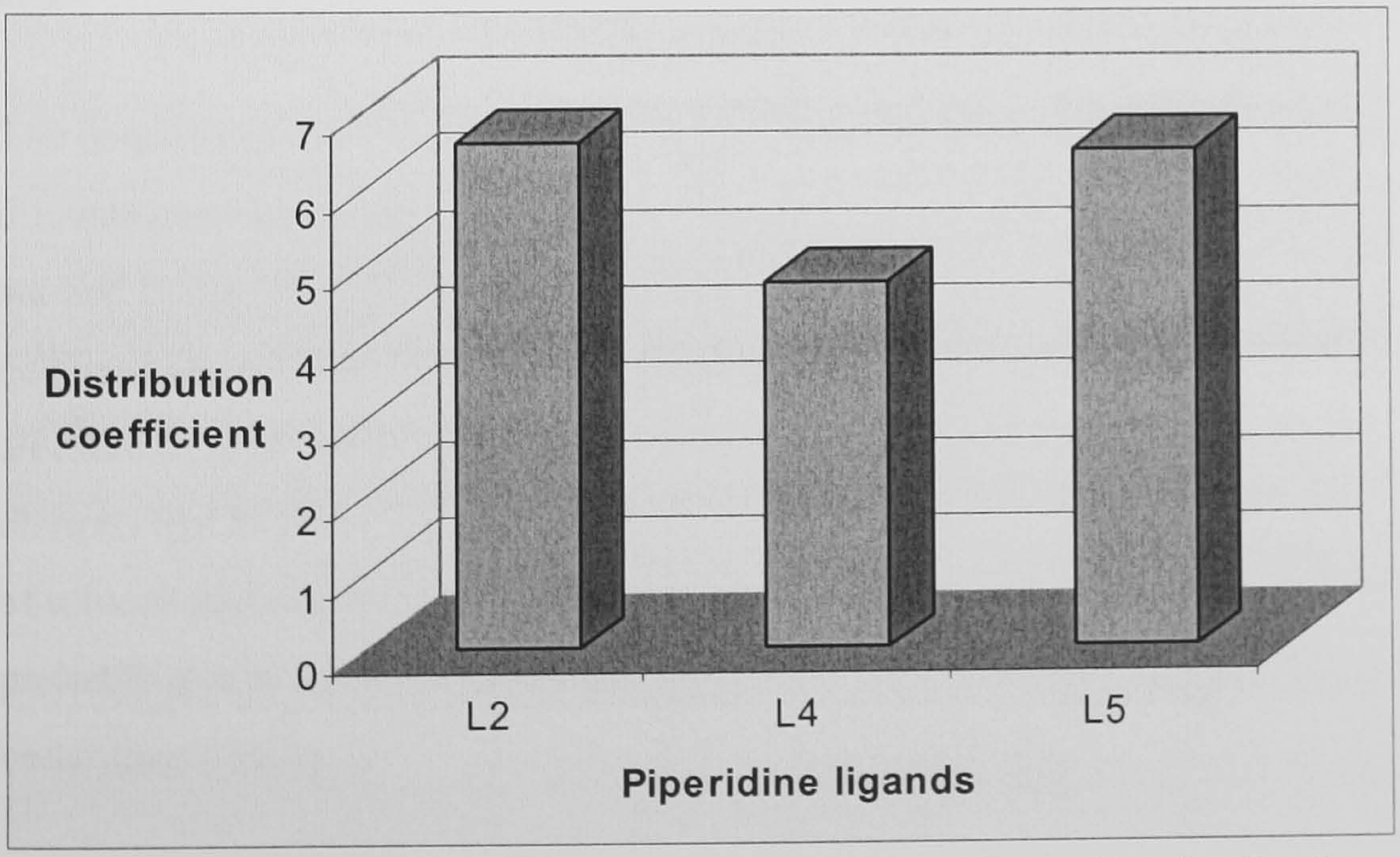


Figure 6.50: The effect of different piperidine ligands on the distribution coefficient of cerium(III).

By comparison of the effect of different ligands on the distribution coefficient of yttrium and cerium(III) and using different piperidine based ligands, the separation of the two elements from each other is more easily obtained in L4 than L2 and L5.

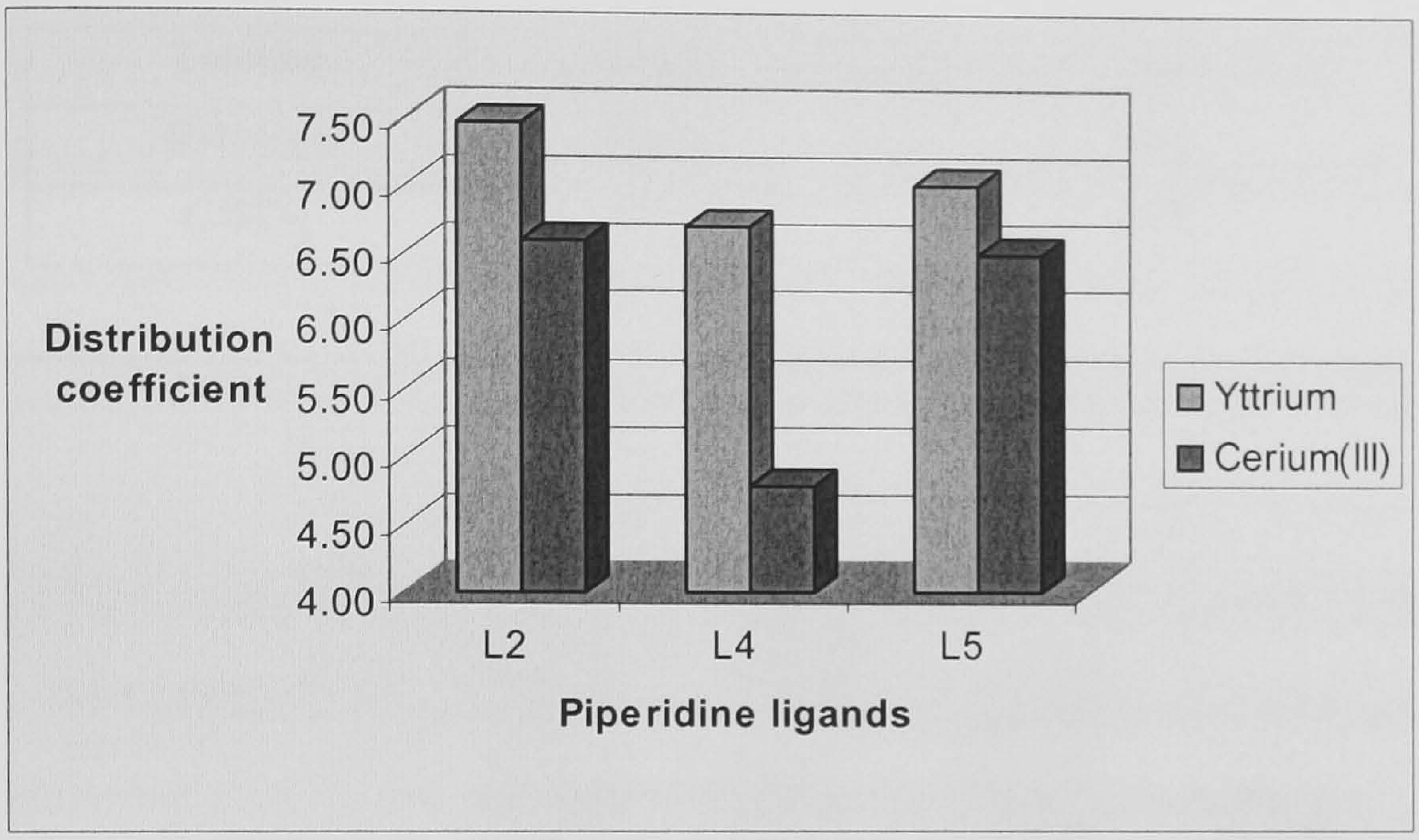


Figure 6.51: Effect of different piperidine ligands on the distribution coefficient of yttrium and cerium(III). (comparison).

6.2.6 Effect of different diluents on the distribution coefficient of yttrium using L2.

The distribution coefficient of yttrium has been studied using different organic diluents namely, benzene (**1**), toluene (**2**), *o*-xylene (**3**) and chloroform (**4**). The other studied factors were fixed at the values at which maximum distribution coefficient occurred i.e. 1:1 (v/v) organic to aqueous phase ratio, room temperature, 0.02M L2 in all diluents, and contact time 10 minutes. Results are presented in Table 6.23. It is obvious that benzene gives the highest distribution coefficient of yttrium, but in case of toluene and *o*-xylene there is a little decrease in yttrium distribution coefficient probably due to the presence of the methyl group, but all the aromatic diluents are better than $CHCl_3$.

Table 6.23: Effect of diluent on the distribution coefficient of yttrium using L2.

Diluents	Yttrium % extraction	Distribution coefficient
Benzene	89.00	8.09
Toluene	88.50	7.69
O-xylene	88.00	7.33
$CHCl_3$	87.00	6.69

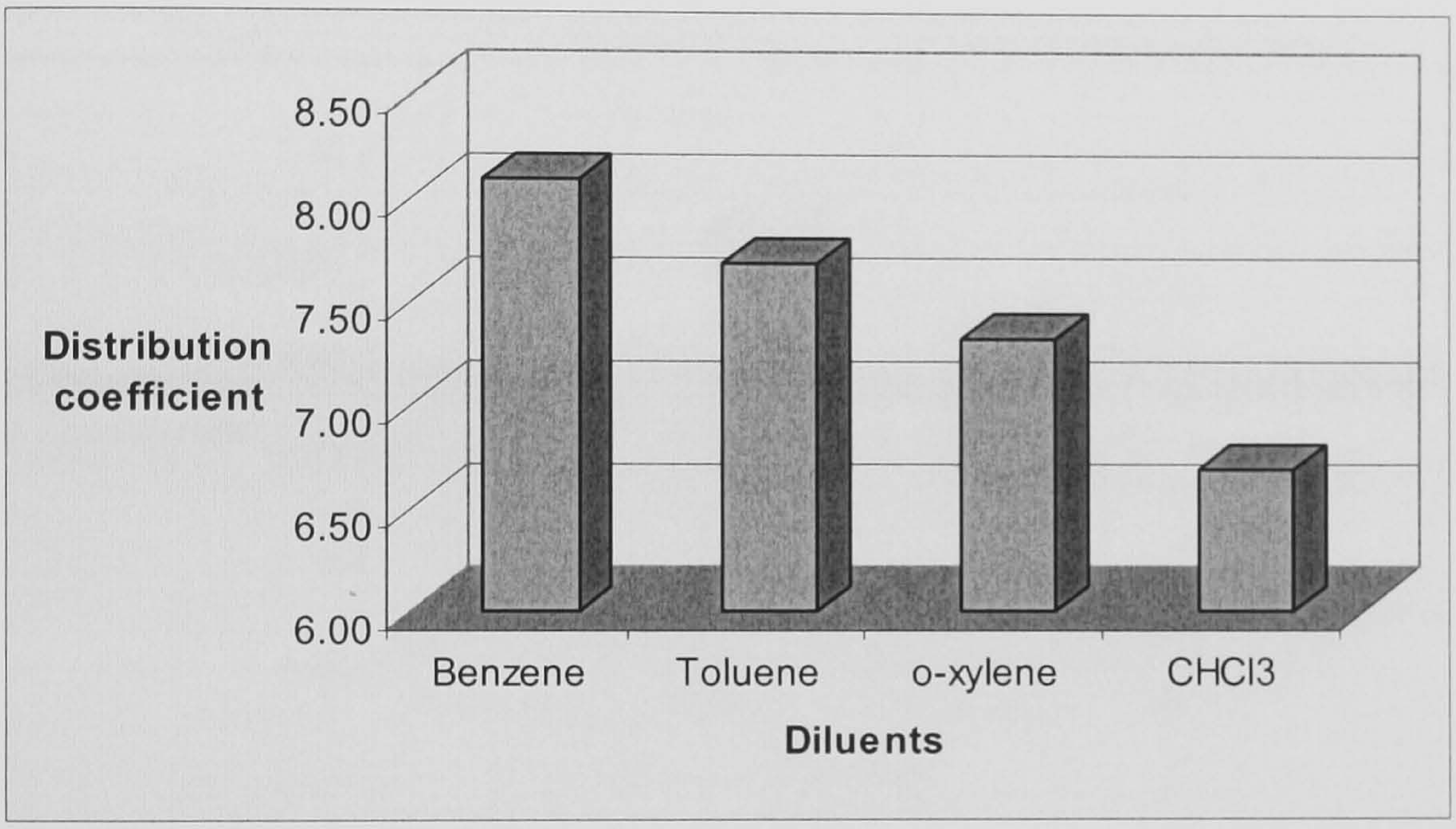


Figure 6.52: Effect of diluent on the distribution coefficient of yttrium using L2.

6.2.7 Effect of different diluents on the distribution coefficient of cerium(III) using L2.

The distribution coefficient of cerium(III) has been studied using different organic diluents namely, benzene (**1**), toluene (**2**), *o*-xylene (**3**), and chloroform (**4**). The other studied factors were fixed at the values at which maximum distribution coefficient occurred i.e. 1:1 (v/v) organic to aqueous phase ratio, room temperature, 0.04M L2 in all diluents, and contact time 10 minutes. Results are presented in Table 6.24. It is noticed that benzene and toluene give the slightly higher distribution coefficient of cerium(III), but all the aromatic diluents are better than $CHCl_3$.

Table 6.24: Effect of diluent on the distribution coefficient of cerium(III) using L2.

Diluents	Cerium(III) % extraction	Distribution coefficient
Benzene	85.50	6.57
Toluene	85.50	6.57
O-xylene	85.00	6.06
$CHCl_3$	84.00	5.05

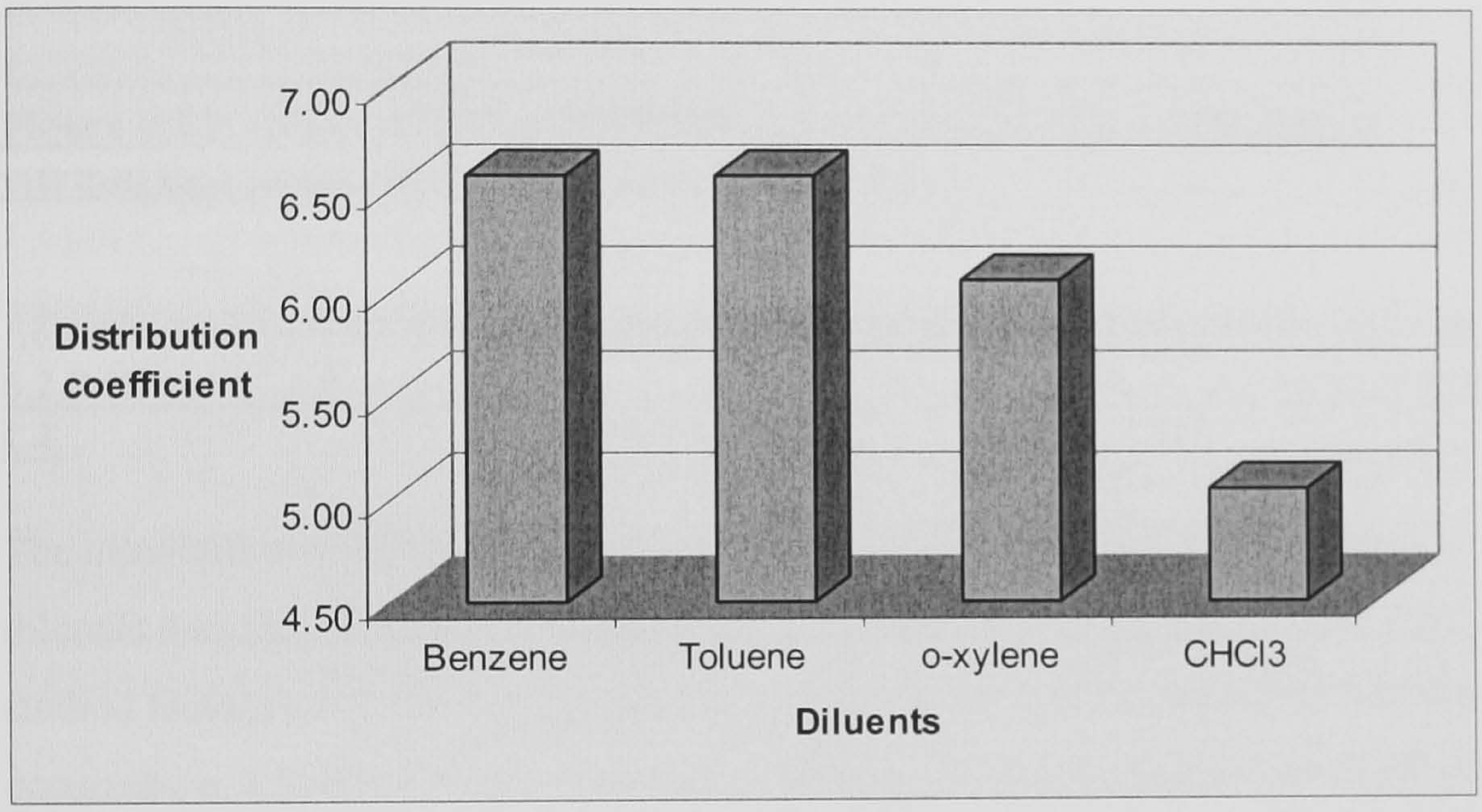


Figure 6.53: Effect of diluent on the distribution coefficient of cerium(III) using L2.

By comparison of the effect of different diluents on the extraction of yttrium and cerium(III) by using of L2, choosing an aromatic diluent does help in the separation of two elements from each other. (Fig. 6.54).

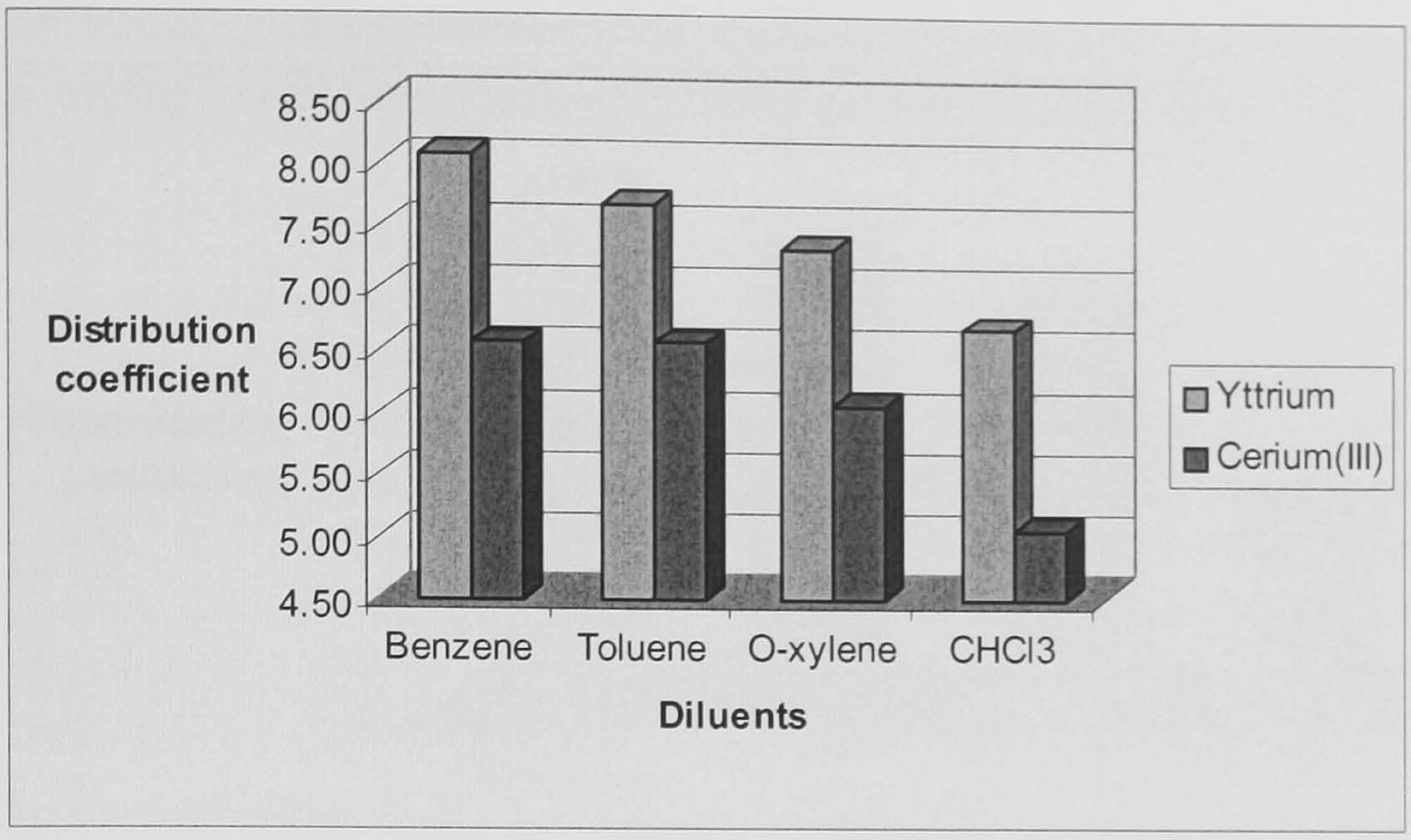


Figure 6.54: Effect of different diluents on the distribution coefficient of yttrium and cerium(III) using L2. (comparison).

6.2.8 Effect of different diluents on the Distribution coefficient of yttrium using L4.

The distribution coefficient of yttrium has been studied using different organic diluents namely, benzene (**1**), toluene (**2**), *o*-xylene (**3**), and chloroform (**4**). The other studied factors were fixed at the values at which maximum distribution coefficient occurred i.e. 1:1 (v/v) organic to aqueous phase ratio, room temperature, 0.02M L4 in all diluents, and contact time 10 minutes. Results are presented in Table 6.25 and Fig. 6.55. It is obvious that benzene gives the slightly high distribution coefficient of yttrium, but in case of toluene and *o*-xylene there are little decrease in yttrium distribution coefficient probably due to the presence of the methyl group, but all the aromatic diluents are better than $CHCl_3$.

Table 6.25: Effect of diluent on the distribution coefficient of yttrium using L4.

Diluents	Yttrium % extraction	Distribution coefficient
Benzene	**88.500**	**7.69**
Toluene	**88.25**	**7.50**
***O*-xylene**	**88.00**	**7.33**
$CHCl_3$	**87.00**	**6.69**

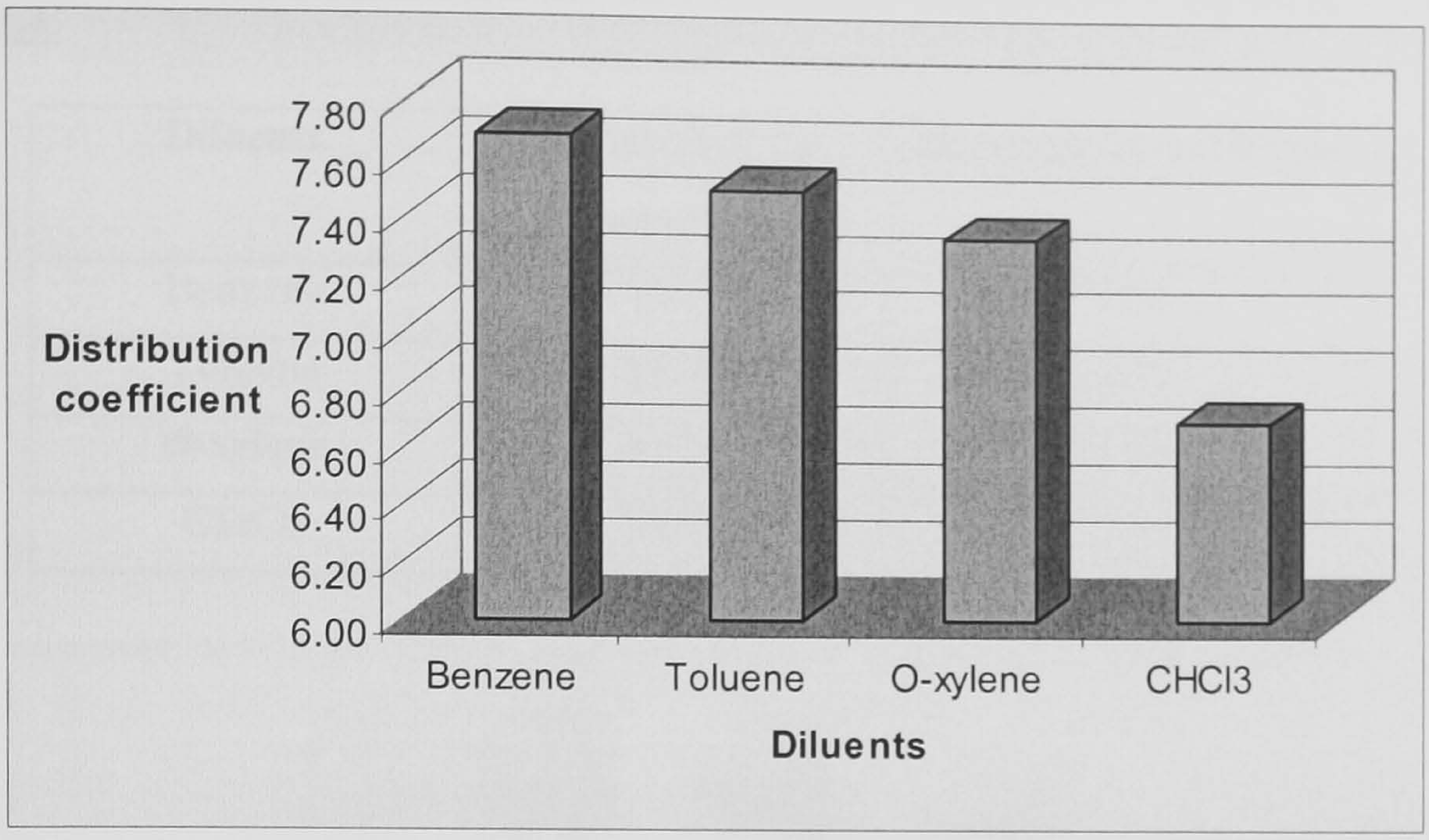


Figure 6.55: Effect of diluent on the distribution coefficient of yttrium using L4.

6.2.9 Effect of different diluents on the distribution coefficient of cerium(III) using L4.

The distribution coefficient of cerium(III) has been studied using different organic diluents namely, benzene (**1**), toluene (**2**), *o*-xylene (**3**), and chloroform (**4**). The other studied factors were fixed at the values at which maximum distribution coefficient occurred i.e. 1:1 (v/v) organic to aqueous phase ratio, room temperature, 0.04M L4 in all diluents, and contact time 10 minutes. Results are presented in Table 6.26 and Fig. 6.56. It is noticed that benzene gives the slightly high distribution coefficient of cerium(III), but in case of toluene and *o*-xylene there are very little decrease in cerium(III) distribution coefficient probably due to the presence of the methyl group, but all the aromatic diluents are better than $CHCl_3$.

Table 6.26: Effect of diluent on the distribution coefficient of cerium(III) using L4.

Diluents	Cerium(III) % extraction	Distribution coefficient
Benzene	80.60	4.15
Toluene	80.50	4.12
O-xylene	80.25	4.06
$CHCl_3$	79.50	3.87

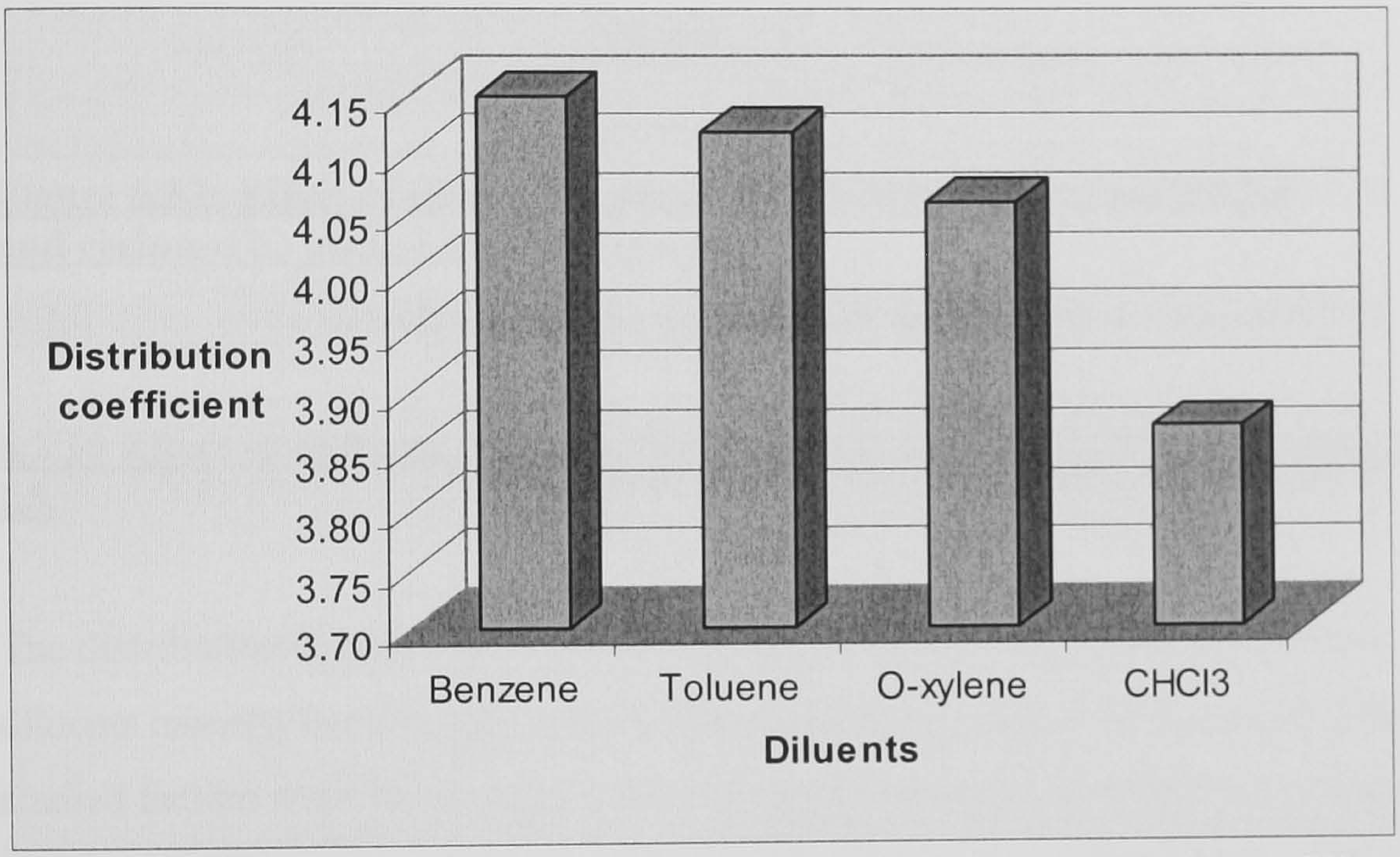


Figure 6.56: Effect of diluent on the distribution coefficient of cerium(III) using L4.

By comparison of the effect of different diluents on the distribution coefficient of yttrium and cerium(III) by using of L4, it can be seen that, it does help in the separation of two elements from each other.

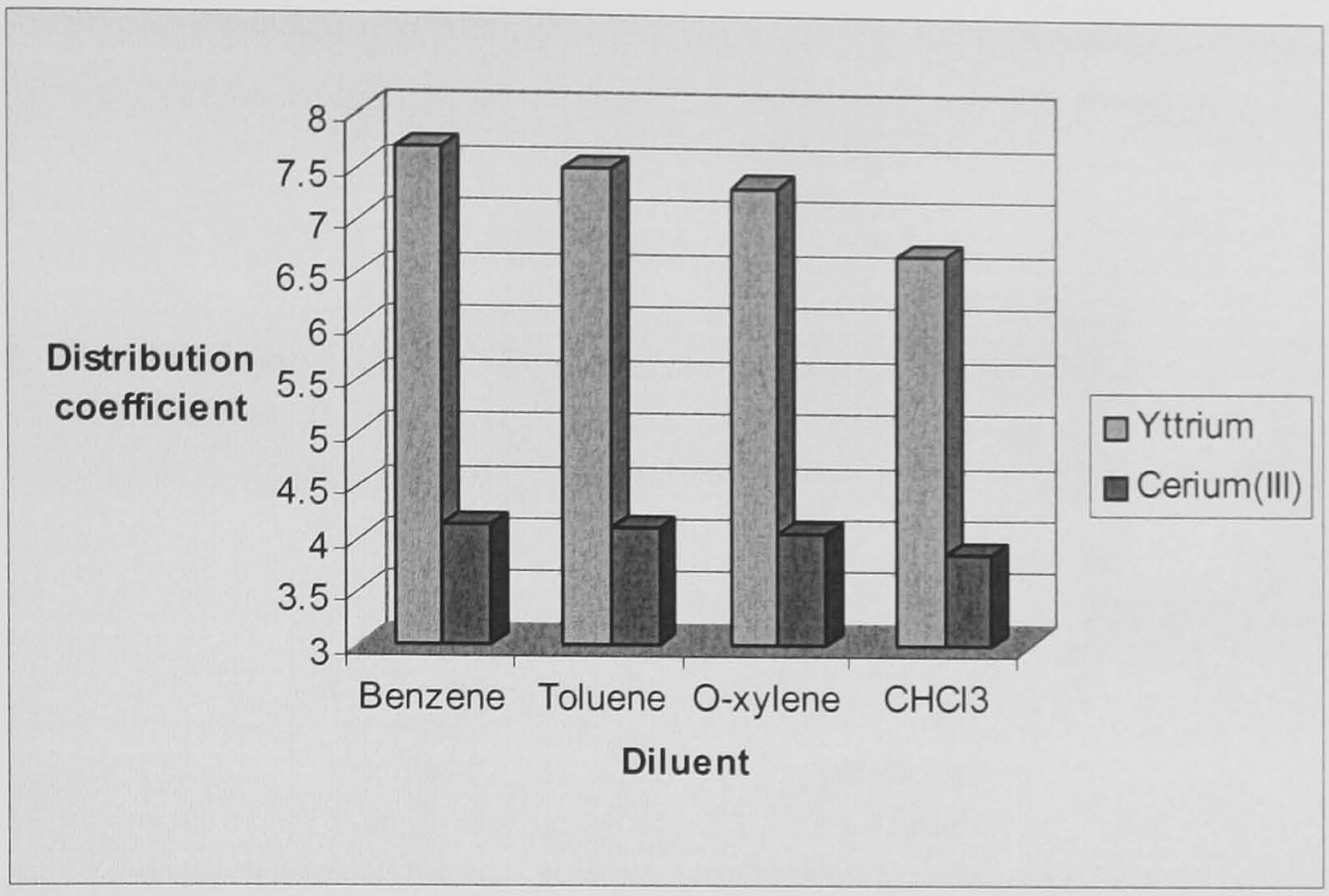


Figure 6.57: Effect of diluent on the distribution coefficient of yttrium and cerium(III) using L4. (comparison).

6.2.10 Effect of different diluents on the distribution coefficient of yttrium using L5.

The distribution coefficient of yttrium has been studied using different organic diluents namely, benzene (**1**), toluene (**2**), *o*-xylene (**3**), and chloroform (**4**). The other studied factors were fixed at the values at which maximum distribution coefficient occurred i.e. 1:1 (v/v) organic to aqueous phase ratio, room temperature, 0.02M L5 in all diluents, and contact time 10 minutes. Results are presented in Table 6.27 and Fig. 6.58. It is obvious that toluene gives the slightly higher distribution coefficient of yttrium than benzene as in other amides, but still all the aromatic diluents are better than $CHCl_3$.

Table 6.27: Effect of diluent on the distribution coefficient of yttrium using L5.

Diluents	Yttrium % extraction	Distribution coefficient
Benzene	88.00	7.33
Toluene	88.50	7.69
O-xylene	87.75	7.16
$CHCl_3$	87.50	6.69

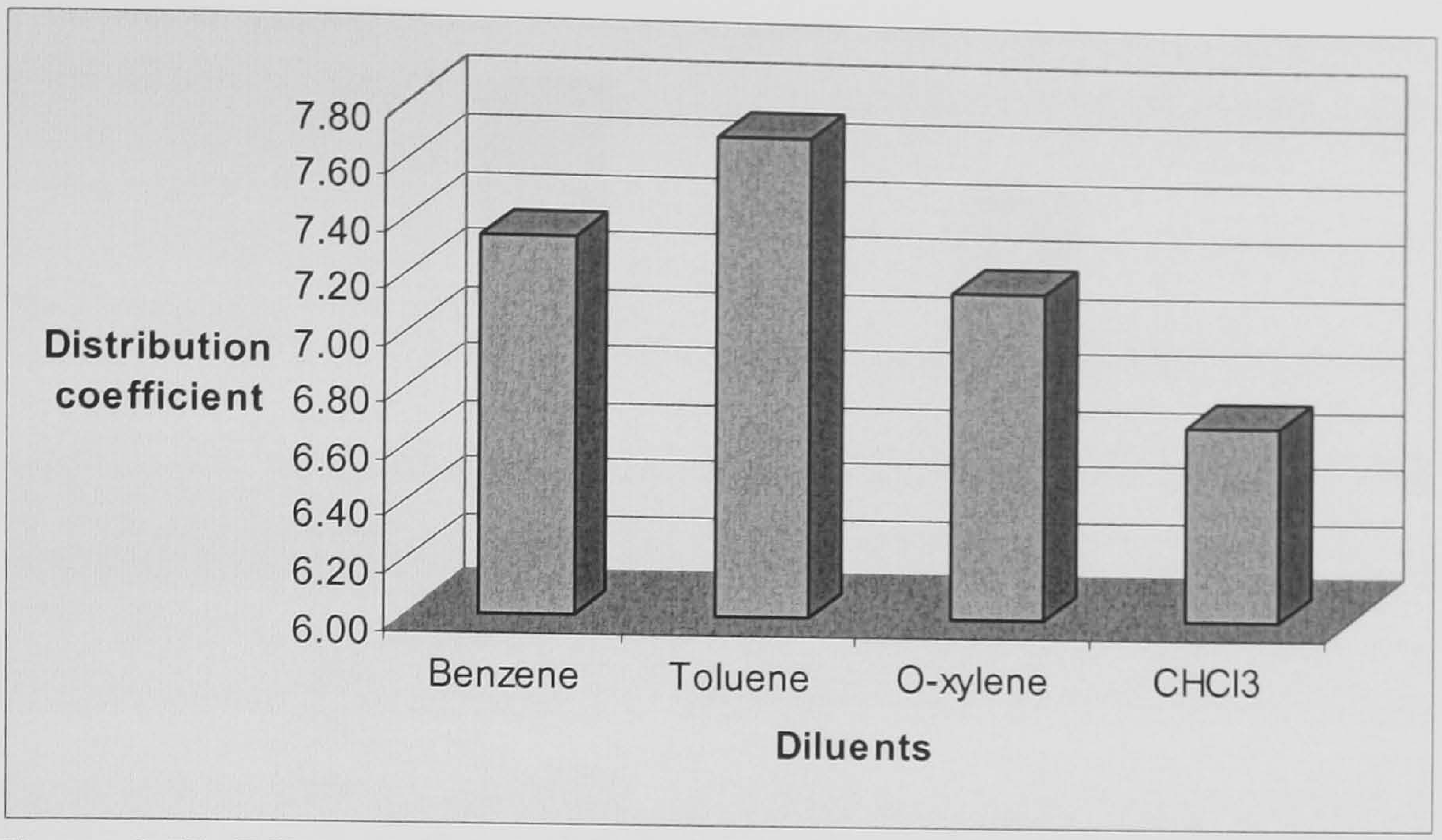


Figure 6.58: Effect of diluent on the distribution coefficient of yttrium using L5.

6.2.11 Effect of different diluents on the distribution coefficient of cerium(III) using L5.

The distribution coefficient of cerium(III) has been studied using different organic diluents namely, benzene (**1**), toluene (**2**), *o*-xylene (**3**), and chloroform (**4**). The other studied factors were fixed at the values at which maximum distribution coefficient occurred i.e. 1:1 (v/v) organic to aqueous phase ratio, room temperature, 0.04M L5 in all diluents, and contact time 10 minutes. Results are presented in Table 6.28 and Fig. 6.59. It is obvious that benzene gives the slightly higher distribution coefficient of cerium(III), but in case of toluene and *o*-xylene there are little decrease in cerium(III) distribution coefficient probably due to the presence of the methyl group, but all the aromatic diluents are better than $CHCl_3$.

Table 6.28: Effect of diluent on the distribution coefficient of cerium(III) using L5.

Diluents	Cerium(III) % extraction	Distribution coefficient
Benzene	**87.00**	**4.15**
Toluene	**86.75**	**4.12**
***O*-xylene**	**86.75**	**4.06**
$CHCl_3$	**86.50**	**3.87**

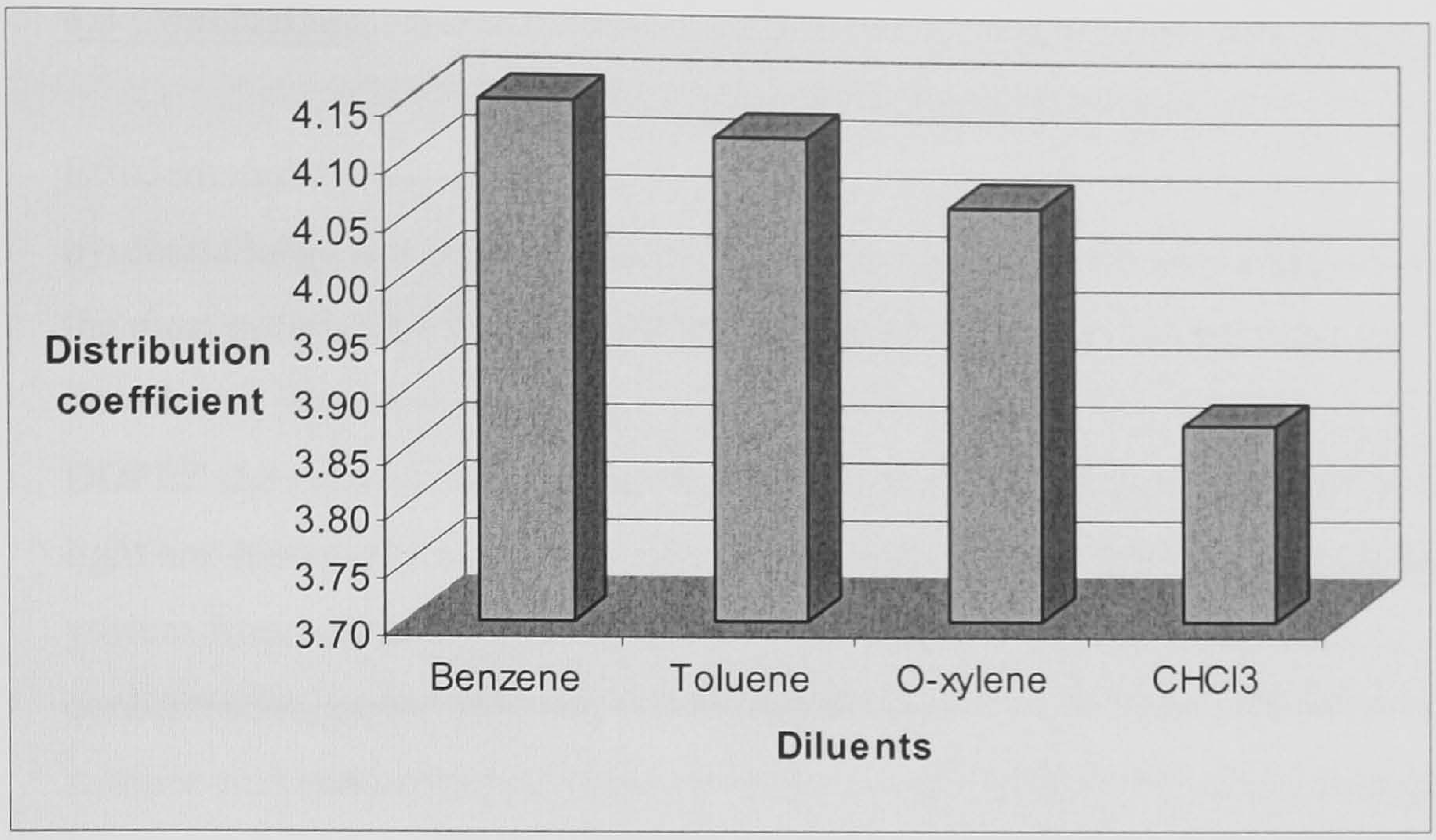


Figure 6.59: Effect of diluent on the distribution coefficient of cerium(III) using L5.

By comparison of the effect of different diluents on the distribution coefficient of yttrium and cerium(III) by using of L5, it can be seen that, choice of diluent can help in the separation of two elements from each other using toluene.

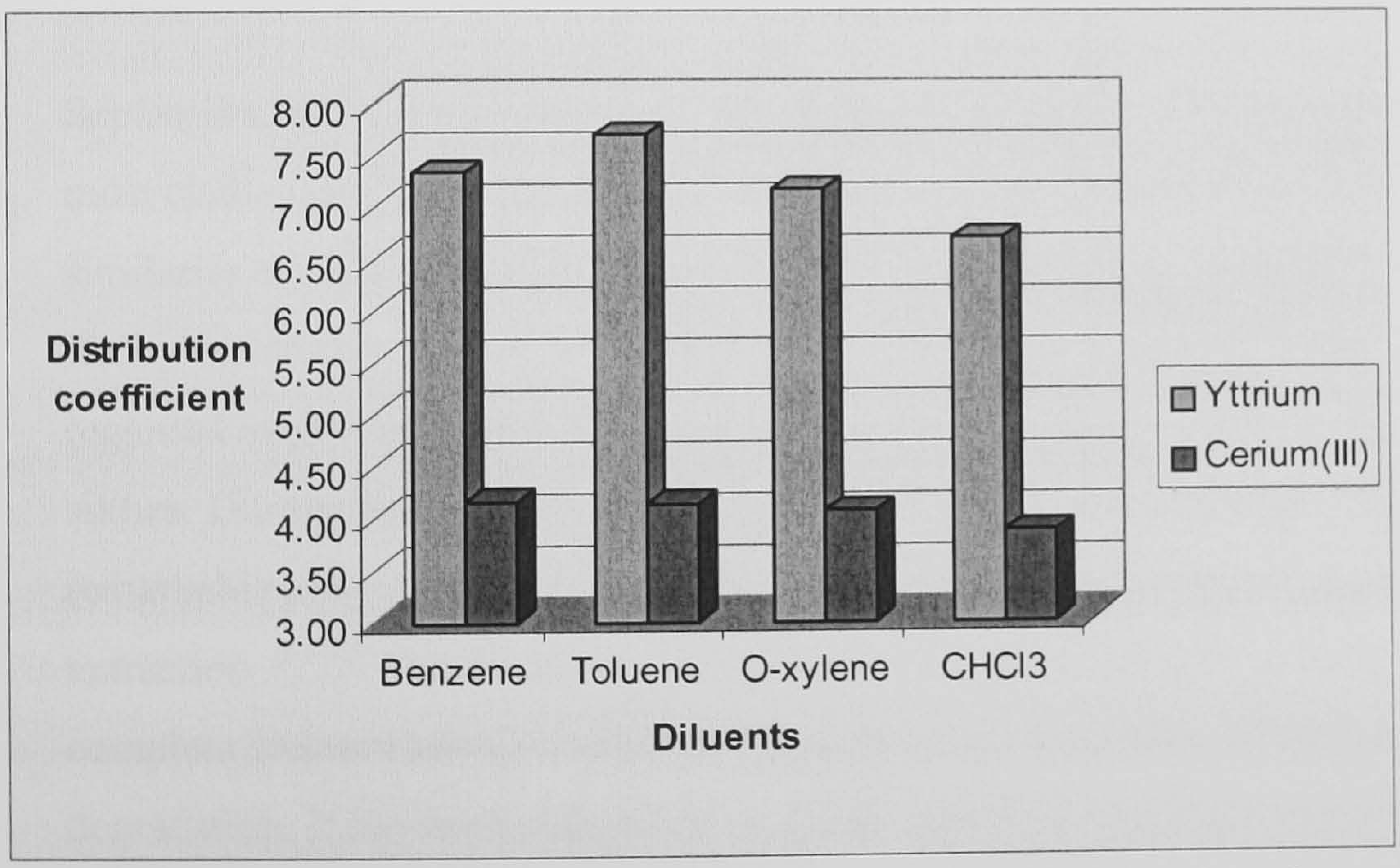


Figure 6.60: Effect of diluent on the distribution coefficient of yttrium and cerium(III) using L5 (comparison).

6.3 Conclusions.

Efficient metal recovery can be facilitated by several different techniques such as pyrometallurgy and froth floatation. (24) Still liquid-liquid solvent extraction shows the most promise for the development of greener processes. To open up new flowsheets, ligands that transport metal sulfates with high selectivity are needed. DOPEZ (L1) can be easily synthesised and has good extraction ability for both light and heavy rare earths. The optimum conditions for liquid-liquid extraction of yttrium from sulfate solution by using DOPEZ dissolved in CCl_4 was 0.02M concentration, cerium(III) was 0.04M, and lanthanum was 0.05M. The effect of sulfuric acid concentration on the extraction using DOPEZ/CCl_4 was investigated. Yttrium extraction increased by increasing sulfuric acid concentration but cerium(III) and lanthanum were decreased by increasing sulfuric acid concentration. The best diluent was CCl_4, equilibration time was 10 minutes, and room temperature. Piperidine derivatives (L2, L4 and L5) are also easy to synthesis with good purity and show promise in the extraction of yttrium and cerium(III) under the conditions studied.

Separation of trivalent lanthanides into their individual component is one of the most challenging endeavors in analytical and separation science, because of the similarity of their chemical properties. Since Siddall III first studied *N,N'*-dialkylamides as extractants for separation of actinides in 1961, (32) they were regarded as alternatives to TBP in the reprocessing of nuclear fuel in the early sixties. During the last forty years, many publications have described the remarkable properties of *N,N'*-dialkylamides in the field of liquid-liquid extraction. (39-41) The principal advantages of diamides are easy synthesis, complete incineration and high stability with respect to chemical and radiolytic degradation. It has been shown that *N,N'*-diamides are potentially good extractants for actinides, especially for U(VI). (34) This Chapter is a novel approach to the possible extraction of rare earth elements by amides of different structures, because no data on diamide solvent extraction of rare earth elements from sulfuric acid solutions have been published to now. Comparing piperazine and piperidine derivatives with other amide-extractants shown that these ligands are the most promising ligand systems for effective separation of yttrium and cerium(III) under the conditions studied.

6.4 Experimental Procedures.

Chemicals were obtained from Sigma-Aldrich Chemical Co., Lancaster Synthesis Ltd., Avocado research Chemicals Ltd., Acros Organics, and the Department of Chemistry Breached Bottle Store, and unless otherwise stated, used as received.

6.4.1 Instrumentation.

NMR spectra were recorded by the author using either a Bruker ARX 250 spectrometer or a Bruker DPX 300 spectrometer, or by Mr. Simon Barrett using a Bruker DRX 500 spectrometer at the Department of Chemistry NMR service. Microanalyses were obtained by Mr. C. Martin Huscroft and Mr. Ian Blakeley at the University of Leeds Microanalytical Service. Mass spectra were obtained by Ms. Tanya Marinko-Covell at the University of Leeds Mass Spectrometry Service. Infra-Red spectra were recorded as KBr discs or nujol mull by the author on a Didac FTIR spectrometer in the Department of Chemistry Inorganic Teaching Laboratory.

6.4.2 Ligand Synthesis.

6.4.2.1 Synthesis of *N,N'*-dioctanoylpiperazine (L1)

Octanoic acid (5.09g, 0.0348 mol) was added to thionyl chloride (20 ml) and heated under reflux for 5 hrs. The excess thionyl chloride was removed under reduced pressure to yield a yellow liquid which was used without further purification. This was added to piperazine (2.99g, 0.03471 mol) and triethylamine (7.04g) in1,2-dichloroethane (250 ml) and heated under reflux for 16 hrs. The solvent was removed *in vacuo* and the resultant solid recrystallized from diethyl ether.

Yield: 7.00g (0.021 mol, 80.5%)

Analysis for $C_{20}H_{38}N_2O_2$

Found: C 70.7 %, H 11.35 %, N 8.5 %

Calculated: C 70.96 %, H 11.31 %, N 8.27 %

^{1}H NMR (250.13 MHz, $CDCl_3$, 298 K): 3.74 (s, 4H, $C\underline{H}_2$ of $C_4H_8N_2$), 3.65 (s, 4H, $C\underline{H}_2$ of $C_4H_8N_2$), 2.46 (t, 4H, $^3J = 4.7$ Hz, $C\underline{H}_2$ of C_7H_{15}), 1.76 (t, 4H, $^3J = 7.2$ Hz, $C\underline{H}_2$ of C_7H_{15}), 1.43-1.41 (m, 16H, $C\underline{H}_2$ of C_7H_{15}), 1.01 (s, 6H, $C\underline{H}_3$ of C_7H_{15}).

$^{13}C\{^1H\}$ NMR (62.89 MHz,$CDCl_3$, 298 K): 172.67 (C=O), 45.77 and 41.93 ($\underline{C}H_2$ of $C_4H_8N_2$), 33.69, 32.07, 31.28, 29.79, 25.64, 22.98 and 14.44 ($\underline{C}H_2$ of C_7H_{15})

MS (ES^+): 339.2 [M^+]

6.4.2.2 Synthesis of *N,N'*-diacetylpiperazine (L3)

Acetyl chloride (9g, 0.1146 mol) was added to piperazine (2.5g, 0.0290 mmol) and triethylamine (10g, 0.0891 mol) in of 1,2-dichloroethane (250 ml) and heated under reflux for 24 hrs. The solvent was removed *in vacuo* and the resultant solid recrystallized from hot acetone (50 ml).

Yield: 8.5g, (0.050 mol, 73.9 %)

Analysis for $C_8H_{14}N_2O_2$

Found: C 55.05 %, H 8.3 %, N 15.6 %

Calculated: C 56.45 %, H 8.29 %, N 16.45 %

^{1}H NMR (250.13 MHz, $CDCl_3$, 298 K): 3.56 (m, 4H, $C\underline{H}_2$ of $C_4H_8N_2$), 3.41 (m, 4H, $C\underline{H}_2$ of $C_4H_8N_2$) and 2.06 ($C\underline{H}_3$)

$^{13}C\{^{1}H\}$ NMR (62.89 MHz, $CDCl_3$, 298 K): 169.68 (C=O), 46.4 and 41.6 ($\underline{C}H_2$ of $C_4H_8N_2$), 21.71 ($\underline{C}H_3$)
MS (ES^+): 171.1 [M^+]

6.4.2.3 Synthesis of *N*-Octanoylpiperidine (L2)

Piperidine (10g, 0.08223 mol) in chloroform (50 ml) was added to a solution of potassium carbonate (10g) in distilled water (50 ml) and the mixture stirred at room temperature for 3 hrs. Octanoyl chloride (5.7g) was prepared as described in 6.4.2.1 and added to the reaction mixture and stirred for 2 hrs. The reaction mixture was cooled, the organic layer separated, dried over magnesium sulfate and the solvent evaporated *in vacuo* to yield a yellow oil.

Yield: 12.25g, (0.058 mol, 78.03 %)

Analysis for $C_{13}H_{25}NO$

Found:	C 71.9 %, H 12.15 %, N 7.1 %
Calculated:	C 73.88 %, H 11.92 %, N 6.63 %

^{1}H NMR (300.13 MHz, $CDCl_3$, 298 K): 3.55 (t, 2H, ^{3}J = 5.6 Hz, $C\underline{H}_2$ of $C_5H_{10}N$), 3.40 (t, 2H, ^{3}J = 5.4 Hz, $C\underline{H}_2$ of $C_5H_{10}N$), 2.31 (t, 2H, ^{3}J = 7.4 Hz, $C\underline{H}_2$ of CH_2-C=O), 1.67-1.53 (m, 8H, $C\underline{H}_2$), 1.32-1.28 (m, 8H, $C\underline{H}_2$) and 0.88 (s, 3H, $C\underline{H}_3$ of C_7H_{15})

$^{13}C\{^{1}H\}$ NMR (75.47 MHz, $CDCl_3$, 298 K): 171.8 (C=O), 47.05 and 42.9 ($\underline{C}H_2$ of $C_5H_{10}N$), 33.79, 32.05, 29.83, 29.44, 26.93, 25.95, 25.83, 24.94 and 22.94 ($\underline{C}H_2$), 14.38 $\underline{C}H_3$ of (C_5H_{10})

MS (ES^+): 212.0 [M^+]

6.4.2.4 Synthesis of *N*-Octanoyl-4-methylpiperidine (L4)

4-Methylpiperidine (10g, 0.100827 mol) in chloroform (50 ml) was added to a solution of potassium carbonate (10g) in distilled water (50 ml) and the mixture stirred at room temperature for 3 hrs. Octanoyl chloride (5.7g mol) was prepared as described in 6.4.2.1 and added to the reaction mixture and stirred for 2 hrs. The reaction mixture was cooled, the organic layer separated, dried over magnesium sulfate and the solvent evaporated *in vacuo* to yield a yellow oil.

Yield: 12.55g, (0.056 mol, 79.94 %)

Analysis for $C_{14}H_{27}NO$

Found: C 73.7 %, H 12.85 %, N 7.2 %

Calculated: C 74.61 %, H 12.07 %, N 6.21 %

^{1}H NMR (300.13 MHz, $CDCl_3$, 298 K): 4.64-4.57 (m, 1H, $\underline{H}$C-N of C_5N ring), 3.88-3.80 (m, 1H, $\underline{H}$C-N of C_5N ring), 3.00 (pseudo t of d, 1H, J_1= 12.60 Hz, J_2 = 2.50 Hz, $\underline{H}$C-N of C_5N ring), 2.54 (pseudo t of d, 1H, J_1 = 12.80 Hz, J_2=2.50 Hz, $\underline{H}$C-N of C_5N ring), 2.33 (t, 2H, ^3J = 7.6 Hz, $C\underline{H_2}$ of C_6H_{13}-CH_2C=O), 1.73-1.55 (m, 5H, aliphatic C$\underline{H}$), 1.37-1.23 (m, 8H, aliphatic C$\underline{H}$), 1.18-1.02 (m, 2H, aliphatic C$\underline{H}$), 1.00-0.94 (m, 3H, $C\underline{H_3}$) and 0.92-0.88 (m, 3H, $C\underline{H_3}$)

$^{13}C\{^1H\}$ NMR (75.47 MHz, $CDCl_3$, 298 K): 169.91 (C=O), 44.37, 40.32 ($\underline{C}$N of C_5N), 33.12, 32.19, 31.91, 30.08, 29.50, 27.87, 27.47, 32.88, 20.98, 20.12 (aliphatic $\underline{C}$) and 12.45 (CH_3 of C_7H_{15})

MS (ES^+): 225.80 [M^+]

6.4.2.5 Synthesis of *N*-Octanoyl-3-methylpiperidine (L5)

3-Methylpiperidine (10g, 0.100827 mol) in chloroform (50 ml) was added to a solution of potassium carbonate (10g) in distilled water (50 ml) and the mixture stirred at room temperature for 3 hrs. Octanoyl chloride (5.7g mol) was prepared as described in 6.4.2.1 and added to the reaction mixture and stirred for 2 hrs. The reaction mixture was cooled, the organic layer separated, dried over magnesium sulfate and the solvent evaporated *in vacuo* to yield a brown oil.

Yield: 13.05g, (0.056 mol, 83.12 %)

Analysis for $C_{14}H_{27}NO$

Found: C 72.61 %, H 12.15 %, N 6.65 %

Calculated: C 74.61 %, H 12.07 %, N 6.21 %

^{1}H NMR (500.13 MHz, DMSO, 303, 313, 323, 333, 343, 353, 363, 373 K): 4.19 (d, 2H, ^2J = 12.6 Hz, (A) C$\underline{H}$N of C_5N), 3.73-3.66 (m, 2H, (B) C$\underline{H}$N of C_5N), 2.91-2.89 (m, 1H, (B) C$\underline{H}$N of C_5N), ~ 2.62 (m, 1H, (B) C$\underline{H}$N of C_5N), ~2.49 (m, 1H, (A) C$\underline{H}$N of C_5N), and 2.26- 0.78 (unable to assign and differentiate between the isomers).

$^{13}C\{^1H\}$ NMR (125.77 MHz, DMSO, 373 K): 53.61 ($\underline{C}H_2N$ of C_5H ring (B), 49.37 ($\underline{C}H_2N$ of C_5H ring (A), 46.57 ($\underline{C}H_2N$ of C_5H ring (B), 42.46 ($\underline{C}H_2N$ of C_5H ring (A), and 33.90, 33.74, 33.47, 33.37, 32.21, 32.07, 31.64, 31.31, 29.83, 29.45, 26.40, 25.99, 25.87, 25.82, 25.16, 22.95, 19.87, 19.37, 19.27, and 14.40 (unable to differentiate between the isomers).

6.5 References.

1 P. N. Pathak, L. B. Kumbhare, V. K. Manchanda, *Radiochim. Acta*, (2001) **89**, 447.

2 E. A. Mowafy, H. F. Aly, *J. Radioanal. Nucl. Chem.*, (2001) **250**, 199.

3 G. Y. S. Chan, M. G. B. Drew, M. J. Hudson, P. B. Iveson, J. O. Liljenzin, M. Skalberg, L. Spjuth, C. Madic, *J. Chem. Soc., Dalton Trans.*, (1997) 649 .

4 C. Y. Yuan, *Proc. Intern. Solvent Extraction Conference*, Liege, Belgium, (1980) **1**, 80.

5 G. X. Xu, C.Y. Yuan, Solvent Extraction of Rare Earths, Science Publishing House, Beijing, China, (1987), 353 (in Chinese).

6 D. M. Rudkevich, Z. Brzozka, M. Plays, H. C. Visser, W. Verboom and D. N. Reinhoudt Angew. Chem. (1994) **106**, 480.

7 P. D. Beer, Z. Chen, P.A. Gale, J. A. Heath, R. J Knubley, M. I. Ogden and M. G. B. Drew *J. Inclusion Phenom. Mol. Recognit. Chem.* (1994) **19**, 343.

8 J. Szymanowski Hydroxyoximes and Copper Hydrometallurgy, CRC press, Inc. London (1993).

9 A. G. Smith, P. A. Tasker and D. J. J. White *Coord. Chem. Rev.* (2003) **241**, 61.

10 M. J. Nicol, C. A. Fleming, J. S. Preston C*omprehensive Coordination Chemistry*, Wilknson G., Pergamon press. Oxford (1987) **6**, 779.

11 P. A. Tasker, P. G. Plieger, L. C. West., *Comprehensive Coordination Chemistry*, McCleverty J A and Meyer T. B., Elsevier, Oxford 759, **9** (2004).

12 H. A. Miller, N. Laing, S. Parsons, A. Parkin, P.A. Tasker and D.J. White *J. Chem. Soc., Dalton Trans.* (2000) 3773.

13 S. Di Bella, I. Fragala, I. ledoux, M. A. Diaz-Garcia and T. J. Marks *J. Am. Chem. Soc.* (1997) **119**, 9550.

14 E. Suresh, M. M. Bhadbhade and D. Srinivas *Polyhedron* (1996) **15**, 4133.

15 S. G. Galbraith, P. G. Plieger and P. A. Tasker *J. Chem. Soc. Chem. Commun.* (2002) 2662.

16 A. Settle Handbook of Instrumental Techniques for Analytical Chemistry, Prentice Hall PTR. NJ (1997).

17 A Bianchi, M. Micheloni, P. Paoletti, *Coord. Chem. Rev.*, (1991) **110**, 17.

18 R. M. Izatt, K. Pawlak, J. S. Bradshaw, R.L. Bruening, *Chem. Rev.* (1991) **91**, 1721.

19 A. Bianchi, K. Bowman-James, E. Garcia-Espana, *Supramolecular Chemistry of Anions*, (1997).

20 K. A. Connors, *Binding Constants: The Measurements of Molecular Complex Stability*, (1987).

21 H. Xie, S. Yi, S. Wu, *J. Chem. Soc., Perkin Trans.*, (1999) **2**, 2751.

22 H. Xie, S. Yi, X. Yang, S.Wu, *New J. Chem.*, (1999) **23**, 1105.

23 M. T. Beck, I. Nagypal, *Chemistry of Complex Equilibria*, Akedemiai, Budapest (1990).

24 S. G. Galbraith, P. A. Tasker, *Rev. Supramolecular Chemistry* (2005) **17**, 191.

25 R. D. Shannon, *Acta Crystallogr., Sect. A*, (1976) **A32**, 751.

26 P. D. Beer, P. A. Gale, Angew. *Chem., Int. Ed. Engl.*, (2001) **40**, 486.

27 C. H. Park, H. E. Simmons, *J. Am. Chem. Soc.*, (1968) **90**, 2431.

28 B. Dietrich, M. W Hosseini, J. M Lehn, Sessions, R. B. *J. Am. Chem. Soc.*, (1981) **103**, 1282.

29 M. Kodama, E. Kimura, *J. Chem. Soc., Dalton Trans.*, (1977) 1473.

30 R. A. Pascal, Spergel, J., Van Engen, D. *Tetrahedron Lett.*, (1986) **27**, 4099.

31 S. Valiyaveettil, J. F. J. Engbersen, W. Verboom, D. N. Reinhoudt, Angew. Chem., (1993) **105**, 942.

32 T. H. Siddall III, *J. Phys. Chem.*, (1960) **64**, 1683.

33 S. Guo-Xin, Physical Chemistry of Extraction System of Uranium (VI) and Thorium (IV) with Amide Extractans, Ph. D. Thesis, Shanghai Institute of Nuclear research, The Chinese Academy of Sciences, (1998).

34 Y. Xing-Cun, B. Bo-Rong, S. Guo-Xin, C. Wei-Guo, *J. Radioanal. Nucl. Chem.*, (2003) **258**, 677.

35 H. Jing-Tian, S. Guo-Xin, B. Bo-Rong *et al.*, *J. Radioanal. Nucl. Chem.*, (1999) **241**, 215.

36 S. Guo-Xin, H. Jing-Tian, B. Bo-Rong *et al.*, *Nucl. Sci.Technol.*, (1998) **9**, 115.

37 G. Thiollt, G.Musikas, *Solv. Extr. Ion Exch.*, (1989) **7**, 813.

38 D. Mirejovesky and H. Takruri, *J. of Pharmaceutical Sciences*, (1986) **75**, 1089.

39 L. Nigond, C. Musikas, C. Cullerdier, *Solv. Extr. Ion Exch*, (1994) **12,** 261.

40 M. C. Charbonnel, C. Musikas, *Solv. Extr. Ion Exch*, (1988) **5,** 151.

41 C. Musikas, H. Hubert, *Solv. Extr. Ion Exch*, (1987) **5,** 151.