National Library
of Canada

Bibliothèque nationale
du Canada

Canadian Theses Service

Service des thèses canadiennes

Ottawa, Canada
K1A 0N4

NOTICE

The quality of this microform is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Reproduction in full or in part of this microform is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30, and subsequent amendments.

AVIS

La qualité de cette microforme dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

La reproduction, même partielle, de cette microforme est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30, et ses amendements subséquents.

NL-339 (r. 88/04) c

Canada

National Library
of Canada

Canadian Theses Service

Ottawa, Canada
K1A 0N4

Bibliothèque nationale
du Canada

Service des thèses canadiennes

NOTICE

The quality of this microform is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Reproduction in full or in part of this microform is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30, and subsequent amendments.

AVIS

La qualité de cette microforme dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

La reproduction, même partielle, de cette microforme est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30, et ses amendements subséquents.

ISBN 0-315-60580-4

NL-339 (r. 88/04) c

Canada

UNIVERSITÉ D'OTTAWA
UNIVERSITY OF OTTAWA

Dedicated to the
Memory of my beloved
Sister, Virginia and Grandmother

"--- thermodynamics deals with differences, that the number of differences to be considered can be reduced greatly by the use of reference states, that the magnitude of the differences can be reduced by the use of deviation functions, and that the choice of reference states and deviation functions is entirely a matter of convenience, which should not be allowed to reduce the accuracy of any calculation.---"

George Scatchard(1950)

ACKNOWLEDGEMENTS

I wish to express my profound gratitude to my supervisor, Professor Alan Duane Westland whose encouragements, professional ideas, advice and criticisms was unceasing from the first day this work was conceived. He has, in the main, been responsible for my present scientific outlook.

I also wish to express my gratitude to Professor John L. Holmes and Professor Edward P. Lai of Carleton University whose advice and concern (they do not know) have been inspiring to me; John Loop, of the Department of Geology, who ran the multitude of samples on the DCP spectrometer and latter taught me the "how to" of the instrument; Mr. Raj Capoor and Dr. Heather Dettman of the NMR Centre who recorded the ^{1}H ,^{13}C and ^{31}P spectra; Mrs. Eva Szabo, who prepared the diagrams; Dr. John Ripmeester of the National Research Council who recorded the solid state ^{31}P NMR and offered valuable information; and to numerous members of the Institute whom I have in one way or another been in contact with throughout the duration of my studies.

My family have also been supportive and I wish to thank my darling wife, Nnennaya, for her patience and understanding for her valuable time that I expended in pursuit of this work; my daughter, Chinedu Ginny-*The Little Alarm Clock*-, who made sure I broke through the "early" morning waking up phobia and my son Mitch Chikadibie who kept me up late into the night.

I am grateful to the Canadian Commonwealth Fellowship under whose Scholarship Programme I was able to undertake this study.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

GLOSSARY OF ABBREVIATIONS

DCP	Direct-Coupled Plasma
AAS	Atomic Absorption Spectroscopy
HDEHP	Di-2-ethylhexyl phosphoric acid
HEHEHP	2-ethylhexylphosphonic acid mono-2-ethylhexyl ester
HEHΦP	2-ethylhexyl phenylphosphonic acid
DDNSA	Didodecylnaphthalene sulphonic acid
DNNSA	Dinonylnaphthalene sulphonic acid
REE	Rare Earth Elements
RE	Rare Earths
ppm	Parts per million
μ	Ionic strength
M	Metal
Ln	Lanthanide
$SF(K_\beta)$	Separation factor

ABSTRACT

This thesis is directed towards the study of the solvent extraction behaviour of the lanthanides and aluminium, bismuth, calcium and zinc whose radii and/or charges are similar to those of the REE. A brief review of the fundamentals and classification of extraction systems and of extractants is presented in Chapter 1. Chapters 2 and 3 are reviews of the properties and uses of the lanthanides and solvent extraction using phosphonate and sulphonate extractants, respectively. Chapter 4 deals with experimental procedures, results, discussions and conclusions.

The extraction of zinc (II), calcium (II), aluminium (III), bismuth (III) and some lanthanide ions from aqueous perchlorate solutions into hexane solutions of 2-ethylhexyl phenylphosphonic acid, HEHΦP, was studied. The mechanisms of extraction are discussed on the basis of the results obtained by slope analysis. Depending upon the size and charge of the ion, the extracted species contain varying numbers of extractant molecules and phosphonate groups as ligands. Monomeric complexes are formed in the presence of excess extractant. High loadings of the extractant phase with the metal ion resulted in suppression of the extraction. Alkali ions were not extracted but alkali perchlorate suppressed the extraction through the effect of ionic strength on the metal ion activity.

To further investigate the mechanism of extraction, ^{31}P NMR of the organic phase following extraction of lanthanum was studied. A polymeric lanthanum-HEHΦP complex which precipitates out in the organic phase is formed at high (saturation) loading of this phase. A structure is proposed for this complex.

The thermodynamics of extraction of these ions from perchlorate solutions into petroleum ether solutions of dinonylnaphthalene sulphonic acid, DNNSA, and HEHΦP were studied. In the case of DNNSA, extraction of the trivalent ions is dominated by the enthalpy of complexing. Electrostriction of large complex micelles by the complexed ion is postulated in order to account for the entropy effect. For the divalent ions, the enthalpy of dehydration of the ion is more important. A strategy for improving the separation factors is proposed.

In the case of HEHΦP, charge density of the cation has a major influence upon the mechanism of the reaction and in turn upon the thermodynamic parameters. The ionic strength of the aqueous phase influences the thermodynamic parameters in the HEHΦP and DNNSA systems. Amongst the REE, lanthanum shows a singular behaviour. The extractions have been compared with those that employ dinonylnaphthalene sulphonic acid and factors that are responsible for the greater selectivity of the phosphonate have been elucidated.

Development of an extraction chromatographic separation procedure for the lanthanides with a view to separating them from other matrix elements and fractionating them among themselves was studied. This was to be achieved by employing an organic polar solvent in the later stages of column elution. However, low recoveries were observed upon ashing the organic eluent and DCP determinations. The presence of phosphate (as KH_2PO_4 or H_3PO_4) was found to lead to depression of analyte signal (concentration) in the DCP.

CHAPTER I

GENERAL INTRODUCTION

With the advent in analytical chemistry of diverse selective methods and their constant improvement, one would have logically predicted a decrease in the importance of separation for analysis, but it appears such is not the case. The growth of technology and natural processes produce complex mixtures and the chemist is required to develop separation procedures for their analysis. In the case of complex samples where detection limits are poor, separation is needed for preconcentration.

The development of gas and high-performance liquid chromatography and ion-exchange have generated methods in which separation of mixtures, identification and determination of the amounts of components form the part of a whole, not isolated stages. These methods and liquid-liquid (solvent) extraction involve phase distribution as a principle. Although liquid-liquid extraction has not yet reached the degree of automation achieved by the other methods, it enjoys a favoured position among them because of its speed, versatility, simplicity, selectivity, and relatively small contamination hazards and the ease with which the analyst can vary conditions (usually pH) to optimize separability. By the use of extremely simple and inexpensive equipment - usually separatory funnels and beakers - the above merits are achieved both for trace and macro levels of analyte. Many liquid-liquid extraction systems result in separation, concentration and colour development all in one step, thus providing an extremely sensitive analytical method. This can be of great advantage in the use of automated methods of analysis both in the laboratory and in the plant. Many flow-injection methods, for example, are based on this principle. Even where coloured complexes are not formed, very sensitive analytical methods can be developed by the use of liquid-liquid extraction together with techniques such as atomic absorption spectrometry. For example, cadmium can be extracted from seawater by the use of either sodium diethyldithiocarbamate or ammonium pyrrolidine dithiocarbamate as chelating agents where a detection limit of ca 10^{-15}g of cadmium per liter of seawater can be achieved in an analysis using electrothermal-atomization techniques [1].

The advent of atomic energy programmes in many countries during and after World War II resulted in the use of liquid-liquid extraction on a large scale for the production of inorganic materials. The production of carrier-free tracers of high specific activity in radiochemistry is simplified considerably by the neat separation possible with liquid-liquid extraction [2]. Liquid-liquid extraction has, however, over the years extended from the nuclear industry to hydrometallurgy, pollution control and treatment and metal waste recovery. There is no doubt that liquid-liquid extraction continues to be popular with analytical chemists.

A knowledge of the principles governing the extractive behaviour of inorganic compounds and the mechanism of the extraction process itself will therefore increase the usefulness and specificity of liquid-liquid extraction.

FUNDAMENTAL PRINCIPLES

The partition law

Liquid-liquid extraction is the process of distributing a solute between two contacting liquids that are practically immiscible. In inorganic separations, as in our present work, the sample is dissolved in an aqueous phase and the other phase is a suitable organic solvent. The latter may comprise an organic reagent (extractant) dissolved in a suitable diluent.

Liquid-liquid extraction as defined above is a two-phase ternary system; it therefore follows from Gibb's phase rule, namely:

$$P + F = C + 2 \qquad 1$$

where P is the number of phases, F the number of degrees of freedom, and C the number of components, that at constant temperature and pressure, a three component system has only one degree of freedom. Thus, if the concentration of the solute in one phase is constant, the concentration of the solute in the other phase is also fixed, according to the distribution law proposed by Berthelot and Jungfleisch [3] and developed by Nernst [4]. This law states that a solute is distributed between two immiscible solvents in such a way that at equilibrium the ratio of the concentrations of the solute in the two phases is constant at a given temperature, *provided the solute has the same molecular weight in each phase*. This may be expressed mathematically as,

$$K_d = C_O / C_A \qquad 2$$

where K_d is the partition (distribution) coefficient (constant), C_O the concentration of the solute in the organic phase and C_A the concentration of the solute in the aqueous phase.

Frequently, experimental results fail to confirm the constancy of K_d due, firstly, to the fact that equation 2 is not strictly thermodynamically correct and secondly, the distributing species may be involved in chemical reactions such as association, polymerization and/or dissociation in either phase. Nernst [4] derived this law thermodynamically as follows: at equilibrium and constant temperature and pressure, the chemical potential (partial molal free energy) of the solute is the same in each phase. That is,

$$\mu_O = \mu_A \qquad 3$$

Substituting $\mu = \mu^o + RT\ln a$

where μ^o is the chemical potential in the standard state (usually taken as an hypothetically ideal one molal solution) and *a* is the activity of the solute at the actual concentration, equation 3 then becomes,

$$\mu^\circ_O + RT\ln C_O + RT\ln\gamma_O = \mu^\circ_A + RT\ln C_A + RT\ln\gamma_A \tag{4}$$

where γ_O and γ_A are the molal activity coefficients in the organic and aqueous phases, respectively. Rearranging equation 4,

$$K_d = \frac{C_O}{C_A} = \frac{\gamma_A}{\gamma_O}\,\frac{\exp\{[\mu^\circ_A-\mu^\circ_O]\}}{RT} \tag{5}$$

If the presence of the solute does not significantly affect the mutual solubility of the two phases, μ°_O and μ°_A can be assumed constant and equation 5 simplifies to the form

$$K_d = K\gamma_A/\gamma_O \tag{6}$$

where K is a constant for a given system. The value of K is the limiting value of K_d at infinite dilution when $\gamma_A/\gamma_O \rightarrow 1$ which can be determined by extrapolating from measurements at low concentrations. From equation 6, it follows that if the aqueous phase activity coefficient can be determined independently, knowledge of the partition coefficient will yield the activity coefficient in the organic phase. The validity of the Nernst distribution law therefore depends on the constancy of the ratio of the activity coefficients. In very dilute solutions, activity coefficients are equal to unity, so the distribution constant is independent of the solute concentration. In solutions of higher concentrations, the distribution law will be followed only if the activity coefficients change in the same direction in both phases and this is practically unlikely.

Other approaches to extraction equilibrium relate extractive properties to the properties of the individual components of the ternary system. These include the electrostatic approach [5,6], the application of the findings of studies on the solubility of gases in liquids to two phase ternary systems [7,8], and the Hildebrand theory of regular solutions [9].

The above equations for K_d hold only when the molecularity of the solute is in the same form in both phases, e.g., it must not dimerize in one phase while existing as a monomer in the other. Such chemical interactions in either phase do not lead to failure of the law but rather, they add complexity to the distribution expression, which can be properly accounted for by using appropriate equilibrium expressions [10 -15]. In this situation, the analyst is concerned with the analytical concentrations of the solute in both phases, and therefore speaks of a distribution ratio, D, which is the total concentration of the solute in all chemical forms in the organic phase divided by the total concentration of the solute in all chemical forms in the aqueous phase. His expectation is to make this high for the wanted solute and low for the unwanted or interfering component(s) of the mixture. Even more important to the analyst is the ratio of the distribution constants or ratio of equilibrium constants of two metal ions, called the separation factor.

Extraction process

Metal ions would not be expected to be extracted from the aqueous phase into the organic phase because of the large loss in electrostatic energy accompanying the process. This can be rationalized by using the Born charging equation [16] to calculate the electrostatic energy, ΔG_T, of transfering a bare ion of radius, r, and charge, Ze from water (dielectric constant ϵ_w) to an organic solvent of dielectric constant, ϵ_o, i.e.,

$$\Delta G_T = \frac{Z^2e^2}{2r}\left\{\frac{1}{\epsilon_o} - \frac{1}{\epsilon_w}\right\} \qquad 7$$

Normally, $\epsilon_o < \epsilon_w$, so that ΔG_T is positive. Considering the so calculated value of ΔG_T and the association (ion-pairing) energy calculated from the theory of Bjerrum

[17] and Fuoss-Kraus [18], a necessary condition for the extraction of an ionic species would be the lowering of the electrostatic energy of transfer by either partial or complete neutralization of its charge and loss of all or some of its water of hydration, increase in the size of the neutral species formed and increase in the hydrophobicity of the neutral species.

Liquid-liquid extraction can be considered as consisting of two steps; complex formation with the dissolved extractant in the aqueous phase and the transfer of the complex from the aqueous into the organic phase. Selectivity will therefore depend, for similar ions, on complex formation in the aqueous phase and for dissimilar ions on the partition of the complex formed between the two phases.

CLASSIFICATION OF EXTRACTION SYSTEMS

To assign all extraction systems to sharply defined classes is difficult and almost impossible. However, three mechanisms for extraction of inorganic cations can be distinguished, namely, extraction of uncharged compounds, of ion-pairs and of coordinatively solvated salts. This classification is based primarily on the type of compound extracted into the organic phase, but the distinction between some types of extraction is sometimes rather arbitrary. A given reagent may function in different ways depending on the conditions of extraction or on the metal ion. Some reagents can at the same time be chelating and solvating in their action. The discussion that follows emphasizes acidic reagents which in the main involve compound formation while the other two classes will be described briefly.

Extraction systems involving compound formation

This comprises a large and important group such as extraction with chelating agents; for example, oxine, cupferron, dithizone, thenoyltrifluoroacetone, diethyldithiocarbamate, dimethylglyoxime, etc. and extraction systems involving liquid cation-exchangers, for example, sulphonic and phosphoric acids; where extractions are more complicated.

Phosphorus-based extractants

As early as 1949 [19], it was recognized that the monobutyl and dibutyl phosphoric acids would extract uranium as well as, or better than, the neutral organophosphate ester tributylphosphate, TBP. Phosphoric acids, (RO)(R′O)(OH)PO, containing larger alkyl groups such as bis(2-ethylhexyl) phosphoric acid, have a lower water solubility and so do the corresponding phosphonic acids, $R(OH)_2PO$ and R(R′O)(OH)PO and phosphinic acids $R_2(OH)PO$ which show equally good extraction characteristics. Acidic organophosphorus extractants were initially developed for nuclear fuel reprocessing but have also become of increasing importance in hydrometallurgical processing.

The mechanism of metal ion extraction into dilute solutions of these acids in suitable diluents is a cation exchange process and may be considered analogous to the cation resin exchange process but cautiously though, since the low dielectric constant of the diluent phase in most cases is quite dissimilar to an aqueous resin phase, even though the latter is 50% hydrocarbon matrix [13]. The chemical and physical properties of these reagents are such that they are capable of competing with water for the available sites in the first coordination shell of the cations, and thus capable of forming extractable coordination solvated complexes.

Peppard and co-workers [20a-j] and others [21-30] have studied the properties of these organophosphorus acid extractants. Definite compounds resulting from the replacement of an acidic hydrogen by an equivalent of metal make extraction by these reagents resemble chelate formation. The situation is not as definite and predictable as chelation but depends on the particular state of these extractants in solution. Complication is caused by the pronounced tendency toward association as dimers and larger aggregates and the fact that solvation of the metal-extractant complex by one or more additional extractant molecules can occur.

The equilibria and quantitative treatment that follows will consider diluents of low dielectric constant since they are used more often. Assuming that the extractant is also dimeric in the aqueous phase, the main equilibria involved in the system are:

The distribution of the dimer between the two phases

$$(HY)_{2,A} \leftrightharpoons (HY)_{2,O} \qquad K_m = \frac{\{(HY)_{2,O}\}}{\{(HY)_{2,A}\}} \tag{8}$$

The dissociation of the dimer in the aqueous phase

$$(HY)_{2,A} \leftrightharpoons (HY_2)_A^- + H_A^+ \qquad K_a = \frac{\{(HY_2)_A^-\}\{H_A^+\}}{\{(HY)_{2,A}\}} \tag{9}$$

The formation of the extractable complex in the aqueous phase

$$M_A^{n+} + n(HY_2)_A^- \leftrightharpoons M(HY_2)_{n,A} \qquad K_f = \frac{\{M(HY_2)_{n,A}\}}{\{(HY_2)_A^-\}^n \ \{M_A^{n+}\}} \tag{10}$$

The distribution of the complex between the two phases

$$M(HY_2)_{n,A} \leftrightharpoons M(HY_2)_{n,O} \qquad K_c = \frac{\{M(HY_2)_{n,O}\}}{\{M(HY_2)_{n,A}\}} \tag{11}$$

where brace brackets represent activities, $(HY)_2$ represents the extractant dimer, the subscripts A and O designating aqueous and organic phases, respectively and M^{n+} the metal ion of charge n, neglecting the water of hydration.

The overall reaction can be written as follows:

$$M_A^{n+} + n(HY)_{2,O} \leftrightharpoons M(HY_2)_{n,O} + nH_A^+ \tag{12}$$

The equilibrium constant for the above reaction is

$$K_e = \Gamma \frac{[M(HY_2)_{n,O}]\ [H_A{}^+]^n}{[M_A{}^{n+}]\ [(HY)_{2,O}]^n} = \Gamma K_c K_f K_a{}^n K_m{}^{-n} \qquad 13$$

where $\Gamma = \gamma_{M(HY_2)} (\gamma_{H_A^+})^n (\gamma_{M_A^{n+}})^{-1} (\gamma_{(HY)_2})^{-n}$ is the activity coefficient product for the species. Under conditions of constant activity coefficient (for example, a constant ionic medium in the aqueous phase, a low concentration of extractant in the organic phase and at tracer metal concentration) Γ is constant and K_e/Γ may be replaced by another constant K'_e while $(HY)_{2,O}$ may be replaced by C_R, the total extractant concentration. If no intermediate complexes of the metal with the organic reagent are formed and there are no other ligands in the aqueous phase which can react with M^{n+}, the ratio $\frac{[M(HY_2)_{n,O}]}{[M_A{}^{n+}]}$ is equal to the partition constant, K_d. Then,

$$K'_e = \frac{K_d\ [H_A{}^+]^n}{C_R{}^n} \qquad 14$$

Expressed logarithmically as

$$\log K_d = \log K'_e + n\log C_R - n\log[H_A{}^+] \qquad 15$$

From this simplified model, it follows that for a given system, log-log plots of K_d vs $[H_A{}^+]$ and K_d vs C_R will be straight lines with slopes equal to -n and n, respectively, that is, the charge on the metal ion in the aqueous phase. Cases where $\log K_d$ depends inversely on a higher power of $\log[H_A{}^+]$ than n may arise due to polymerization of metal species in the organic phase [31], the reverse of this (i.e. lower n dependency) occurs either by hydrolysis of the metal ion in the aqueous phase or when the extracted complex contains some other anionic ligand. Most real systems are therefore more complex than that represented by equation 12. Mathematical description of the extraction reactions of such systems have been treated by various investigators [10-12, 32-37]. Although the extraction with these acids is frequently difficult to control for reasons mentioned above, they have the advantage of rapid extractions and usually high loading capacity. Numerous analytical separations of closely related groups like the lanthanides and actinides based on the use of these reagents have been accomplished.

Sulphonates

Alkyl and aryl sulphonic acids have also been investigated for the extraction of metal ions from aqueous solutions and have been used in studies of equilibria involving formation of various aqueous metal complexes [38-41]. The most useful of these for solvent extraction are the alkylated benzene and naphthalene sulphonates, for example, dodecylbenzene, tripentylmethylbenzene, didodecylnaphthalene (DDNSA) and dinonylnaphthalene sulphonic (DNNSA) acids. Extraction with sulphonic acids is restricted because of their solubility in aqueous electrolyte solutions thus requiring slightly acidic aqueous media. Micelle formation both in the aqueous and organic phases complicates the physicochemical interpretation and quantitative treatment of the equilibrium extraction data. In wet organic diluents, DNNSA is known to polymerize extensively [42-44] and exhibits selectivities similar to solid polystyrene cation-exchangers that contain the same functional group [43-46]. The micelles are the active organic phase species involved in the extraction of metals.

The equilibria involving these acids can be represented as follows

$$M_A^{n+} + (HD)_{m,O} \leftrightharpoons M(H_{m-n}D_m)_O + nH_A^+ \qquad 16$$

where m represents the degree of polymerization of the extractant HD, other symbols having the same definitions as before. The difference between the sulphonic acid and mono-acidic organophosphorus extractant systems results from the extensive aggregation of the former in the organic phase. Regardless of the charge on the metal ion the $\log K_d$ vs $\log[HD]$ plot is always of unit slope, but $\log K_d$ vs $\log[H_A^+]$ plots give slopes of -n as with acidic phosphorus extractants.

Extraction systems involving ion-association

In this class, extractable species are formed by virtue of electrostatic interaction between the metallic species in the aqueous phase and the extractant in the organic phase. Much of the ion-association theory is due to Bjerrum [17]. The most used ion-association reagents are amines, quaternary phosphonium and arsonium compounds and dye cations of the type, RH^+ (e.g. Rhodamine B), for the extraction of oxyanions of metals with halide and pseudohalide ions, anionic inorganic coordination complexes and anionic coordination complexes involving organic ligands, to give ion-pairs effectively extracted into chloroform and other organic solvents.

The main interest in these systems lies in their selectivity towards anionic metal complexes formed in the aqueous phase rather than simple anions. Thus extractability of the anionic species depends on the aqueous phase conditions more than on the differences in the specific affinities of the anionic species for the extractant. Selectivity of the extraction process depends on the degree of hydration of the anion, which is a function of size. Large, singly charged anions which do not have a large energy of hydration are extracted readily by the similarly large organic cations. Ion-association in which the cation-anion ratio is 1 : 1 are generally more easily extracted than those in which the ratio is 2 : 1 or 1 : 2, due to the greater hydration of ions of higher charge and their resultant tendency to remain in the aqueous phase. Thus, the basis for their extraction is bulkiness and weak interaction with water.

The existence of these unhydrated complexes will therefore mean that the ion-pairing energy decreases the electrostatic energy of transfer to such an extent that makes extraction possible. From the Born charging equation, the larger the cation and anion of the ion-pair, the better the extraction.

High molecular weight amine salts ($R_3NH^+X^-$ for example) and quaternary ammonium salts, $R_4N^+X^-$, show excellent extraction capabilities and are used in process chemistry for recovering fissionable metals from irradiated fuel materials. The extraction equilibria with these extractants in organic diluents of low dielectric constant are complicated by polymerization, and this polymerization can be perserved in the ion-associate also [18,47], . Further complication arises from the decrease of the dielectric constant of the aqueous phase, by the high concentration of electrolyte needed and the presence of dissolved organic solvent, to a point where ion-association in this phase becomes possible [48].

The equilibria essentially involve anion-exchange and can be written as follows:

$$B_A^- + (R_3NH^+X^-)_O \rightleftharpoons (R_3NH^+B^-)_O + X_A^- \qquad 17$$

where B_A^- is the metal species in the aqueous phase and other symbols have the same definitions as before. The distribution ratio, D, is affected by the structure of the amine, its concentration in the organic phase diluent and the anion, X_A^-, involved. Selective separations have been achieved for metals which can form anionic chloro-complexes, for example, the separation of cobalt from nickel, since cobalt readily forms stable chloro-complexes [49].

Quaternary phosphonium and arsonium extractants are soluble in water. The polarity of the organic solvents used in extracting their ion-pairs do not lead to the complications observed with amine extractants in low dielectric constant solvents.

Chelating agents possessing reactive groups which enable them to form charged species have been used in the extraction of ion-pairs. These are formed when the chelating agents complex metal ions without loss of hydrogen ions. For example, the coloured complex, $Fe^{II}(1,10\text{-phenanthroline})_3^{2+}$, in which molecular phenanthroline occupies the six coordination sites of Fe^{2+}. Such complexes enhance both the extractability and the selectivity of the extraction process [50]. The presence of ClO_4^- results in the formation of an ion-associate extractable into chloroform and has been used for the selective separation and determination of iron [51,52].

Extraction systems involving coordinative solvation

This class is not as well defined as the previous two. Systems involved are rather diverse and some are not easily distinguishable from and are sometimes classified under ion-association. The main difference arises, firstly, by the fact that water molecules must be incorporated into some of the extracted complex, and secondly, neutral inorganic molecules or complexes are extracted by virtue of solvation by the extractant. The metal ions surrounded by the anion interact weakly with water molecules. The small size and high charge of the cation does not favour extraction of the complex into the organic phase, because of strong solvation.

Due to its high charge density, the hydrogen ion is much more hydrated and more solvated by basic organic solvents than small cations. This is responsible for the extraction by basic organic solvents of protonated anionic complexes that consist of ion-pairs containing the solvated proton. The presence of a suitable acid is a necessary requirement for the formation of an extractable compound.

The organic solvent, which in most cases is the extractant, (i.e. requires no diluent), plays an important role in determining the success of the extraction process and its choice should be carefully considered. Organic solvents, like alcohols, ethers, ketones and neutral organophosphorus esters, which have electronegative groups can in many cases provide the necessary solvation in the organic phase thereby helping to compensate for the loss of hydration. Definite isolable compounds are formed in some systems while there is sometimes indefinite solvation of the extracted species in others.

The displacement, not necessarily complete, of the water molecules around the species to be extracted is always an important factor. Solvents containing the P — O bond compete favourably with water and can replace it in the first hydration shell of the cation. Such extractants are better than those containing the C — O bond, where the presence of water in the extracted species is a necessary part; the water molecules in the extracted species of these latter solvent systems usually act as a bond in an outer sphere ion-pair consisting of the solvated proton and the anionic complex. The greater donicity of the phosphoryl group (P → O) is a consequence of the basicity of the O atom and its ready steric availability which facilitates solvation. Examples of the use of this class in inorganic analysis are, the separation of Fe(III) as the chloride by extraction into diethyl ether from 6 M HCl and the extraction of uranium from HNO_3 by TBP.

EXTRACTANTS AND DILUENTS

The question that has always arisen is whether it is preferable to search for new extractants or to obtain further more reliable information on those already available. The answer is ambiguous and indeed both types of study are essential. While it is important to pursue the discovery of new and selective extractants, it is equally important to accumulate a good knowledge of the already existing ones.

The main reason for investigating new extractants is the search for selectivity since such compounds will greatly decrease the number of stages and cycles and cost of separating the required metal ions. For metal-extractant complexes that involve direct bonding, the general principle for designing selective extractants should take maximum compatibility of the properties of the central metal ion and the extractant molecule into account [53]. Such factors are: the nature of the metal and those atoms in the extractant that directly interact with the central atom, the size of the metal ion, its coordination number, the type of active atoms in the extractant molecule, the properties of the rest of the molecule and its geometry. The strength of the metal-extractant bond plays a very important role and has led to the concept of soft and hard acids and bases. The theory of extraction has also been considered from the stand-point of the relationship between the structure of the extractant and extraction efficiency [54,55].

A reagent to be employed in liquid-liquid extraction should meet the following requirements:

(i) be relatively inexpensive
(ii) have a very low solubility in the aqueous phase
(iii) have very high solubility in the organic phase
(iv) be non-flammable, non-toxic and non-volatile
(v) be stable
(vi) have high metal loading capacity
(vii) have good extraction kinetics
(viii) not form emulsion with aqueous phase
(ix) have good coalescing properties when mixed with a diluent
(x) the extracted metal should be easily stripped off it.

Extractants can be classified by considering the type of compound formed as was the case with classifying extraction systems discussed above. Table 1 lists some extractants that have been used in liquid-liquid extraction.

Table 1

Classification of some extractants that have been used
in liquid-liquid extraction of metals

Cationic (or acidic)	
Versatic 9 and 911	Carboxylic acids
H2MEHP	Mono-2-ethylhexylphosphoric acid
HDEHP	Di-2-ethylhexylphosphoric acid
HEHΦP	2-ethylhexyl phenylphosphonic acid
HEH[EHP]	2-ethylhexylphosphonic acid mono-2-ethylhexyl ester
Cyanex 227	Di-2,4,4-trimethylpentyl phosphinic acid
OPPA	Di-p-octylphenyl phosphoric acid
DNNSA	Dinonoylnaphthalene sulphonic acid
HDBP	Di-n-butyl phosphoric acid
H2MiDP	2,6,8-trimethylnonyl-4-phosphoric acid
$(C_6H_5)_4B^-$	Tetraphenylborate

Anionic (or Basic)	
Alamine 336	Tri-n-octylamine + tri-n-decylamine
Aliquat 336	Tri-n-(octyl+decyl)methyl ammonium chloride
$TLMANO_3$	TRidodecylmethyl ammonium nitrate
Amberlite LA-1	N-dodecyltrialkylmethylamine
Amberlite LA-2	N-lauryltrialkylmethylamine
TNOA	Tri-n-octylamine
$(C_6H_5)_4P^+$	Tetraphenylphosphonium
$(C_6H_5)_4As^+$	Tetraphenylarsonium

Table 1 cont'd

Solvating	
TBP	Tri-n-butyl phosphate
DBBP	Di-n-butyl butyl phosphonate
TOPO	Tri-octyl phosphine oxide
MIBK	Methyl isobutyl ketone
Cyanex 471	Tri-isobutyl phosphine sulphide
Chelating	
The LIX series	Oximes
Kelex extractants	Oxines
Macrocyclic	
Dibenzo - 18 - crown - 6	
Monobenzo -15- crown - 5	
Dicyclohexano -18- crown - 6	
Sym - dibenzo -16- crown -5- oxyacetic acid	
Dibenzo- 8,12- diazacyclopentyl -15- crown -7,12- dien	

Some extractants may belong to more than one class depending on the environment where they are used, for example, tertiary amines may be classifed as anionic extractants in acid solutions but under solvating when they are neutralized, i.e., used as salts in neutral solutions; dialkyl phosphoric and phosphonic acids are classified as cation-exchanging and chelating when chelate formation is proven and also as solvating.

Most extractants are rarely used in the "as received form", but need to be diluted with an "inert" organic liquid (diluent). The diluent is used to dissolve and improve the physical properties of the extractant, without practically having extractant properties itself. The diluent and extractant form the organic phase and in the majority of cases, the diluent comprises the major portion of the phase.

Diluents for hydrometallurgical applications are usually relatively inexpensive crude oil fractions and may be aliphatic, aromatic or mixture of the two. To consider diluents as inert and not to enter into the mechanism of extraction may be far from the truth. Investigators have found that not only are diluents not "inert" in the solvent extraction process, but they can play a significant role in determing the success of an operation [56,57], hence the preference of the terminology "carrier" diluent.

A diluent should have the following requirements:

(i) be invariably soluble with the extractant

(ii) have a high solvency with the extractant to minimize both the problem of third phase formation and low loading capacity of the solvent

(iii) have a low vapour pressure at room temperature and high flash point, thus decreasing losses due to volatility as well as fire hazards.

(iv) have very low solubility in the aqueous phase

(v) have a low surface tension to prevent emulsification

(vi) be cheap and readily available

(vii) have low viscosity and density for a good and fast phase separation.

The effects of the diluent on the form in which the extractant exists in the organic phase have recieved particular attention, especially in the case of organophosphates [58a-f] and amine extractants [59a-f]. Generally, acidic and basic extractants are polymerized or self-associated in non-polar diluents. The mono basic organophosphates can polymerize to a large extent depending on the polar nature of the diluent. In polar diluents such as alcohols and ketones, the extractants have been found to exist as monomers [20a-j,21-30] and dimers in diluents of low dielectric constant such as toluene, hexane, etc. The average degree of polymerization in wet benzene for mono-n-octyl phosphoric acid has been found to range from 12 to 92 [60]. The presence of polymeric forms of the extractant in the organic phase will affect its distribution between the aqueous and organic phase which in turn will affect the equilibrium distribution of the metal between the two phases [12,58a-f].

Aggregation in the solvent phase affects the loading capacity of the solvent. For example, in low polarity diluents where the extractant exists as dimers in the solvent phase, the extraction equilibria is represented by equation 12, whereas in more polar diluents where the monomeric species is predominant, the equilibria can be represented as

$$M_A^{n+} + n(HY)_O \rightleftharpoons (MY_n)_O + nH_A^+ \qquad 18$$

At low loading of acidic extractants in solvents of low polarity wherein distribution ratios are high, it has been found that MY_n is less commonly extracted than $M(YHY)_n$

[61,62] but at saturation loading the reverse is obtained. Equations 12 and 18 represent two distinct extraction mechanisms in their own right, but such cases are unlikely to be exclusive to any one system because of monomer - polymer (dimer) equilibria. Aggregation of the extractant generally increases with increasing concentration and loading capacity of the solvent [63].

It has also been found that the degree of aromatic or aliphatic nature of a diluent can have rather surprising, not easily explainable but not common effects on the extraction of metals by different solvent systems [64]. A diluent cannot be assumed not to enter into the mechanism of the liquid - liquid extraction process; therefore, its choice should also be taken into account in developing an extraction process. In this present work, the distribution ratios of the ions studied were found to be higher in hexane than in toluene or petroleum ether (100-120°C boiling range). Similar effects have been observed for the extraction of Cf and Am with 2-ethylhexyl phenylphosphonic acid in heptane and toluene diluents [65]. Although higher separation factors are achieved in aromatic diluents, the distribution ratios are practically low necessitating the use of very high concentrations of the extractant. The antagonism or otherwise of the extraction of a metal by a diluent may be due to some impurity in the diluent which for one reason or another cannot be removed. Purification of diluents for bench-scale work is often embarked on but not necessary or advisable if industrial application of such liquid-liquid extraction process using commercially available material is expected. With respect to understanding and quantifying extraction processes, a commensurate amount of work has not been done on the relationship between the physicochemical properties of the diluent and the distribution of metals [66].

The addition of a modifier to overcome third phase or emulsification tendencies in solvent extraction systems is a common practice. These reagents are usually long-chain alcohols but TBP is also used sometimes. Third phase formation is basically a solubility problem and can be overcome in most cases by the addition of a third component to the solvent. A modifier should possess the same requirements as a diluent. A modifier can also affect the extractive properties of the solvent [67].

CHAPTER II

THE RARE EARTH ELEMENTS

The group of elements characterized by the filling up of the 4f energy levels have alternatively been called lanthanons, lanthanides, or rare earths. The latter term arose because of the rarity of the minerals from which these elements were obtained. Recent geochemical investigations have shown that these elements are by no means rare but dispersed. These names will be used interchangeably hereafter without any attached meaning and will include elements from La-Lu (atomic no. 57-71) but yttrium will be included occasionally. The geochemical coherence and uniqueness, both in elemental state and in compounds, of this group of elements under most natural conditions is a result of the common (+3) oxidation state, although anomalies occur.

Occurrence in nature

The REE are not especially rare in nature but are found in low concentrations widely distributed throughout the Earth's crust and in high concentrations in a considerable number of minerals. The REE are lithophiles i.e. when allowed to distribute between silicate, metal and sulphide phases in co-existence, they predominantly concentrate in the silicate. The scarcest, thulium, is as abundant as bismuth and even more so than Ag, Au, Cd, Pt, Pd or Se . As a group the RE constitute $8 \times 10^{-3}\%$ by wt. of the Earth's crust.

The cooling of molten rocks (fractional crystallization) and superheated water solutions that have percolated through rocks under great pressure frequently produces minerals containing up to 50% REE. This fractional crystallization naturally results in partial separation of the REE so that some minerals are relatively richer in the lighter elements (the so-called cerium group) whereas others are richer in the heavier (the so-called yttrium group) [68-72]. From the presence and composition of such minerals, geochemists can learn a great deal about the conditions, such as temperature and pressure, that prevailed during the formation of the rock, i.e., the petrogenetic processes. This has led to the significant growth of REE geochemistry. The relative abundances of REE in chondritic meteorites are commonly taken as a standard of comparison and it is assumed that their composition may serve as a quantitative guide to the composition of the earth as a whole [73]. It is now generally accepted that the relative values of the REE in chondritic meterorites represent their overall relative abundance in the universe. Such information is of importance to prospectors.

The fact that these elements have not been separated into minerals containing individual members of the group at any time in the Earth's history, even after repeated geochemical concentrating processes, attests to the great similarity in their properties.

Electronic structure, oxidation state and ionic radii

Although spectroscopic data indicate that the first 4f-electrons appear in cerium, lanthanum has essentially identical chemical properties with the other elements and is prototypical of the RE series. This suggests that the influence exerted on the properties of the lanthanides by a change in their electronic configuration due to the formation of the 4f-subshell is small.

The electronic configuration of the elements and yttrium is shown in Table 2 along with the known oxidation states and effective ionic radii. An alternative suggestion for the electronic configuration involves moving a single electron from the 4f-shell to the 5d-shell to achieve the outer lanthanum cofiguration except where it destroys the symmetry of the half-full or full f-shell. Whichever of the two suggestions is true is of little importance because the RE typically form compounds

Table 2

Electronic configuration, known oxidation states and ionic radii of the REE and yttrium

Element	Ground state electronic configuration	Known oxidation states	Ionic radii (A°)[a]		
			M^{2+}	M^{3+}	M^{4+}
Y	4d $6s^2$	+3		0.900	
La	5d $6s^2$	+3		1.032	
Ce	4f 5d $6s^2$	+3 +4		1.01	0.87
Pr	$4f^3$ $6s^2$	+3 +4		0.99	0.85
Nd	$4f^4$ $6s^2$	+3		0.983	
Pm	$4f^5$ $6s^2$	+3		0.97	
Sm	$4f^6$ $6s^2$	+2 +3		0.958	
Eu	$4f^7$ $6s^2$	+3	1.17	0.947	
Gd	$4f^7$ 5d $6s^2$	+3		0.938	
Tb	$4f^9$ $6s^2$	+3 +4		0.923	0.76
Dy	$4f^{10}$ $6s^2$	+3		0.912	
Ho	$4f^{11}$ $6s^2$	+3		0.901	
Er	$4f^{12}$ $6s^2$	+3		0.890	
Tm	$4f^{13}$ $6s^2$	+3		0.880	
Yb	$4f^{14}$ $6s^2$	+2 +3	1.02	0.868	
Lu	$4f^{14}$ 5d $6s^2$	+3		0.861	

a) ref. 74 for coordination number = 6

which are ionic and trivalent [75]. Other so-called "anomalous valency states" of +2 or +4 in addition to the typical +3 are exhibited by a few of the REE. These are to be expected when the extra stability of an empty, half-full and full f-level is allowed for. These configurations exhibit a pseudo "inert-gas" structure for the RE series. Although few solid compounds exemplifying the +4 state have been prepared [76], only Ce^{+4} has a sufficiently long half-life with respect to reduction to exist in aqueous solutions. All of the lanthanides have been obtained in the +2 state by trapping in solid alkaline earth halide matrices [77] but dissolution in aqueous systems results in rapid oxidation to the +3 state of all the species except Eu(II). Eu(II) has been shown to have a comparatively short half-life with respect to oxidation in aqueous solution [78,79]. The +2 state in solid compounds has also been observed for Yb, Sm and Tm and the +4 state for praseodymium and terbium in $Pr_6O_{11}$and Tb_4O_7, respectively. These states are of sufficient chemical stability to be of importance. The existence of these anomalous oxidation states for Ce, Eu and Yb is utilised industrially in their separation from the other RE.

On a comparative basis, the atoms and cations of the RE are large [80], explaining why the metals are strong reducing agents and their compounds generally ionic. The small differences in the size of the Ln^{3+} ions, as shown in Table 2, (are a result of the effective shielding of the 4f-electrons by the overlying $5s^2$ and $5p^6$ shells) explains the close resemblance of the properties of the REE and their geochemical coherence in nature. This contraction is sufficient to cause differences in the *degree* to which some, but not all, of the properties associated with a given oxidation state are exhibited. For example, considering only the +3 ions, there arises due to decreasing ionic radii, many recorded examples of decrease in coordination number, decrease in basicity, decrease in ionic character in solid binary compounds, etc.

These differences in degree are utilized as the basis for all procedures of fractional separation of the REE, be it the classical procedures of crystallization or precipitation, or the more modern procedures of solvent extraction, ion-exchange or extraction chromatography.

The contraction is also sufficient for the radii to drop below that for yttrium in the preceding transition series and since yttrium forms a +3 ion with a noble gas core, it is generally found in nature along with the lanthanides and has chemical properties similar to Dy and Ho. In instances where the ionic radii of the REE are comparable to other ions, substitution of these elements in their minerals may occur. The charge difference, if any, may be compensated for by addition or removal of an anion in an interstitial position in the crystal structure.

The lanthanide contraction is also responsible for the remarkable parallels between the elements that follow the lanthanides in nuclear charge and their congeners in the preceding periodic series, e.g., between Hf and Zr, Ta and Nb, W and Mo, etc.

APPLICATIONS

Carl Auer von Welsbach's invention of the incandescent gauzes and mantles for gas lamps in 1885 generated interest into the possible practical uses of the REE. Welsbach's lamps are still in use today in remote areas and in signal devices for railroads. Further intensified search for industrial applications of the REE in the form of metals, alloys, or compounds was brought about by the development of technology, mainly nuclear technology, which require materials with the most varied properties. The REE are used industrially mainly as a mixture in the form of metals (known as mischmetal) or compounds, except in cases where the specific properties of individual members of the group are needed.

The following paragraphs will highlight usage of the REE with regard to their chemical, optical, magnetic and nuclear properties and applications in metallurgy.

Applications based on chemical properties.

Either the naturally occuring or synthetic mixtures of the REE's is utilized in most of the examples to be mentioned here. Rare earth oxides are used as catalysts in the hydrogenation, dehydrogenation, and oxidation of various organic compounds; the anhydrous chlorides in polyesterification processes; the most important being in crude petroleum cracking [81,82a,b]. In the latter, RE containing zeolite catalysts (e.g., $Na_2O.Al_2O_3.nSiO_2.H_2O$) are substantially superior in activity and selectivity to the amorphous silica alumina formerly used for gasoline production. REE catalysts are used in the pollution control of exhaust gas, CO, NO_x and unburnt hydrocarbons [83]. Mischmetal ignites readily and this property is utilized in lighter flints and artillery shell liners [84].

At high temperature, Gd_2O_3 and Y_2O_3 become conductive and CeO_2 ceramics doped with any of these and Y_2O_3-stabilized ZrO_2 are used as solid oxygen electrodes. These are the so-called lambda-sensors used to optimize the air-fuel ratio in automobiles [85]. Ceramic applications of the REE includes the use of mixed rare earth oxides especially CeO_2. Ce-rich oxides mixtures are used in glass polishing and also for the improvement of stability against discoloration of glass by cathode rays, gamma rays, and X-rays [86,87] and solarization by ultra-violet rays from the sun [88]. The coordination chemistry of the REE has also been utilized, for example, the use of paramagnetic gadolinium complexes (e.g., with diethylenetriaminepenta-acetic acid and the phylate ligand) to enhance medical NMR imaging [89,90].

Applications based on optical properties.

The absorption and emission spectrum of the REE is characterized by narrow lines (a characteristic of inner core electrons) which produces attractive coloured glasses [91]. This property is utilized in optical glass. High purity rare earth oxides (98-99.999%) are required for phosphors in colour television picture tubes, X-ray imaging and fluorescent lighting tubes. Eu_2O_3 doped with Y_2O_3 [92] or yttrium oxysulphide (Y_2O_3S) [93] or yttrium orthovanadate (YVO_4) [94] produces the red phosphor in colour television. Gadolinium gallium garnets and the recently developed $Ba_3(PO_4)_2$-Eu and $BaSO_4$-Eu phosphors are used in medicine in X-ray radiography intensifying screens to increase film exposure and hence reduce X-ray dosage [95,96]. The sharp line emission spectrum of the REE accounts for their use in lasers [97-99]. Nd-doped yttrium-aluminium garnet (YAG;$Y_3Al_5O_{12}$) is used in cutting, scribing semi-conductors, drilling and welding [100]. Communication apparatus using infrared-trigged phosphors consisting of SrS and/or BaS doped with REE and/or EuO and a fusible salt e.g., LiF, have been developed for use in recoverying infrared signals [101].

Applications based on magnetic properties.

Here again, the presence of the 4f electrons and their interaction with the electrons of other elements is utilized. Yttrium-iron garnets (YIG) and gadolinium-iron garnets (GIG) are used as ferrite materials in microwave filters [102] in the communication industry. The demagnetization resistance of rare earth/cobalt intermetallic mixtures of the type $LnCo_5$ is used in the construction of permanent magnets. The elements Y, La, Ce, Pr, Nd or mischmetal may be used. The recently developed Nd-Fe-B permanent magnets (e.g., the alloy $Nd_2Fe_{14}B$) [103-105] have approximately 40% more energy than $SmCo_5$ and have the potential of replacing alnicos and ferrites in many applications. Magnetic "bubble" memories based on gadolinium-gallium garnets for storage of information is a recent application found for the REE [106].

Applications based on nuclear properties.

The REE, especially, Gd, Sm, Eu, Dy, and Er are used as control and shutdown materials because of their high capture cross-section for thermal neutrons. Yttrium, because of its low neutron cross-section is used as structural metal and as fuel matrix (diluent) material [107]. Cerium and yttrium hydrides are used as neutron moderators in reactors.

Metallurgical applications.

The REE find considerable use in alloys and scavengers for non-metallic impurities. Magnesium containing several percent of mischmetal have proved helpful in producing alloys that have superior high temperature properties utilized in jet engine parts and precision casting if small amounts of zirconium or other metals is added. Magnesium alloys containing up to 3% Nd or Y have been used in bone surgery. Addition of mischmetal or mixed RE silicides to cast iron produces a more malleable nodular iron [108,109]. The addition of mischmetal to certain alloys increases their tensile strength, improves their hot workability and imparts a special high temperature oxidation resistance to them [110-112]. However, calcium and magnesium compounds have partly replaced the REE in ferrous metallurgy but nevertheless metallurgical applications are still one of the three major areas of REE applications (the other two being catalysis/chemical and glass/ceramics).

Miscellaneous applications.

These include certain medicinal preparations, for example, Nd-isonikotinate as treatment for thromboses, Ce^{4+} in analytical chemistry, REE in metallothermic reactions because of their high reducing capacity, use of $LaCl_3$ as interference supressor in the determination of certain elements by atomic absorption spectroscopy [113]. The extraction of plutonium and other transuranic elements from liquid uranium uses REE as carriers. The use of RE hydrides, for example, lanthanium-nickel hydride ($LaNi_5H_6$) [114] permits safe storage of hydrogen at ambient temperatures and moderate pressures and is expected to find wide application in catalytic hydrogenation of organic compounds [91,115]. The REE market would increase significantly if they are proven suitable as catalysts as is the considerably cheaper lanthanum-cobalt oxide which approaches the platinum types in efficiency.

CHAPTER III

REVIEW OF SOLVENT EXTRACTION WITH ORGANOPHOSPHONIC MONO-ACIDIC ESTERS AND SULPHONIC ACIDS.

The purpose of this review, which is not exhaustive per se, is to provide brief background information on the use of organophosphonic acid and sulphonic acid extractants that are useful in solvent extraction for the hydrometallurgical processing of metals and have potential use in analytical chemistry.

ORGANOPHOSPHONIC ACIDS

Organophosphorus acidic extractants can be represented generally as $R_1R_2PO(OH)$, where R_1 and R_2 may be alkyl, alkoxy, phenyl, phenoxy, or any combination of these or any substituted variant. The nomenclature phosphoric, phosphonic and phosphinic corresponds to such compounds having two, one and no alkoxy or phenoxy substituents attached to the P atoms, respectively. The search for more selective and versatile extractants has resulted in the evaluation of esters of orthophosphoric, phosphonic and phosphinic acids and similar compounds containing polyfunctional groups. Phosphorus-based extractants, especially tributylphosphate (TBP), are commonly employed for the isolation of higher valent metal ions such as the lanthanides and actinides. Monoacidic extractants such as diesters of phosphoric acid have been the subject of several studies [20a,c,e,116-119] and have been used in the separation of many metal ions on a commercial scale. HDEHP has received much attention because of its versatility and availability. Monoesters of phosphonic acids have been reported to possess higher separation factors for successive members of such chemically similar groups as the lanthanides and actinides [20f,65,119-121] and other metal ions. Despite this advantage, these have been less studied until recently.

The vast amount of information on these extractants has necessitated their evaluation with regards to the nature of R_1 and R_2 since the active group $>PO(OH)$ responsible for their extractive properties is common to the three groups. The nature of the extractant in all extraction systems affects its distribution and dissociation and the stability of the complex formed with the metal ion and its consequent distribution between the phases. By studying various dithizone derivatives, Freiser et al. correlated structure with both the properties of the extractant and its metal complexes [122]. With the realization that any modification of the extractant by changing those parts of the molecule which do not directly participate in the formation of the extracted metal complex can essentially alter the extractant, the literature is rich in acidic organophosphorus extractants that have been evaluated for the extraction of metal ions. The types of substituent influence the acidic nature of the reagent and the electronegativity of these substituents will thus be of importance in determining the pK_a of these acids. The pK_a has been found to be practically independent of the nature of the alkyl chains but mainly reflects the number of alkoxy groups bound to the P atom [123,124]. This is supported by the fact that there is a negligible difference in the electronegativities of n-, sec-, iso-, and tert- butyl groups [125]. An example of this has been studied by replacing one of the 2-ethylhexyl groups in HDEHP by n-butyl-, isobutyl- or sec-butyl- group; which failed to alter the R_f values in the use of paper chromatography to test the extraction of the REE [126]. Structure also affects the solubility of these reagents in the aqueous phase. Thus in most cases, a short alkyl chain length results in excessive solubility whereas long chain length, while decreasing solubility, may also result in lower metal loading capacity as a result of steric effects. Monoacidic organophosphorus extractants are dimeric in solvents of low dielectric constant.

In general, it is well known that the stability of a complex normally decreases with increase in acidity of the extractant. However, substituents which by their inductive effect can change the acidity of the extractant without greatly affecting the stability of its complexes can be introduced into the extractant. Thus, the effect of the nature of the extractant on the extraction system must involve an understanding of the individual equilibria. Under similar conditions, pK_a increases in the order phosphoric < phosphonic < phosphinic and the separation efficiency (measured by the separation factor) of an extractant to separate a given pair of ions has been found normally to increase in that order also [127]. In the extraction of the lanthanides, extraction efficiency (measured by the distribution coefficient) has been found to remain practically unchanged [128] within the di-n-alkylphosphoric acids when the alkyl substituent is butyl, pentyl, hexyl and octyl in which the acid strength decreases [129]. A rigorous comparison of isomeric mono-acidic organophosphorus extractants indicates that in each of the three groups the separation efficiency strongly increases with increased branching of the alkyl substituents, especially near the etheric oxygen of the P atoms [124,130,131]. However, any enhancement of the separation efficiency of the extractant as a result of changes in the structure simultaneously causes a decrease in their extractive power [128,132]. Alkyl group chain branching enhances steric hinderance around the P-atom. Thus, an application of mono-acidic organophosphorus extractants would have to be based on a compromise between the separation and extraction efficiencies.

At low acidity, extraction by acidic organophosphorus extractants is a cation-exchange process. Thus, in so far as steric effect of the ligand, composition and structure of the extracted species is concerned, the strength of the complexes formed with metal ions should be dependent on the ionic radii, structure and electrostatic charge on the metal ions. It is evident from equations 13 and 14 in

Chapter One that the more stable the extracted complex, the higher will be the distribution coefficient of the metal ion. It seems natural therefore that the extractability of metal ions of the same charge should increase with decrease in size. This has been observed for such chemically similar groups of elements as the lanthanides and actinides. Extractability increases with increase in metal ion charge. Several authors have found that at high acidities, the distribution coefficient increases with increase in the hydrogen ion concentration and have remarked that under such conditions, the extraction mechanism is by solvation.

Despite the recent rapid proliferation of the phosphonate-type extractants, only a few have found commercial use, although not as widely as HDEHP. In recent years, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH[EHP]) produced under the names PC 88A (or P507) by Daihachi Chemical Company Japan and SME 418 by Shell Chemical Company has been attracting a lot of attention. It has been investigated for the extraction of a host of metal ions such as In(III) [133-136], Ga(III) [133,137], Mo(VI) [138-140], Pb(II) [141], Co(II) and Ni(II) [124,127,142-147], Cu(II) and Zn(II) [148], Th [149] and the lanthanides [150-152]. In the first ever reported extraction of U(VI) by an acidic organophosphonate, HEH[EHP] was found to excel over HDEHP by about a factor of two [153]. This extractant, as is true for phosphonates in general, has been shown to overcome such problems as high acidity required in extraction and stripping and emulsion formation which attend extractions with HDEHP. This difficulty in back extraction has limited the utilization of HDEHP in the separation of higher valent elements or heavy RE and group separations of mixtures containing large amounts of heavy REE. The mean separation factor with PC 88A between adjacent RE has been found to range from 2.0-3.04 depending on the anion in the aqueous phase. Cheng et al. [154] have studied the extraction of RE from HCl with HEH[EHP] in molten paraffin wax (in which it was dimeric) as solvent. They found that the same extraction mechanism observed in liquid-liquid extraction using HEH[EHP] in n-dodecane also applied in solid-liquid extraction and obtained a mean separation factor for adjacent RE of 2.78. They argue that the following merits; economy, safety, non-volatility and easy recovery makes extraction in molten wax attractive and reported the first observed tetrad effect of pH (at 50% extraction efficiency, E=50%) for the lanthanides. HEH[EHP] exhibits a separation factor for Co relative to Ni several dozen times that obtained with HDEHP. Reversed-phase chromatography using paper impregnated with HEH[EHP] as stationary phase and aqueous HCl and mixed solvent containing NH_4SCN as mobile phases showed promise for the separation of some noble metal ions [155]. Paper treated with a non-volatile diluent (n-dodecylbenzene) showed a great similarity to solvent extraction, which is likely due to dimerization of the ester in the stationary phase [156]. Reversed-phase column chromatography has been used in the determination of thermodynamics of extraction and separation of Y and Er by using HEH[EHP] coated on a resin that is predominantly macroporous styrene-DVB copolymer [156-159]. Duolite ES-63, a phosphonate-type ion exchanger has been used in the separation of pure lanthanum from La_2O_3 containing Nd_2O_3 and Pr_6O_{11} [160]. Zhai et al. used a polyether-type polyamide material treated with HEH[EHP] as a stationary phase in the reversed-phase extraction chromatographic separation of Sm and Gd, using 0.33 M HCl as the mobile phase [161]. Uranium (VI) in 0.01-1 M H_2SO_4 was quantitaively transported across a microporous polytetrafluoroethylene membrane impregnated with HEH[EHP] in kerosine containing 10% 1-decanol [162]. The use of supported liquid membrane (SLM) has been attracting attention as a promising alternative to liquid-liquid extraction and ion exchange for the separation and concentration of various metal ions [163]. Liquid membrane separation combines a solvent extraction and stripping process in a single step. The extractant (membrane liquid) is held in the pore structure of the support by capillary force (usually a polymeric solid) and the metal ions in the feed solution selectively form complexes with the extractant as carrier and diffuse through the membrane and the stripping occurs at the other side of the membrane. A new method based on liquid-liquid extraction, centrifugal partition chromatography [164], employing HEH[EHP] as organic stationary phase without solid support has been used in the separation of the lanthanides [165]. The attraction here, is that it is easy to change stationary phases empirically based on data on liquid-liquid extraction, which is not possible in the case of HPLC [166].

Peppard et al. [20f,119] found that in toluene carrier diluent and aqueous HCl, HEHΦP was about 200 times as strong an extractant for lanthanides as HDEHP. HEHΦP gave an average separation factor between successive lanthanides of 2.8 which is somewhat better than the 2.5 for HDEHP in extractions from HCl. Using HEHΦP as the stationary phase in reversed-phase chromatography, Fidelis and Siekierski [167] achieved a mean separation factor of 3.02 for the heavy lanthanides. A Cf/Cm separation factor of 105 was attained with HEHΦP, compared to 37 with HDEHP. Peppard et al. used HEHΦP to study the extraction behaviour of Eu(II) and Eu(III) [168]. A separation process was developed by Baybarz et al. [169] using HEHϕP in diethylbenzene from 1-1.5 N HCl for the actinides, but it was not applied because the presence of zirconium causes enhancement in their extraction and also promotes the extraction of several other metal ions [170]. Much of the equipment in the Oak Ridge National Laboratory transuranium processing plant was made of zirconium alloy. The strong extraction of zirconium by HEHΦP affects the scrub section of the separation. This difficulty was sufficient to force abandonment of the phosphonate process. Other workers have also observed the zirconium enhancement [171,172]. Yagodin et al. [172] reported an increase in the enthalpy of extraction of europium with HEHΦP by ca 2.5 kcal/mol in the presence of zirconium and hafnium. However, it should be noted that where such difficulty is not experienced, HEHΦP has proven to be a better extractant than the widely used HDEHP and HEH[EHP] [20f]. This is why we chose to continue with fundamental studies with this extractant. Quadrivalent Ti, Sn and Zr salts of phosphates and phosphonates have been found to be useful ion exchangers [173]. Baybarz [174] studied the dissociation constants of the heavy actinides with complexing agents using HEHΦP as the extracting agent. Previous work done in this laboratory on columns packed with phenylated Kel-F powder impregnated with HEHΦP and conditioned with 0.1 M $HClO_4$ isolated the REE as a group from the matrix elements and a clean chromatographic fractionation of Eu from La, Pr and Nd with HNO_3 was achieved [175].

The β-ketophosphonates have also been evaluated for liquid-liquid extraction. These extractants function by a cation exchange mechanism at low aqueous acidity (less than 2×10^{-4}) in perchlorate medium because of the enolate tautomer but behave as neutral extractants (like TBP) at higher aqueous acidity [176].

Some of the other organophosphonic acid extractants which have been evaluated for solvent extraction are: α-monooctyl anilinobenzylphosphonic acid [177,178]; monooctyl α-(2-carboxyanilino)benzylphosphonic acid [179]; 2-ethylhexyl phenacylphosphonic acid [180]; octyl dichloromethyl and n-octyl n-octylphosphonic acid [123]; n-octylphenylphosphonic acid [123,181]; n-octylchloromethylphosphonic acid [181]; 1-methylheptyl phenylphosphonic acid [120]; monoisodecylisodecyl and mono(3,5,5-trimethylhexyl)3,5,5-trimethylhexylphosponate [182]; n-decyl phenylphosphonic acid [183]. Pugia et al. [184] have used a crown ether phosphonic acid monoethyl ester in chloroform to extract alkali metals. They found that depending on the number of methylene groups joining the crown and phosphonate residues, complexation was either within the crown ether or through the monoethylphosphonate centre.

SULPHONIC ACIDS

A brief introduction to this class of extractants was given in Chapter One and an excellent review up to 1973 is given in reference [43]. This section will consider very briefly the subsequent applications of sulphonic acids in liquid-liquid extraction.

The sulphonic acids considered are those in which the sulphonate group ($-SO_4^-H^+$) is the active centre. In this group, dinonylnaphthalene sulphonic acid has been the most widely used and studied. Didodecylnaphthalene sulphonic (DDNSA) acid was introduced to study the effect of side chain size on the extraction characteristics of the sulphonates. Soldatov et al. [185] have found that DDNSA is less aggregated and has less water uptake capacity than DNNSA, but their selectivity for metal ions is about the same.

In dry organic solvents, dimers have been reported for DNNSA [42b,186,187] but under liquid-liquid extraction conditions, a considerable amount of water is extracted into the organic phase and the aggregation number is increased [43,188]. In their investigation of the thermodynamics and infrared spectroscopy of the hydration of DNNSA in heptane, Soldatov et al. [187] concluded that water molecules are more strongly bonded in DNNSA-micelles than in a resin network of crosslinking corresponding to about the same water uptake. The composition of the micelle when DNNSA in n-heptane is equilibrated with either 0.5 or 1.0 M $HClO_4$ as aqueous phase has been found to be $(DNNSA)_7.54(\pm 3)H_2O$ [189-191]. This composition has been shown to be essentially constant with temperature and independent of concentration above the critical micelle concentration (10^{-6} M) [190]. The authors showed that this is the actual composition of the micelle (i.e. the micelle is monodispersed) not a mean value for a mixture of species as was earlier proposed [192]. Ideality of the organic phase solution was also confirmed by the non-penetration of the heptane molecules into the aqueous core of the micelle. Several workers have proposed the existence of a ternary phase assemblage at equilibrium, namely, aqueous, organic and micellar phases because of the large aggregation of the sulphonates.

The sodium and lithium salts in n-heptane when pre-equilibrated with 1.0 M sodium and lithium perchlorate as aqueous phase gave micelle compositions $(NaDNNS)_4.28H_2O$ and $(LiDNNS)_4.28H_2O$, respectively [193]. In a similar experiment, it was found that solutions of DNNSA in heptane equilibrated with 1.0 M $NaClO_4$ or $LiClO_4$ at pH = 2 showed the formation of sodium hydrogen dinonylnaphthalene sulphonate involving five DNNSA moieties containing forty eight water molecules and lithium hydrogen dinonylnaphthalene sulphonates involving six DNNSA moieties containing forty four water molecules [194]. Bryan et al. [195] have reported the following composition for the DDNSA and the strontium salt micelles $(DDNSA.xH_2O)_{11}$ ($x = 7$-8) and $\{Sr(DDNS)_2.11H_2O\}_6$, respectively. It should be noted that there are conflicting reports on the aggregation number of the sulphonates in actual extraction media. Micelle formation in nonpolar solvents have been shown to be mainly due to strong (acid-base) interaction between polar groups in the micelle core [196]. Thus, with respect to the fact that the energy of hydration of a gaseous spherical ion is proportional to e^2/r, cations should affect the micelle aggregation number.

Patel and Thornback [197] have proposed that in a multi-element nuclear reprocessing plant, DNNSA could be used as a possible downstream-end clean up of rhodium. Rhodium in nitric acid media is a major valuable by-product of the nuclear industry. Khan and Morris [198] have also separated rhodium from iridium, platinum, palladium and silver and purified it in dilute HCl by combining precipitation and solvent extraction using DNNSA in n-heptane. Solvent extraction employing DNNSA or DDNSA have been used in the removal of cobalt and other metal ions from liquid radioactive wastes [199,200], purification of wet phosphoric acid [201], hydrolysis and complexation of Am(III) in the presence of acetic and tartaric acids [202], complexing of Th(IV), Np(IV), and Pu(IV) by various complexing ions [203], extraction of Fe, Zn, Cu, Ni, Cr and other metal ions from waste metal sludges, waste mineral acids and metal finishing waste solutions [204,205] and extraction of various metal ions.

The sulphonates although effective extractants show little selectivity for related groups of metal ions. Extractability increases with increase in the formal charge of the free metal ion. In the past two decades, in order to introduce selectivity into the extraction of metal ions from the aqueous phase into the organic phase, the size selectivity of crown ethers have been exploited as a means to synergize extraction with sulphonates and liquid ion exchangers in general [194,206-213]. Synergistic effects have been related to the matching of the ion size to the crown cavity diameter and has been explained to be due to interactions between the crown molecules and the metal ions, with the presence of the anion of the liquid exhanger to balance the charge of the metal ion and preserve electrical neutrality in the organic phase. McDowell et al. [214] suggested the possible existence of interaction of additional sulphonic acid molecules with the complex molecule (metal-crown-micelle) in the organic phase. Depending on the crown:sulphonate ratio, Ensor et al. [212] found that the micellar extraction mechanism by the sulphonates is preserved; thus, the crown-metal complex is solubilized into the sulphonate micelle [215-218]. Crowns developed for cesium and strontium have been used in conjunction with DNNSA and DDNSA in the PUREX TBP and kerosine matrix for their separation [210,213]. Synergistic enhancement has been achieved in the extraction of hexavalent actinides by combining DNNSA and neutral organophosphorus extractants [219]; extraction of trivalent elements with an organic solvent consisting of DNNSA and HDEHP [216-218] or HEHΦP [217], where the organophophorus acids were primarily introduced to suppress emulsification. Carboxylic acids have also been used in combination with DNNSA [220]. Osseo-Asare and Kenney [221] have reported a catalytic effect on the extraction of nickel with the oxime LIX63 by sulphonates which was due to the solubilization of both the metal and the extractant by the micelles resulting in an increase in the interfacial concentration of these species.

Supported liquid membrane (SLM) utilizing DNNSA and a crown ether dissolved in n-dodecane as carrier, the crown to synergize the carrier, has been used in the removal of Cs^+ from strongly acidic solutions [222]. Högfeldt and Muraviev [223] have reviewed the stability and ion exchange properties of Amberlite XAD-2 impregnated with DNNSA and concluded that solvent-impregnated resins have properties intermediate between those of solid resins and liquid extractants.

OBJECTIVES OF THE RESEARCH

This research evaluates the possibilities of fractionating the rare earth elements (REE) by solvent extraction with 2-ethylhexyl phenylphosphonic acid, HEHΦP, and separating them as a group from other matrix elements. Other elements studied in this thesis occur in some REE minerals and their ions have charge and/or size similar to the REE. Ions with different charge and/or size were included to study extractability. HEHΦP is a fairly specific extractant for large polyvalent ions and its novelty in analytical chemistry was pursued.

The research was directed mainly towards the investigation of extraction mechanisms and the thermodynamic parameters affecting the extraction process. Extraction mechanisms were studied by the slope analysis method and ^{31}P NMR spectroscopy and thermodynamic parameters were obtained by the examination of the temperature coefficient of extractability. At the molecular level, thermodynamic parameters provide valuable information about extraction mechanisms.

Thermodynamic parameters with dinonylnaphthalene sulphonic acid (DNNSA) as extractant were also investigated in order to compare the sulphonate and phosphonate liquid cation-exchangers. DNNSA in low polarity solvents has been shown to behave in much the same way as do solid resins containing the same functional group.

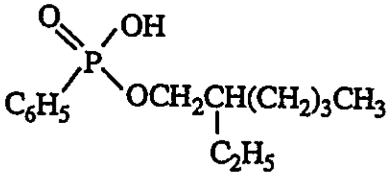
Analysis of solutions containing all the REE, even by the most specific and powerful methods like ICP and ICP-MS, still suffer from inter-element spectral interferences. This is particularly the case if the relative amounts of the REE are different from typical geological samples. Isolation from matrix elements and rapid fractionation of the group into at least two sub-groups is therefore desirable and was pursued in this investigation. This will be done by using HEHΦP as a bulk extractant on an inert support from which one half of the group will be eluted with acid and the other half stripped off with a polar organic solvent.

The methodology used was directed towards direct coupled plasma or atomic absorption spectrometry and spectrophotometry finish.

CHAPTER IV

MATERIALS AND METHODS.

Synthesis of HEHΦP

HEHΦP was prepared according to the method of Kantipuly [175]. This entailed the alcoholysis of phenylphosphonic dichloride with 2-ethyl-1-hexanol. Both reagents were obtained from Aldrich Chemical Co. A 1:1.5 molar ratio, respectively, of the above reagents in benzene were mixed in a pressure bottle and stirred for 48 hours at room temperature. The pressure was released carefully and the mixture washed several times with water to remove unesterified phenylphosphonic acid. The mixture was taken up in ether and shaken with 10% NaOH solution. The aqueous phase was scrubbed with benzene to remove alcohol and any diester and then acidified with concentrated hydrochloric acid to liberate the monoester, HEHΦP. This was taken up in anhydrous diethyl ether, dried with $MgSO_4$ and filtered. Solvent was removed under reduced pressure. The purity of the product was found by ^{31}P NMR spectroscopy to be 99% or better. The structure,  $C_6H_5P(=O)(OH)OCH_2CH(C_2H_5)(CH_2)_3CH_3$, was confirmed by proton and ^{13}C NMR spectroscopy. The spectra are shown in Figures 1 and 2, respectively. All the spectra were obtained with a Varian XL-300 instrument. Anal. Found: C = 62.07%; H = 8.63%. Calc. for $C_{14}H_{23}O_3P$: C = 62.21%; H = 8.57%.

The ^1H NMR spectrum was obtained in $CDCl_3$ with the instrument operating at 300 MHz. The chemical shifts are relative to TMS. The multiplet resonances at 7.82 - 7.38 ppm are due to the aromatic protons and those at 1.52 - 0.79 ppm are due to the fifteen aliphatic protons and those at 3.91 - 3.86 ppm are due to the methylene protons on the $O{=}P{-}OCH_2{-}$ moiety . The ^{13}C NMR spectrum was obtained in

FIG. 1: ^{1}H NMR spectrum of HEHΦP in $CDCl_3$

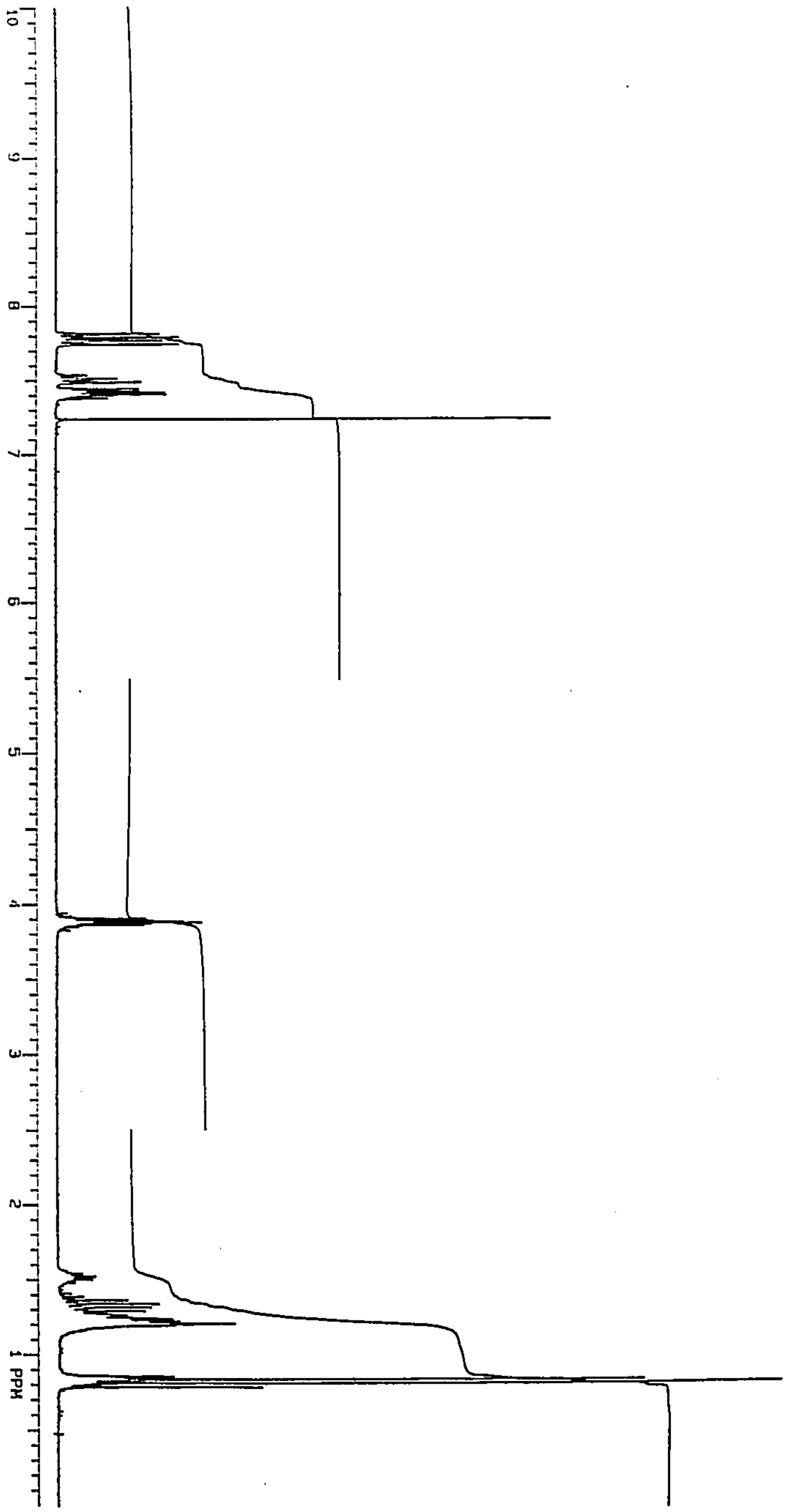
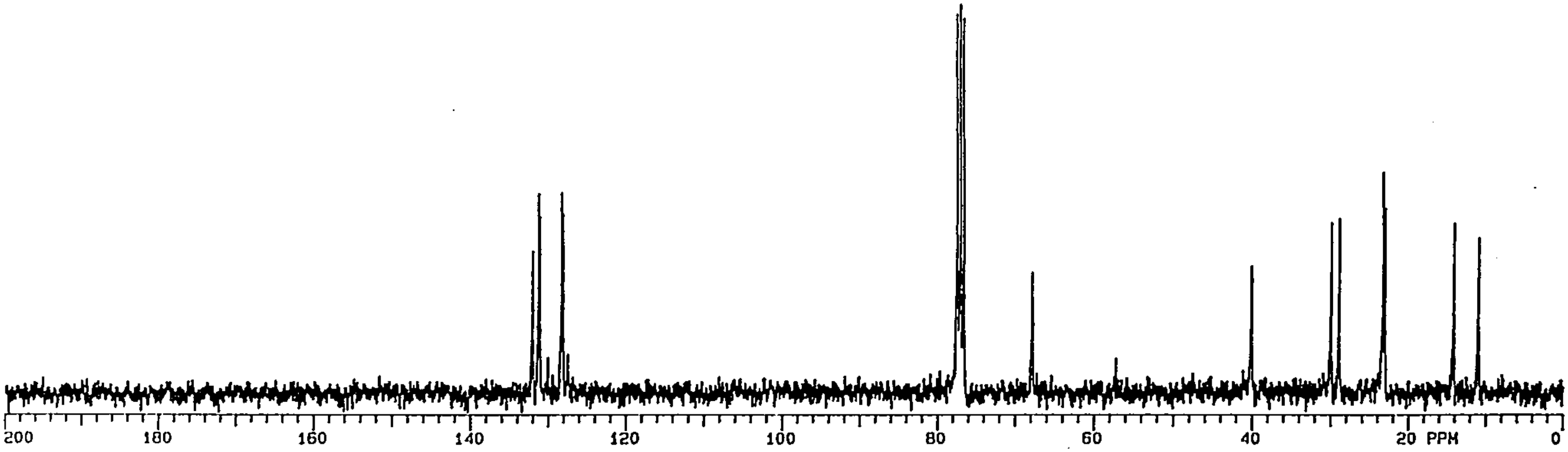

10
9
8
7
6
5
4
3
2
1 PPM

FIG. 2: ^{13}C NMR spectrum of HEHΦP in $CDCl_3$


200
180
160
140
120
100
80
60
40
20 PPM
0

$CDCl_3$ with the instrument operating at 75.429 MHz. The chemical shifts are relative to TMS.

Purification of DNNSA

Dinonylnapthalenesulphonic acid (DNNSA) was obtained from Morton Thiokol, Inc., Alfa Catalog Chemicals, Danvers, Massachusetts, as a 50% solution in kerosene. An anion exchange clean-up [224] was used to obtain a pure solvent free DNNSA. Dowex 1X8-100, 50 - 100 mesh in the chloride form obtained from Sigma Chemical Co. was soaked overnight in water. The water was decanted and the wet resin soaked in 2 M HCl for 2 hours, washed free of acid, packed in a column and washed with 1 - 2 M NaOH until there was no positive chloride test. This way, the resin was converted to the OH^- form. The DNNSA solution in an equal volume of 99.9% ethanol was introduced into the column. After adsorption of DNNSA, the column was washed free of neutral impurities (until the effluent was clear) with 99.9% ethanol. The adsorbed DNNSA was eluted with 1 M HCl in 99.9% ethanol. The eluant was evaporated to dryness under reduced pressure at 50 - 55°C. The product was taken up in ether, dried with $MgSO_4$, filtered and the solvent removed under reduced pressure. The product was a dark yellow-coloured viscous liquid and its purity was confirmed by proton and ^{13}C NMR spectroscopy. The spectra obtained with a Varian XL-300 Spectrometer are shown in Figures 3 and 4, respectively.

The ^1H NMR spectrum was obtained in $CDCl_3$ relative to TMS. The resonance at 5.03 ppm is assigned to the acidic proton of DNNSA and H_2O on the basis of the disappearance of the peak upon deuterium exchange with D_2O (see Figure 5). The multiplet resonances at 1.73 - 0.59 ppm and 7.80 - 7.59 ppm are due to the thirty-two equivalent aliphatic protons on the dinonyl and the five aromatic protons

FIG. 3: ^1H NMR spectrum of DNNSA in $CDCl_3$

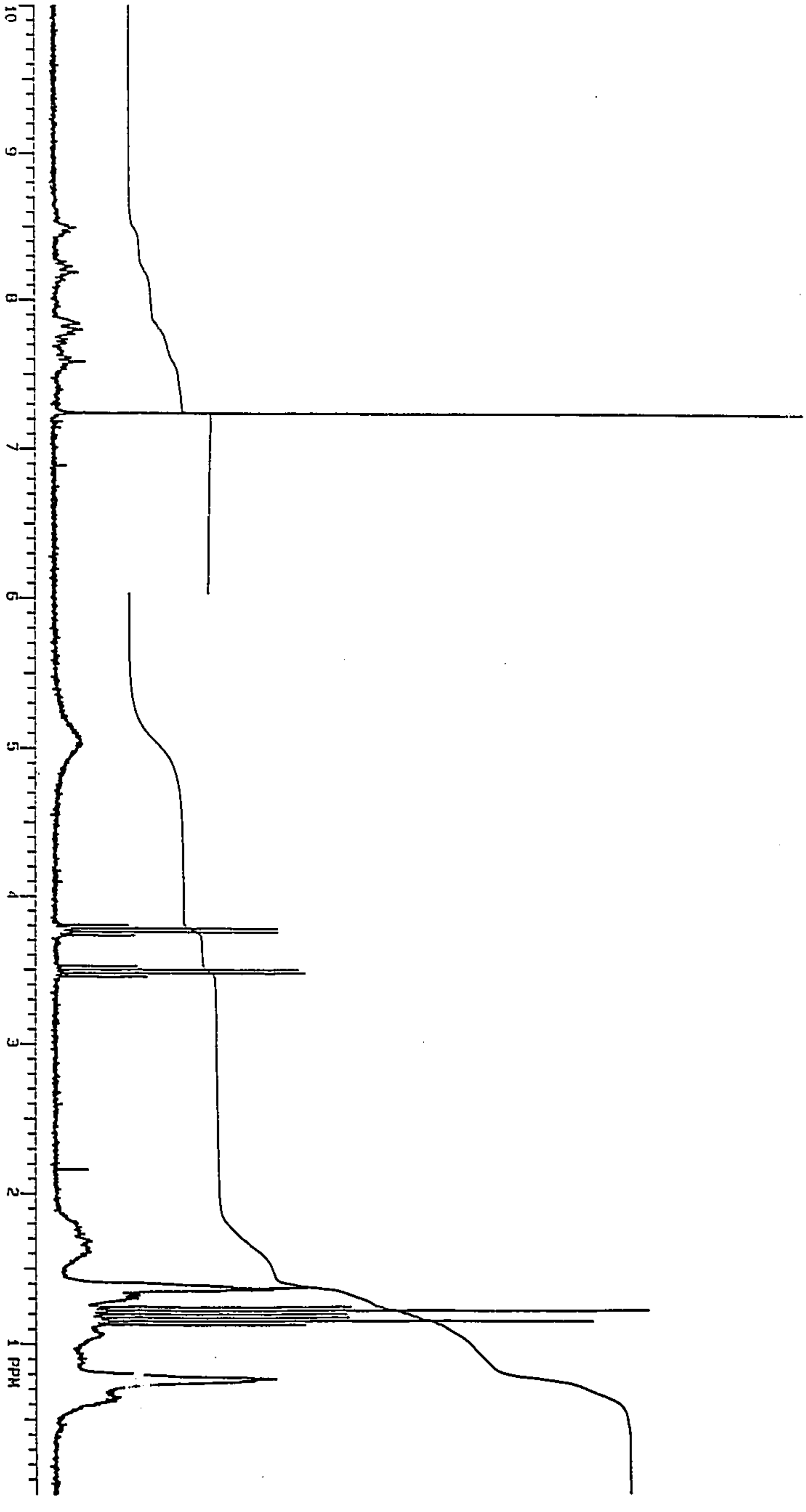

10
9
8
7
6
5
4
3
2
1 PPM

FIG. 4: ^{13}C NMR spectrum of DNNSA in $CDCl_3$

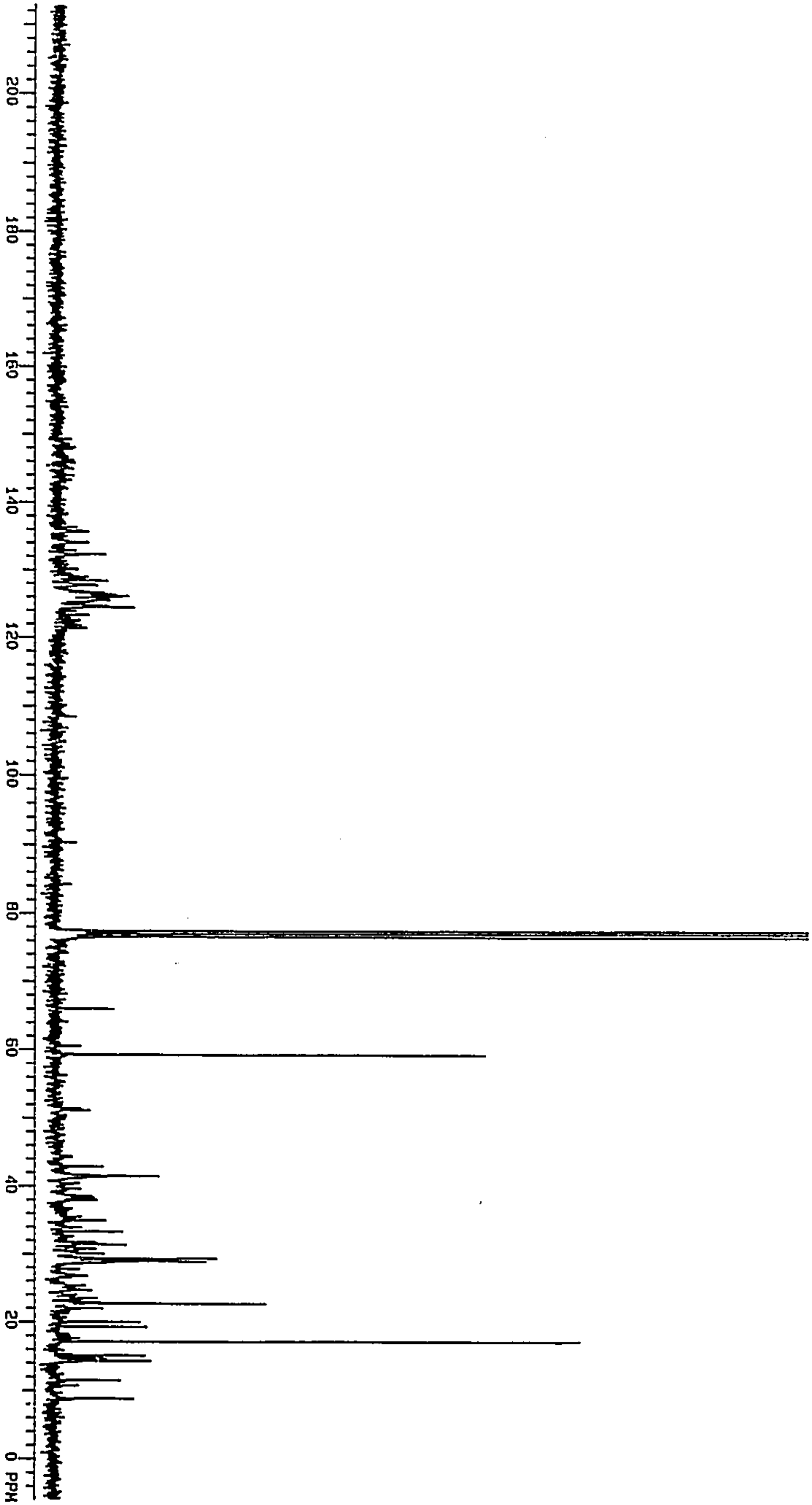
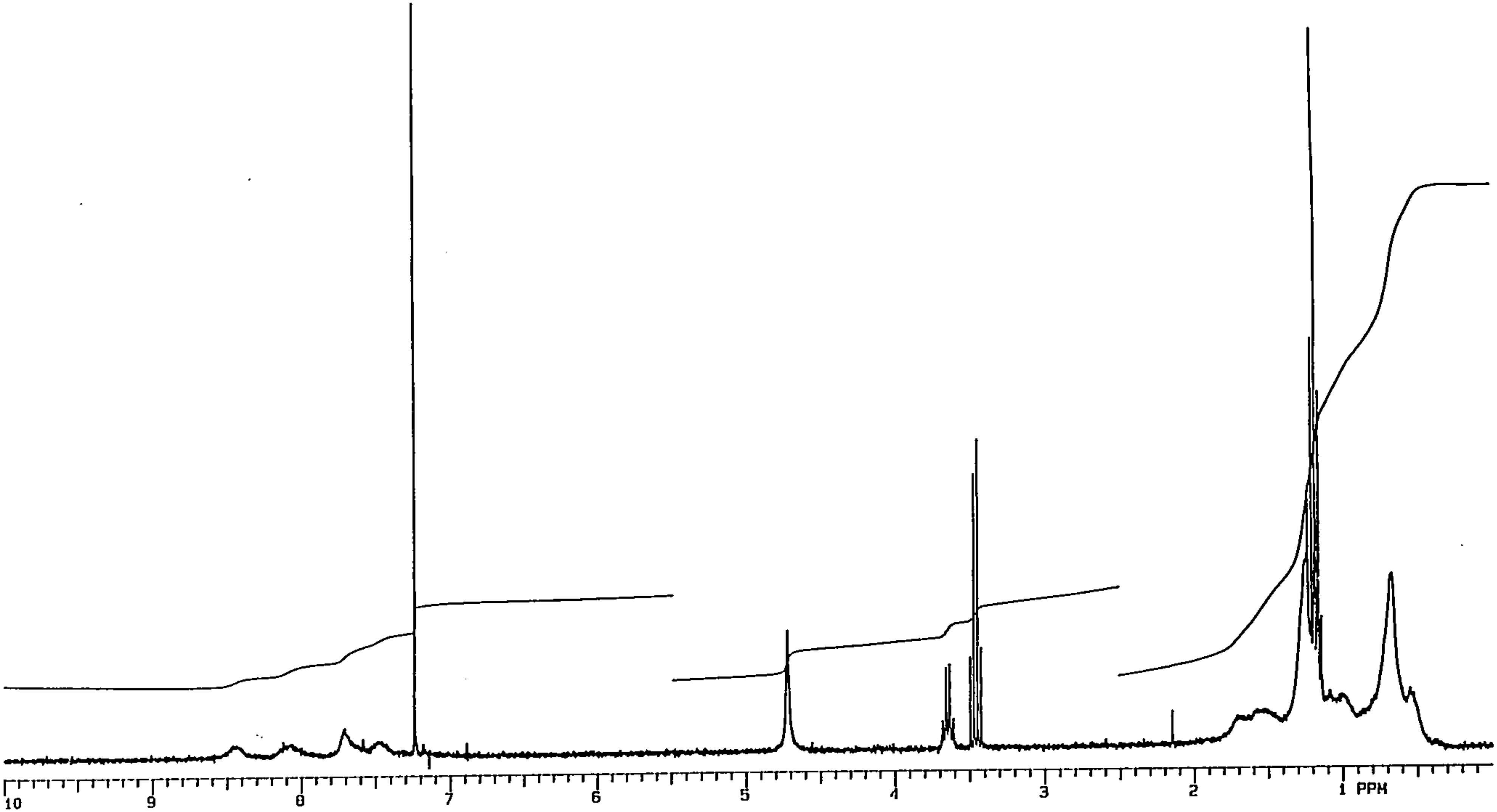

200
180
160
140
120
100
80
60
40
20
0 PPM

FIG. 5: ^1H NMR spectrum of D_2O exchange of DNNSA in $CDCl_3$


10
9
8
7
6
5
4
3
2
1 PPM

on the naphthalene residues, respectively. Those at 3.76 and 3.48 are due to the α-methylene protons on the two nonyl groups. The ^{13}C NMR spectrum was obtained in $CDCl_3$ relative to TMS.

Preparation of metal ion solutions

Atomic absorption standard solutions of the REE in nitric acid were obtained from Aldrich Chemical Co., Inc. The perchlorates were prepared by evaporating aliquots to dryness and cautiously fuming twice with 70% $HClO_4$ (B. D. H. Analar grade), evaporating each time to dryness. The resulting perchlorate salts were taken up in 6 M $HClO_4$ and diluted to the required volume. Acidities were established by titrating with standard NaOH using phenolphthalein as indicator. Appropriate weights of reagent grade chemicals: $Bi(NO_3)_3.5H_2O$ (Baker), $CaCO_3$ (Baker) and Zn metal (Fisher) powders were dissolved in HNO_3 and granular Al metal (Fisher) was dissolved in 6 M HCl and treated in the same manner as the atomic absorption standard solutions.

Determination of distribution ratio, D

The organic phases had extractant concentrations in the range 0.01 - 0.1 molar HEHΦP in practical grade (Anachemia) hexane or Analar grade petroleum ether (100 - 120°C) and 0.01 molar DNNSA in petroleum ether. Normally, a 5 ml volume of the organic phase was stirred magnetically with 5 ml of metal ion (10^{-4} molar) in vials held in a thermostatted bath at the required temperature. Ten minutes were allowed to attain a constant temperature and chemical equilibrium was attained in 5 minutes but routine stirring times were longer than this. After equilibration, the phases were allowed to settle for 15 minutes before separating. In the case of zinc and calcium with DNNSA at room temperature, it was necessary to centrifuge before separating the phases. Analyses of both aqueous and organic fractions yielded mass recoveries of greater than 98%. Therefore, for much of the data that follows, the aqueous phase was analyzed and the metal content of the organic phase found by difference. The concentrations at temperatures other than room temperature were corrected for the effect of expansion.

The coefficient of expansion of the aqueous phase was assumed to be the same as that of pure water. The densities of the organic phase were measured by immersing a filled pycnometer in the thermostat bath and weighing after thermal equilibrium had been attained.

The distribution coefficient K_d at temperature T was given by the relation

$$K_d(T) = \frac{[M]_{org,RT}}{[M]_{aq,RT}} \times \frac{\rho_{w,RT}}{\rho_{w,T}} \times \frac{\rho_{org,T}}{\rho_{org,RT}} \qquad 1$$

where RT is room temperature, ρ_w is the density of water and ρ_{org} is the density of the organic phase.

The lanthanides and aluminium were determined by direct-coupled plasma emission, DCP, spectrometry and the former sometimes by spectrophotometry using Arsenazo III. Zinc and calcium were determined by atomic absorption spectrometry. Bismuth was determined by spectrophotometry as the yellow complex, BiI_4^- [225]. The aqueous phases were run without treatment but the organic phases were wet-ashed with $HClO_4$ and HNO_3 prior to analysis. The small amount of phosphate formed by wet-ashing the extractant was found not to interfere in the determination of bismuth.

Analyses were run in duplicate. Some, but not all, of the equilibrations were run in duplicate as well. The distribution ratio, D, was calculated by dividing the concentration of the ion in the organic phase by that in the aqueous phase.

DCP spectrometry

The instrument used was a single-channel Beckman Spectraspan V direct current plasma atomic emission spectrometer. A functional block diagram of a DCP spectrometer is shown in Figure 6. The spectrometer used in this work consists of a dc power supply with gas controls for monitoring and adjusting flows of argon to the dc plasma jet, a three-electrode (two graphite anodes and a tungsten cathode) plasma jet in an inverted "Y" configuration with argon flowing through the ceramic sleeves (see Figure 7), an echelle grating monochromator, a microprocessor-based control and data acquisition system, an Okidata µ 88A microline printer, a dynamic background compensator (DBC-33) and an auto-sampler. The DCP temperature in the excitation region is in the region 6000 - 7000° K. Used in combination with a quartz prism the echelle grating monochromator provides a two-dimensional spectral pattern 4" x 5" (10.2 x 12.7 cm) in area covering wavelengths from 180nm to 800nm and allows simplified photographic (spectrograph) operation for qualitative analysis. This dc plasma-echelle spectrometer system offers acceptable levels of selectivity, sensitivity, speed and economy for the analysis of trace elements.

The wavelengths used and some of the fixed instrumental parameters are listed in Table 3. The wavelengths were selected on the basis of maximum sensitivity while at the same time minimizing spectral interference. The wavelengths were normally "peaked" with a high standard solution of the particular element to be determined. The system was calibrated using single element standard and blank solutions. This was always checked by measuring several standards in those instances when the analyte concentrations were low. The instrument data acquisition and control system is designed to establish a two-point calibration curve with the blank and a single standard solution. The photomultiplier tube(s) in the detector converts sample light

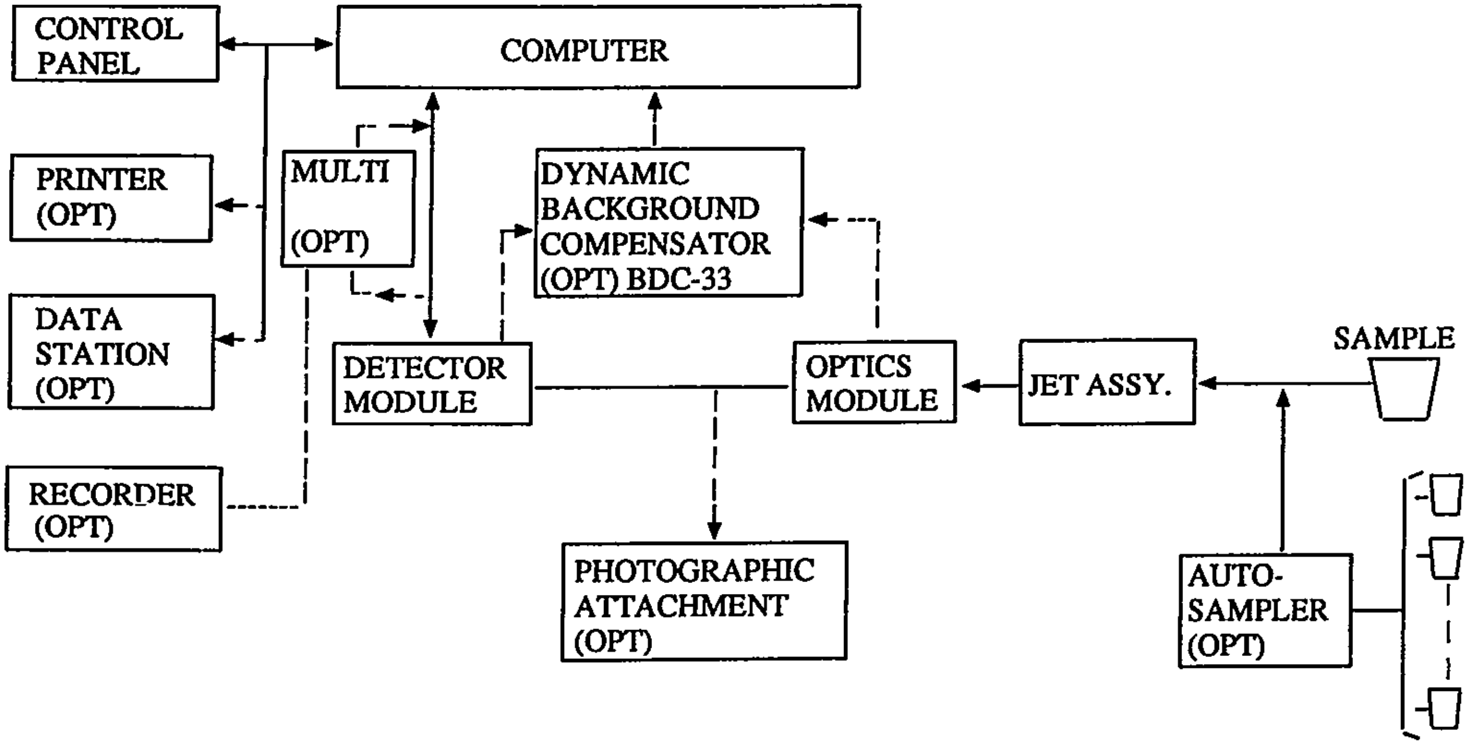


Figure 6: Functional block diagram of a DCP spectrometer

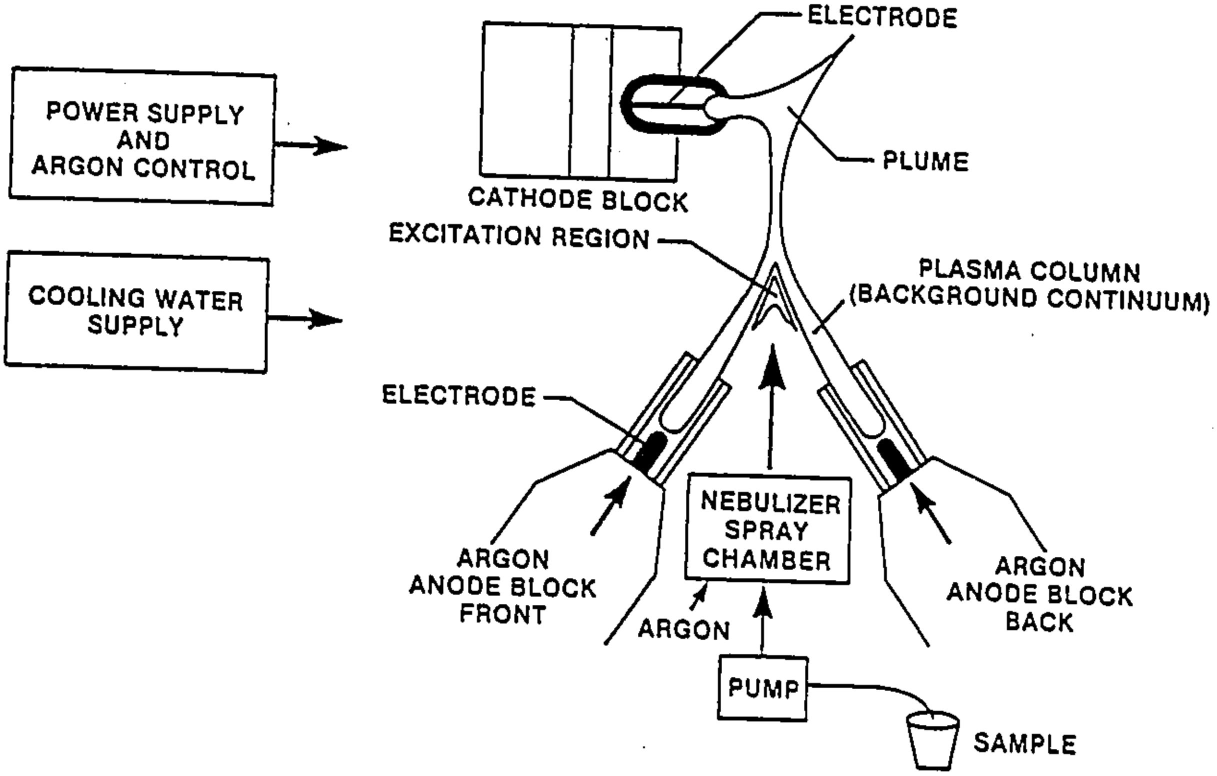


Fig. 7: Schematic diagram of the DC plasma jet.

Table 3

Analytical DCP wavelengths and instrument settings

Element	Wavelength (nm)	Instrument settings
La	398.89	
Pr	414.31	Spectral bandpass = 0.017nm
Nd	430.36	Entrance slit 50 x 300 μm (horizontal x vertical)
Sm	359.26	Exit slit 100 x 300 μm (horizontal x vertical)
Gd	364.62	Argon supply: Commercial grade (99.5%) ;
Tb	367.64	typical flow rate of 7 liters/min.
Dy	353.17	Sample uptake rate: 2 ml/min (approx.)
Er	369.25	
Lu	261.54	
Al	308.215	

intensity to a proportional electric current, which is first converted to voltage and amplified. The microprocessor uses the calibration curve established with the standard and blank solutions prior to the sample to convert the measured voltage to the analytical concentration of the sample by interpolation. Experience shows that there is a linear relationship between voltage and analyte concentration. All blank, sample and standard solutions contained 5000 μg per ml strontium to provide a uniform matrix so that the plasma temperature is uniform from sample to sample and also to minimize differential enhancements caused by the presence of Na or K which is particularly necessary in order to obtain a linear calibration curve for aluminium [226]. Fixed wavelength intensity measurements were based on duplicate 5-second integrations during a single nebulization period.

Column preparation.

A known amount of phenyl modified Kel-F prepared according to the method of Kantipuly [175] was stirred with an appropriate weight of HEHΦP in hexane. The solvent was evaporated under a heat lamp, while stirring occasionally with a glass rod. The coated phenyl Kel-F was hydrated by stirring in 0.1 M $HClO_4$ equilibrated with HEHΦP for one hour. A glass column was made hydrophobic by exposing to dimethyldichlorosilane vapours in an oven. The wet slurry of phenylated Kel-F in $HClO_4$ was transferred to the column fitted with a glass wool plug at the bottom. The packing was allowed to settle with constant tamping. A reservoir with a ball joint to enable application of overpressure was fitted on top of the glass column. The column was conditioned by washing with 0.1 M HNO_3 equilibrated with HEHΦP with the application of pressure to remove air bubbles.

A 0.05 or 0.1 ml aliquot of mixed RE solution (yielding 250 μg ml^{-1} or less of each) in 0.1 M HNO_3 was placed on top of the column, washed in with 50 ml of 0.1 M HNO_3. One half of the lanthanide series, i.e., La - Gd, was eluted with 200 ml of 0.9 M HNO_3 and the other half, Tb - Lu, with 20 ml of 99.9% ethanol. The flow rate was 0.5 ml per minute. All acid eluents were pre-equilibrated with HEHΦP to prevent depletion of that coated on the support. Acidities were determined as previously mentioned. The eluates were evaporated to dryness and wet-ashed twice with $HClO_4$ and HNO_3. The final residue was taken up in 20 ml of 0.5 M HNO_3 containing 5000 μg per ml strontium and the concentrations of the metal ions were determined by DCP.

Preparation of NMR samples.

Lanthanum nitrate (99.99%) was obtained from Johnson Matthey Co. The perchlorate was prepared by cautiously fuming twice with 70% $HClO_4$ (B. D. H., Analar grade), evaporating to dryness each time. The perchlorate salt was taken up in 1 M $HClO_4$ and final acidites were fixed to the required values either by dilution or addition of acid. Spectra grade n-hexane and toluene were also obtained from B. D. H. chemicals. Equal volumes of 0.1 M HEHΦP in n-hexane or toluene and an aqueous solution of appropriate acidity containing 0.1 M lanthanum were shaken for 15 minutes or more at 25°C. The phases were separated and the ^{31}P NMR spectra of the organic phases were recorded on a Varian XL-300 instrument. 10 mm outside diameter sample spinning tubes were used. The chemical shifts, δ, are relative to 85% H_3PO_4. The spectra of the organic phases following extraction with acid solutions without lanthanum were also recorded.

$La(EH\Phi P)_3$ solid polymer was prepared by contacting equal volumes of 0.033 M aqueous solution of $La(NO_3)_3.6H_2O$ with 0.1 M n-hexane solution of HEHΦP for

15 minutes. Some white gelatinous solid appeared in the organic phase. The phases were separated and the aqueous phase equilibrated with a second portion of 0.1 M HEHΦP in n-hexane. The two organic portions were combined and the solvent removed under vacuum. The oily residue was treated with acetone, whereupon crystals appeared. The solid was removed by filtration and recrystallized from acetone. The product was air dried at 105°C for one hour. Anal. Found: C = 53.15%, H = 6.90%; Calc. for $La[(C_8H_{17}O)(C_6H_5)PO_2]_3$, C = 53.25%, H = 7.03%. The ^{31}P solid state NMR spectrum at ambient temperature was recorded on a Bruker MSL-300 Spectrometer with a Doty Scientific probe. The chemical shift is relative to solid $(NH_4)_3PO_4$. The radiofrequency amplitude was 40 kHz and the magic angle spinning rate was 3 - 5 kHz.

CHAPTER V

RESULTS AND DISCUSSION

Extraction isotherms

Figure 8 shows extraction isotherms for Dy^{3+} and Zn^{2+} for extractions with HEHΦP. As the plots are not linear, it is evident that the ions do not obey Henry's Law in one or both phases in each case. The ionic strength of the aqueous phases is very largely determined by the fixed concentration of acid present. The aqueous phases containing these rather low concentrations of metal ion should have nearly constant ionic strength and should therefore obey Henry's Law to a good approximation. The situation is otherwise for the organic phase, however. It is shown later that the stoichiometric ratios of HEHΦP to Dy^{3+} and Zn^{2+} are 5:1 and 3:1, respectively, in the complexed species when the extractant is in large excess. As the extractant concentration was only 0.01 molar, a large fraction of the extractant was bound to the metal ions in the organic phases that were relatively concentrated in metal ion. For example, in the most concentrated zinc solution (0.0015 M), if there is a 3:1 mole ratio of HEHΦP to zinc, 45% of the extractant would be bound to zinc. The curvature of the extraction isotherms suggests that with such a high degree of loading, the stoichiometry of the extracted species cannot be maintained at 3:1.

There is an additional reason for the curvature. As the extractant is deprotonated upon complexing, the acidity of the aqueous phase is increased. This would have a considerable effect in the case of zinc extraction where the initial acid concentration of the aqueous phase was 0.01 M. However, in the dysprosium case, the high acidity, 1.0 M, would not be changed appreciably by the complexing.

Except for the NMR investigations, in the experiments described below, the metal ion concentrations were kept small relative to the extractant concentration so that both phases invariably obeyed Henry's Law. ^{31}P NMR investigation of the most

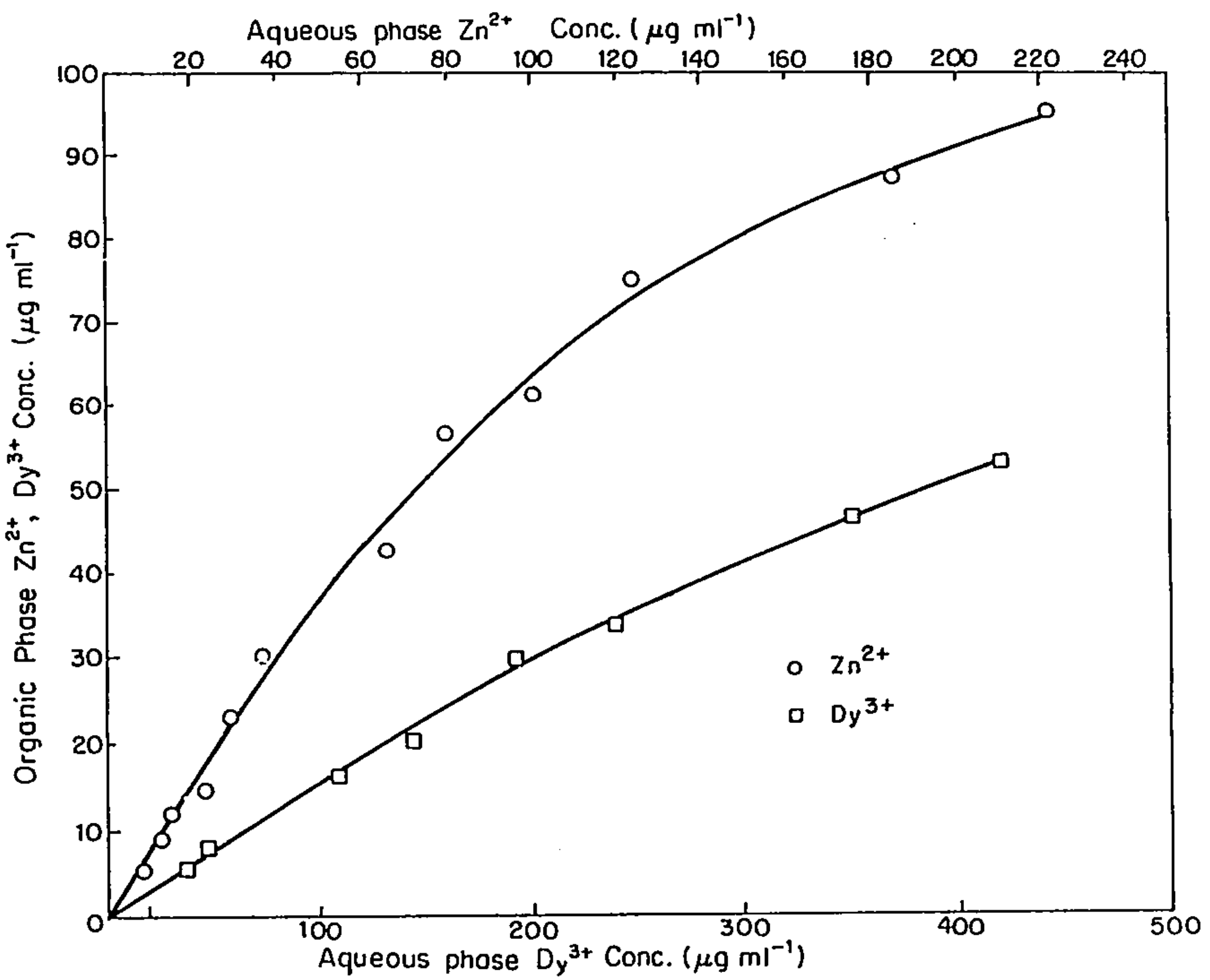


Fig. 8: Extraction isotherms for Zn^{2+} from 0.01 M $HClO_4$ and Dy^{3+} from 1.0 M $HClO_4$ into 0.01 M HEHΦP in hexane at room temperature

concentrated metal-carrying organic phase showed only 4% complexing. Therefore, to a first approximation $[HY] \equiv C_R$, the total extractant concentration; HY being present almost exclusively in the dimeric form in hexane.

Degree of polymerization of the extracted species

Assuming that the metal ion M^{n+} is extracted as a j-merized complex of composition $(MY_n.xHY)_j$* into hexane with HEHΦP form aqueous $HClO_4/NaClO_4$ solution, the extraction equilibrium can be written as follows [227]:

$$jM^{n+} + j(n+x)/2(HY)_2 \rightleftharpoons (MY_n.xHY)_j + njH^+ \qquad 2$$

The equilibrium constant is

$$K_e = \frac{[(MY_n.xHY)_j]\ \ [H^+]^{nj}}{[M^{n+}]^j\ [(HY)_2]^{j(n+x)/2}} \qquad 3$$

Then, the distribution ratio of M^{n+} is given by

$$D = \frac{C_{M,O}}{C_{M,A}} = \frac{j\,[(MY_n.xHY)_j]}{C_{M,A}} \qquad 4$$

which leads to

$$C_{M,O} = jK_eC_{M,A}{}^jC_R{}^{j(n+x)/2}C_H{}^{-nj} \qquad 5$$

assuming no side reaction (hydrolysis and/or complex formation) in the aqueous phase, where $C_{M,A}$, C_H and $C_{M,O}$ denote the metal and hydrogen ion concentrations in the aqueous phase and metal ion concentration in the organic phase, respectively.

Taking logarithm of equation 5,

$$\log C_{M,O} = \log\{jK_eC_R{}^{j(n+x)/2}\} + j\log C_{M,A}C_H{}^{-n} \qquad 6$$

Therefore, the degree of polymerization, j, of the metal-extractant complex can be found from the slope of the plot of $\log C_{M,O}$ versus $\log C_{M,A}C_H{}^{-n}$ at constant

---

* When the extractant is in excess.

concentration of the extractant in the organic phase, C_R. The straight line plots of unit slope as shown in Figure 9 implies that j=1, i.e., the metal ions are extracted as monomers, $MY_n.xHY$. Deviation of the slopes from unity at high organic phase loading should be expected and will be due to the fact that the uncomplexed extractant concentration is not constant and/or other species different from $MY_n.xHY$ may be extracting.

The number of free HEHΦP dimer molecules involved in the extracted species can be determined by expressing the distribution ratio of the metal ion as follows (j=1):

$$D = \frac{C_{M,O}}{C_{M,A}} = \frac{K_e \, C_R^{(n+x)/2}}{C_H^{\,n}} \qquad 7$$

$$\text{or } \log(DC_H^{\,n}) = \log K_e + (n+x)/2 \log C_R \qquad 8$$

The extraction equilibrium constants given in Table 4 have been obtained from the intercepts of the plots of $\log(DC_H^{\,n})$ versus $\log C_R$ shown in Figures 10 and 11 at constant hydrogen ion concentrations. The slope of the plots is equal to (n+x)/2. The non-linearity in the $\log K_e$ for the lanthanide ions may be attributed to the varying aqueous phase acidity.

Acid dependencies

Log-log plots of the distribution coefficient against acid concentration are shown in Figures 12 and 13. The slopes indicate that K_d is inversely second power and third power dependent upon the initial aqueous phase acidity for the M(II) and M(III) ions, respectively. The ionic strength was adjusted to a constant value with $NaClO_4$ throughout each series of measurements.

Peppard et al. [20f] obtained the same third power dependence in the extraction of M(III) ions with HEHΦP in toluene. Second power dependence has been reported for the extraction of Ca^{2+} with n-octyl esters of phenyl and chloromethyl phosphonic acids [181].

The results suggest that the neutral complexes enter the organic phase and the ion charge is neutralized by the extractant in anionic form. It follows that the perchlorate ion does not enter the complex. Were it to do so, the order of dependence upon acid concentration would be less than that observed.

Extractant dependencies

Studies of the dependence of extraction upon extractant concentration provide information about the composition of the extracted complexes. From the results reported elsewhere [228], extraction of lanthanum and praseodymium is third power dependent upon extractant concentration while the order drops to 2.5 for the heavier lanthanides. The neodymium and samarium plots are intermediate with slopes of 2.8 and 2.7, respectively. The plots indicate third order dependence for Ca^{2+} and Bi^{3+} and an order of 1.5 for Al^{3+} and Zn^{2+}. Peppard et al. reported third order dependence for M(III) ions when extracted with the extractants mentioned above [20f]. Calcium exhibited an order of 2.5 when extracted with n-octyl chloromethylphosphonic acid and 3.0 with n-octyl phenylphosphonic acid [181]. An extractant dependence of order 1.5 has been observed for the extraction of Zn^{2+} with HEHEHP [148] and HDEHP [229]. The order is thus variable, depending upon the ion charge and size and upon the particular choice of extractant.

The extractions with HEHΦP follows the equations:

$$La^{3+}(Pr^{3+},Bi^{3+}) + 3(HY)_2 \rightleftharpoons M(HY_2)_3 + 3H^+ \qquad 8$$

$$Ln^{3+} + 2.5(HY)_2 \rightleftharpoons LnY(HY_2)_2 + 3H^+ \qquad 9$$

$$Ca^{2+} + 3(HY)_2 \rightleftharpoons Ca(HY_2)_2(HY)_2 + 2H^+ \qquad 10$$

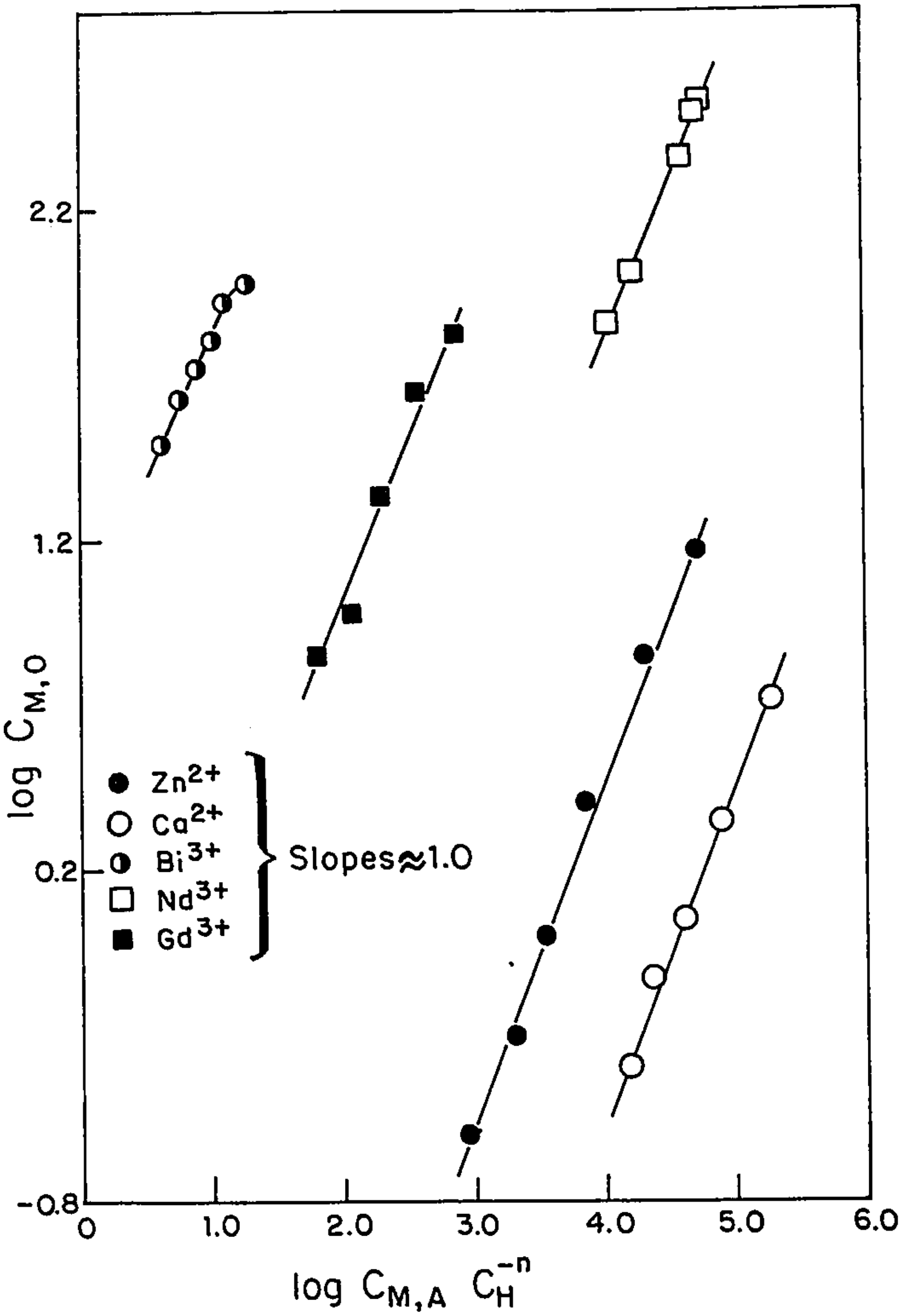


Fig. 9: Determination of j-value for the extraction of Zn^{2+} (μ=0.25); Bi^{3+} from 1 M $HClO_4$; Ca^{2+} (μ=0.05): Gd^{3+} (μ=2.0) and Nd^{3+} at varying acidity into 0.025 M HEHΦP in hexane.

Table 4

Extraction equilibrium constants for the M(II) and M(III) ions studied

Metal ion	$[HClO_4]$	log K_s
Zn^{2+}	0.025	-0.32 ± 0.06
Ca^{2+}	0.01	-0.01 ± 0.07
Bi^{3+}	1.0	5.29 ± 0.06
La^{3+}	0.10	1.49 ± 0.05
Pr^{3+}	0.15	2.34 ± 0.04
Nd^{3+}	0.20	2.14 ± 0.04
Sm^{3+}	0.25	3.02 ± 0.02
Gd^{3+}	0.50	3.33 ± 0.06
Dy^{3+}	1.0	4.39 ± 0.04
Er^{3+}	2.0	4.98 ± 0.03
Lu^{3+}	5.0	6.30 ± 0.04

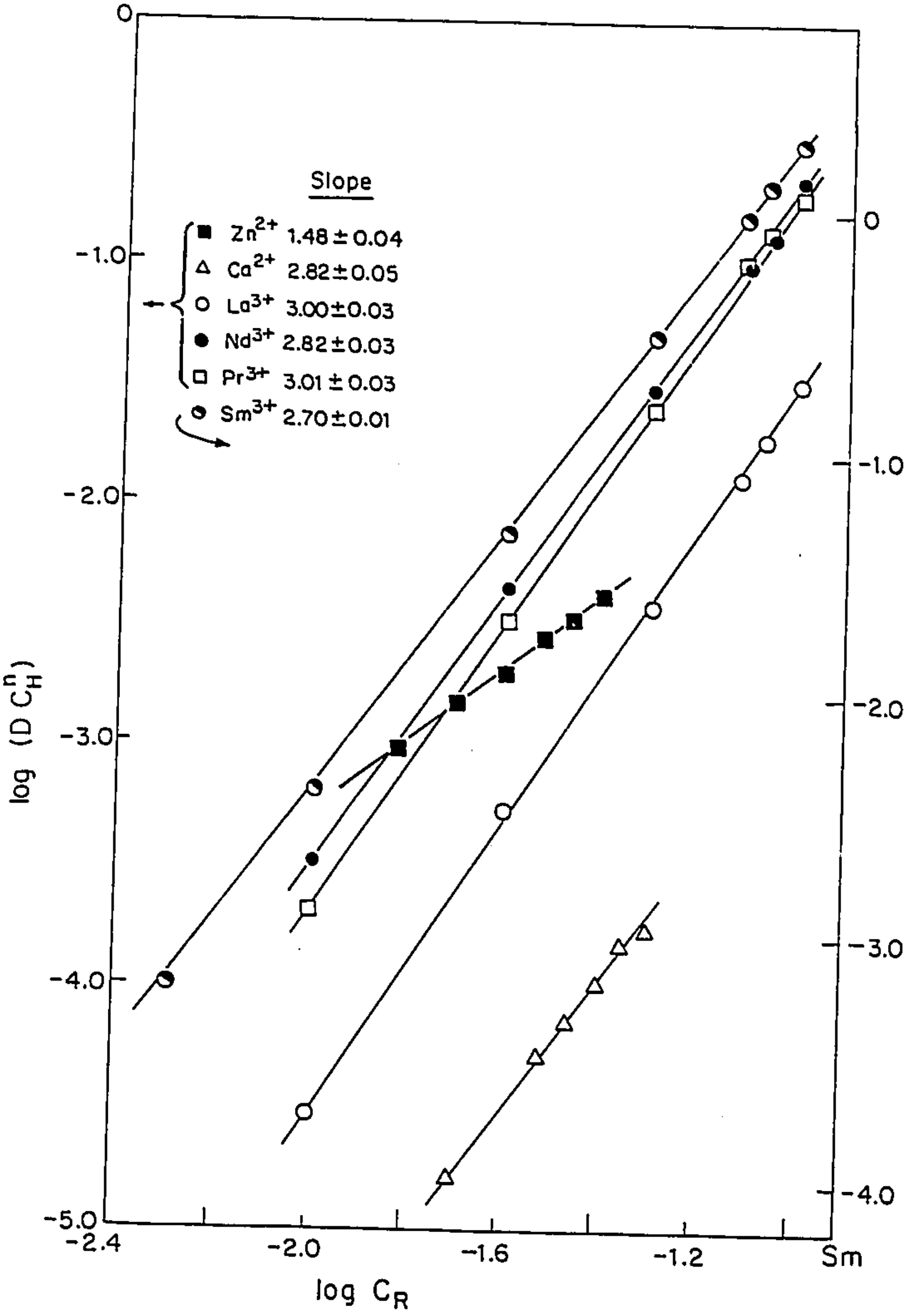


Fig. 10: Determination of (n+x)-values for the extraction of Zn^{2+}, Ca^{2+}, La^{3+}, Nd^{3+}, Pr^{3+} and Sm^{3+}.

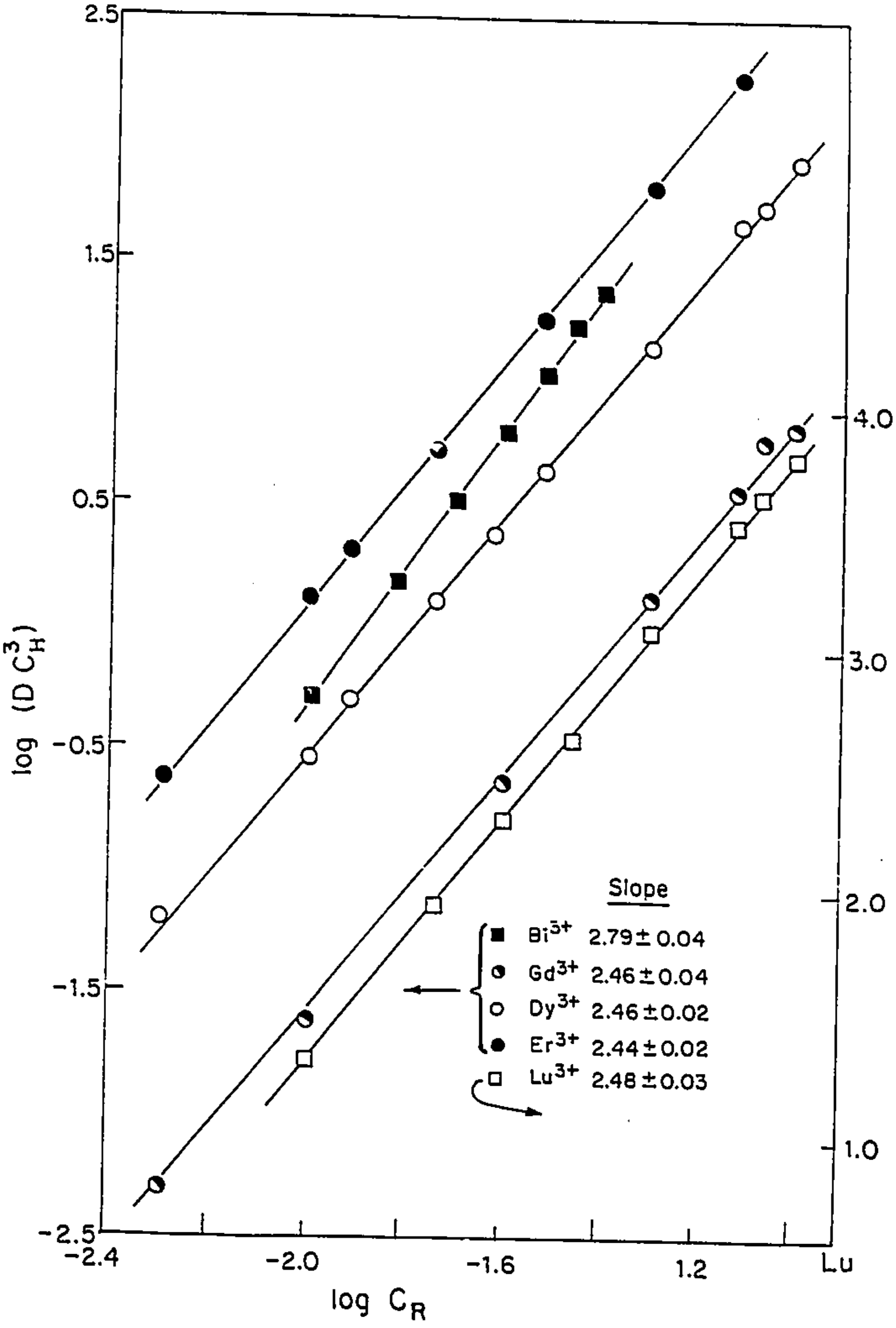


Fig. 11: Determination of (n+x)-values for the extraction of Bi^{3+}, Gd^{3+}, Dy^{3+}, Er^{3+} and Lu^{3+}.

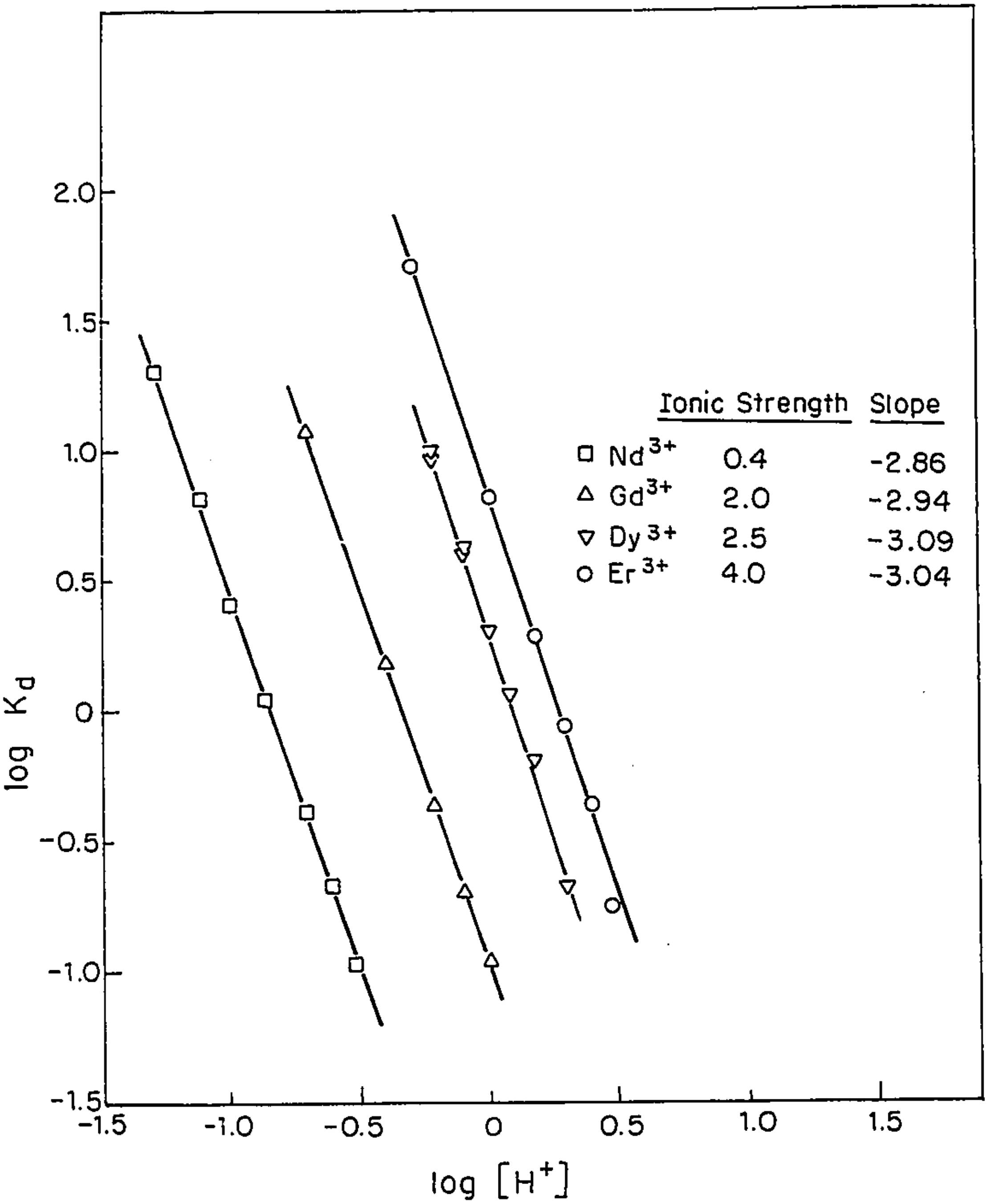


Fig. 12: Hydrogen ion dependence of the extraction of Nd^{3+}, Gd^{3+}, Dy^{3+} and Er^{3+} into 0.025 M HEHΦP in hexane; aqueous phase $HClO_4$+$NaClO_4$ at 25°C.

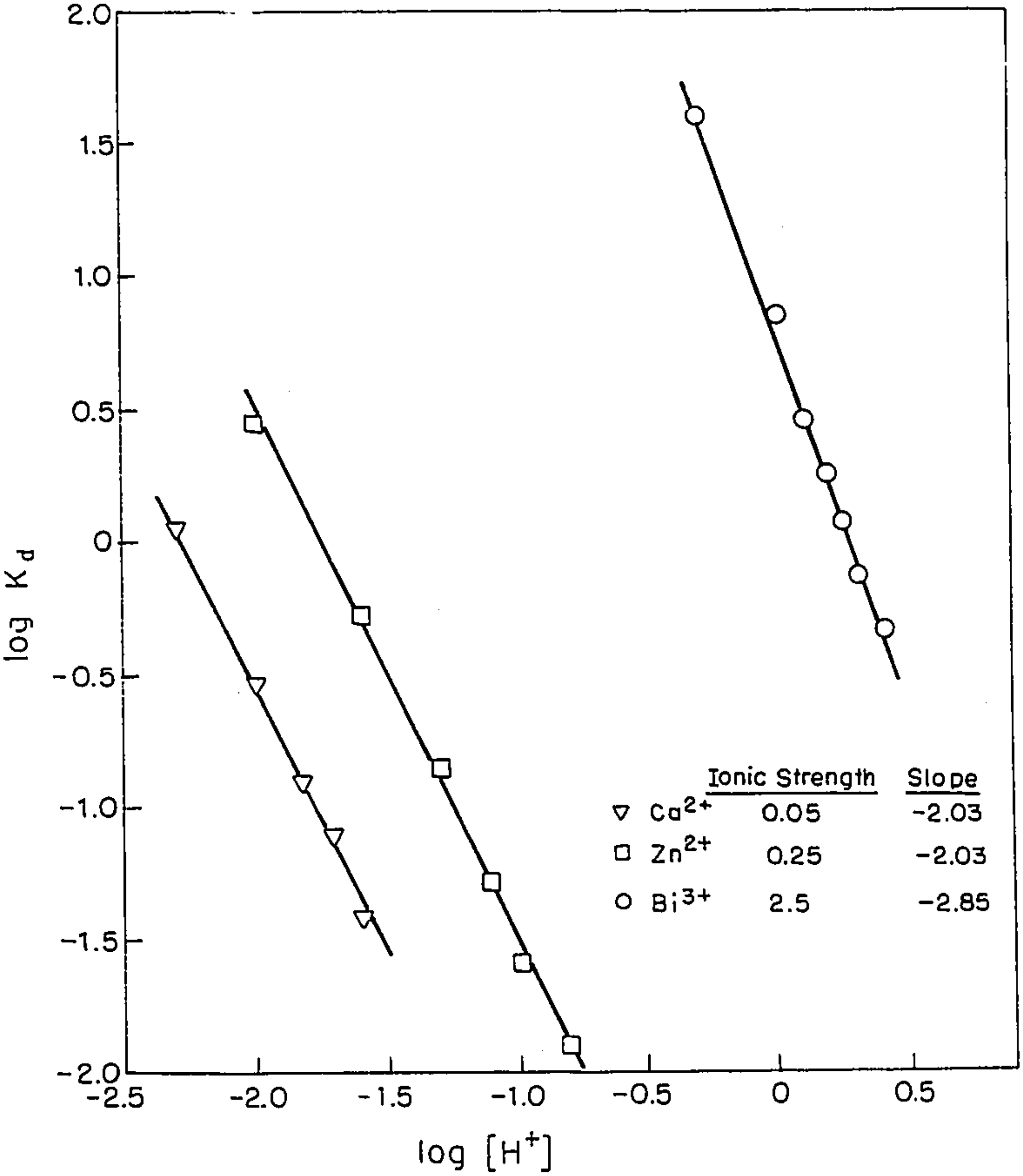


Fig. 13: Hydrogen ion dependence of the extraction of Ca^{2+}, Zn^{2+} and Bi^{3+} into 0.025 M HEHΦP in hexane; aqueous phase $HClO_4$+$NaClO_4$ at 25°C.

$$Zn^{2+} + 1.5(HY)_2 \rightleftharpoons ZnY(HY_2) + 2H^+ \qquad 11$$

$$Al^{3+} + 1.5(HY)_2 \rightleftharpoons AlY_3 + 3H^+ \qquad 12$$

in which the charged species and uncharged species are in the aqueous and organic media, respectively and $(HY)_2$ is the dimer of HEHΦP [20g,230]. It is owing to the dimeric nature of the extractant that either integral or half-integral powers, n, arise in an equilibrium relation.

The formula of the metal complex in equations 2-4 may appear inconsistent with the formulae given in equations 9-13. This is not so, however, as the formula $LnY_3.2HY$, for example, is strictly empirical while the equivalent $LnY(HY_2)_2$ may be termed semi-structural.

The number of extractant molecules that react with a given ion appears to decrease with the electric field about that ion. The field is proportional to the ionic function, ze/r, where ze is the charge and r is the radius of that ion. Thus the largest rare earth ion, La^{3+}, binds three extractant dimers. With a decrease in radius, the later lanthanides replace one of the dimers with a monomer unit.

The radius of the calcium ion is about equal to that of Dy^{3+} but it carries only a double charge. Evidently the smaller electrical field permits the Ca^{2+} ion to react with as many as three extractant dimers. The smaller radius of the Zn^{2+} ion combined with the fact that it is of the pseudo rare gas type, gives this ion a considerably stronger field. It consequently accomodates only 1.5 $(HY)_2$ molecules. Aluminium being a stronger Lewis acid than any of the trivalent ions studied, completely deprotonates the extractant and therefore binds only 1.5 dimer molecules as would be expected from the theory.

Effect of alkali salt

As HEHΦP is a liquid cation exchanger, it was thought that it might extract some of the alkali ion used in some of the experiments to adjust the ionic strength. Sodium perchlorate added to the aqueous phase at concentrations as high as 3 M had a large inhibitory effect on extractions. Organic phases that had been equilibrated with 1 M alkali perchlorate in 0.01 M perchloric acid were found to contain less than 1 μg ml^{-1} alkali ion. Therefore, the activity of the organic phase was not affected by the presence of the alkali salt. The inhibitory effect on extractability is therefore due to the reduction of the activity of the other ions in the aqueous phase. The influence is quite large as can be seen from Figure 14 which shows the effect of ionic strength on the distribution coefficient of Nd^{3+}. The behaviour is compatible with plausible values of the activity of Nd^{3+} ion.

^{31}P NMR investigation of species forming in the organic phase in extractions with HEHΦP

Investigation of extraction mechanisms and species forming in the organic phase have been mostly studied using equilibrium distribution data. The use of varied extraction conditions by different workers, resulting in a large variation of activity coefficients of the species, especially in the aqueous phase, have given rise to conflicting reports of extraction mechanisms. Sidall and Stewart [231] pointed out the potential of nuclear magnetic resonance spectroscopy in elucidating the structure/mechanism of species formed in the organic phase following extraction with neutral organophosphorus esters. Other workers have used NMR spectroscopy to investigate the species formed in the extraction of uranium with HDEHP, a closely similar extractant [232-235]. Recently, Kalina [236] has used lanthanide induced

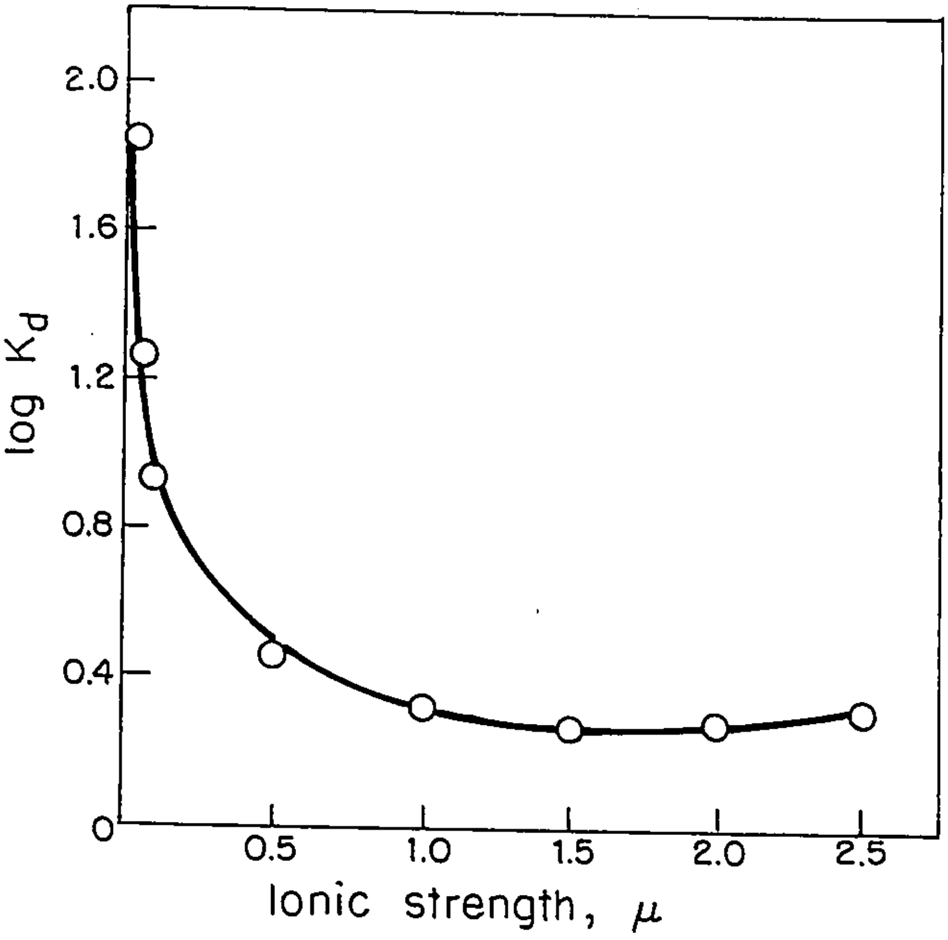


Fig. 14: Effect of ionic strength, $\mu(HClO_4+NaClO_4)$, on the extraction of Nd^{3+} into 0.025 M HEHΦP in hexane at 25°C.

shifts to determine the structure of species formed in the solvent extraction of lanthanides with neutral organphosphorus extractants.

Extraction carried out at low loading with various concentrations of HEHΦP, as shown above, at fixed aqueous phase acidity gave a 6 : 1 ratio for HEHΦP : lanthanum. The extraction equilibrium is therefore described by the following equation:

$$La^{3+} + 3(HEH\Phi P)_2 \rightleftharpoons La[H(EH\Phi P)_2]_3 + 3H^+ \qquad 14$$

in which the charged species and uncharged species are in the aqueous and organic phases, respectively. At high loading, de-dimerization occurs as a result of the competition between hydrogen bonding and bonding to metal ions. The consequent ionization of the monomers results in the formation of the extractable metal ion extractant complexes. Ejection of a solid phase from the extraction system suggests that a polymeric compound is formed [237,238]. The empirical composition of the isolated solid corresponded to that of a simple salt. To take into account the extraction of polymeric species, Sato [239] suggested the following reaction in solvent extraction of In(III), La(III) and Bi(III) analogous to that with the closely related HDEHP:

$$nLa^{3+} + 3n/2(HEH\Phi P)_2 \rightleftharpoons \{La(EH\Phi P)_3\}_n + 3nH^+ \qquad 15$$

A single peak was obtained for all the ^{31}P spectra recorded at room temperature. In some cases the single peak corresponded to resonances from the free ligand and the complex undergoing exchange. On lowering the temperature, two peaks corresponding to separate resonances by the free ligand and the complex were observed. The $La(EH\Phi P)_3$ polymer was not soluble in n-hexane but formed a gel in toluene or THF. A slurry of gel and solvent was formed and filtered. No peak(s) was observed in the spectrum of the filtrate. The isolated solid was shaken with hexane, filtered and no peak(s) was also observed for the filtrate. Table 5 summarizes the low temperature ^{31}P chemical shifts for the free ligand and the slurry of gel in toluene of the isolated compound. Figure 15a, b, c, d and e show the solid state NMR spectrum of La(EHΦP)$_3$, the solution spectra of the gel in toluene and the free ligand in n-hexane, toluene and THF, respectively. The broad signal obtained with the gel is as a result of poor exchange due to viscosity. The difference in chemical shifts for the free ligand indicates a solvent effect. A single peak at room temperature of chemical shift 4.4 ppm was obtained for the solid state ^{31}P NMR spectrum of the La(EHΦP)$_3$ solid polymer.

Table 6 shows the ^{31}P chemical shifts of the species formed in the organic phase following extraction at different acidities. Representative spectra are shown in Figure 16. Extraction from 0.1 M $HClO_4$ using n-hexane solution resulted in a white gelatinous solid appearing in the organic phase, and the spectra of one portion was recorded in-situ. A second portion was filtered and even after repeated filtration more solid precipitated in the filtrate. The solution was then dialyzed in hexane using an extraction timble and no peak(s) was observed in the spectrum of the final portion of the hexane "dialysate". The small amount of complex extracted when toluene is the diluent does not obviously yield any precipitates since there would still be excess extractant. The peak observed for the in-situ spectrum in n-hexane (Fig. 16a) was due to the unprecipitated complex since no spectrum was observed for the solid obtained after dialysis when dispersed in n-hexane. The composite peak obtained with toluene, Fig. 16e, did not split even at 198K; either exchange and/or viscosity broadening, but most likely the latter, is operational at such low temperature. Also toluene is more likely to be wetted than n-hexane, so that the water content may be freezing out and will lead to the broadening observed in the former solvent. The effect of saturating

Table 5

^{31}P Chemical shifts

Compound	Solvent	Temperature (K)	^{31}P chemical shifts δ (ppm)
Solid $La(EH\Phi P)_3$		ambient	4.4
$La(EH\Phi P)_3$ (gel)	toluene	198	37.3
$La(EH\Phi P)_3$	n-hexane	198	14.0
0.1 M HEHΦP	n-hexane	198	18.1
0.1 M HEHΦP	toluene	212	20.4
0.1 M HEHΦP	THF	198	19.8

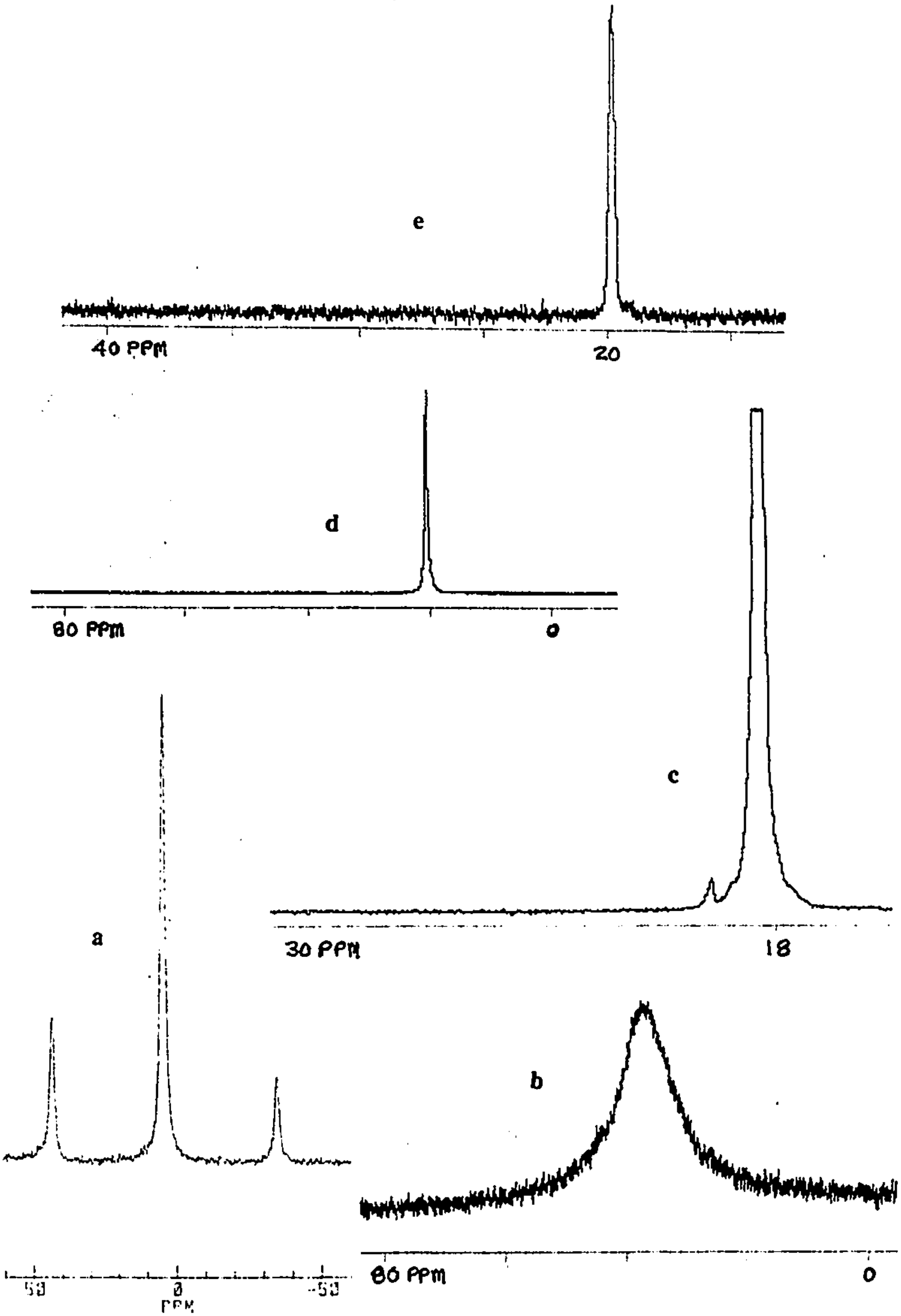


Fig. 15: ^{31}P NMR spectra for a) solid La(EHΦP)$_3$, b) La(EHΦP)$_3$ gel in toluene,c) 0.1 M HEHΦP in n-hexane, d) 0.1 M HEHΦP in toluene, e) 0.1 M HEHΦP in THF.

Table 6

^{31}P chemical shifts for the extraction of lanthanum at different acidities into 0.1 M HEHΦP solutions

Acidity (M)	Solvent	Temperature (K)	^{31}P chemical shifts δ (ppm)
0.1	toluene	212	20.4
0.1	toluene	198	20.5
0.1	n-hexane	198	14.0
0.5	n-hexane	198	14.2,18.6
1	n-hexane	198	18.4
2	n-hexane	198	18.4
3	n-hexane	198	18.4
4	n-hexane	198	18.6
5	n-hexane	198	18.3

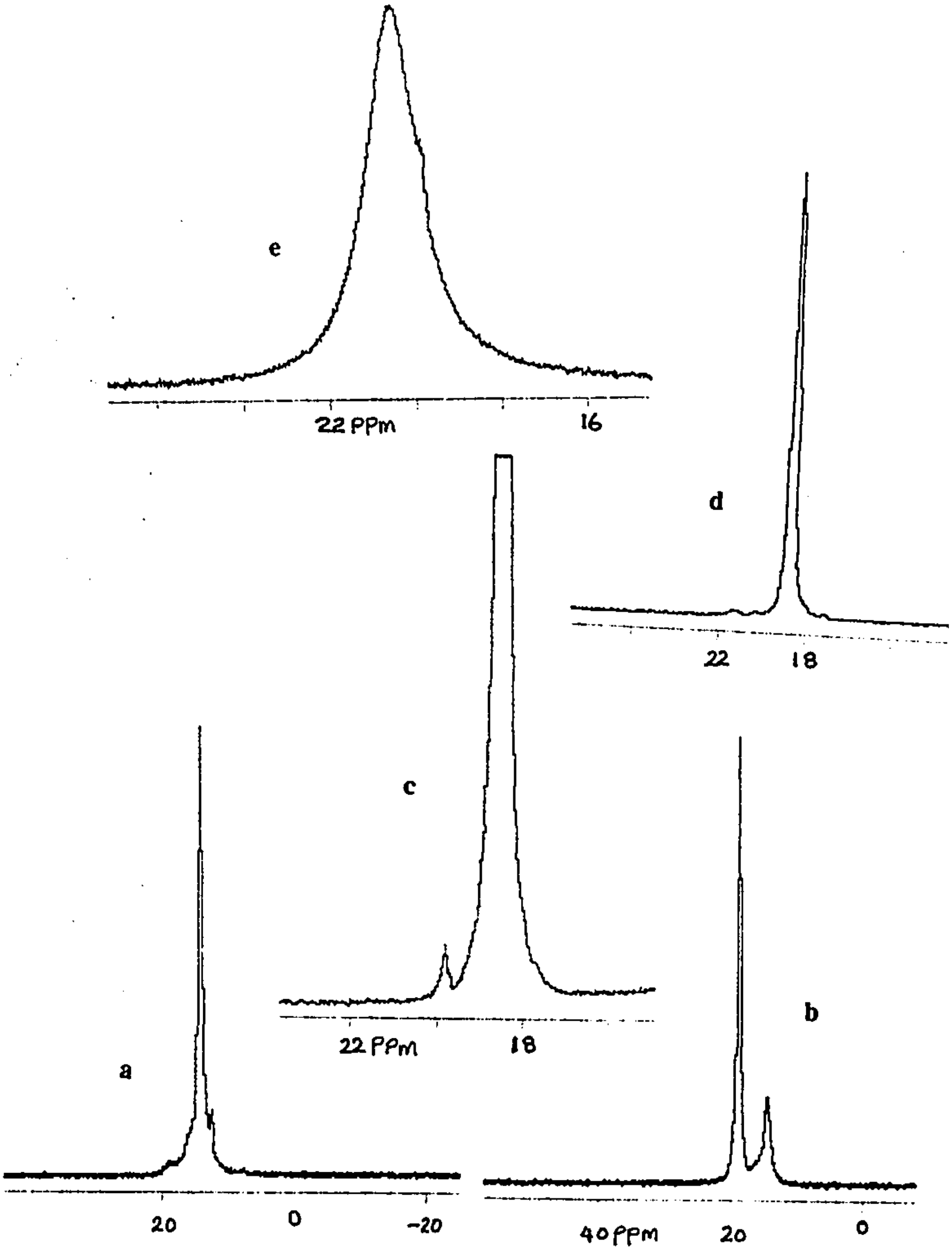


Fig. 16: ^{31}P NMR spectra for the extraction of lanthanum into n-hexane phase containing HEHΦP from a) 0.1, b) 0.5, c) 1.0 d) 2.0, M $HClO_4$ and into toluene phase containing HEHΦP from e) 0.1 M $HClO_4$ at 198 K.

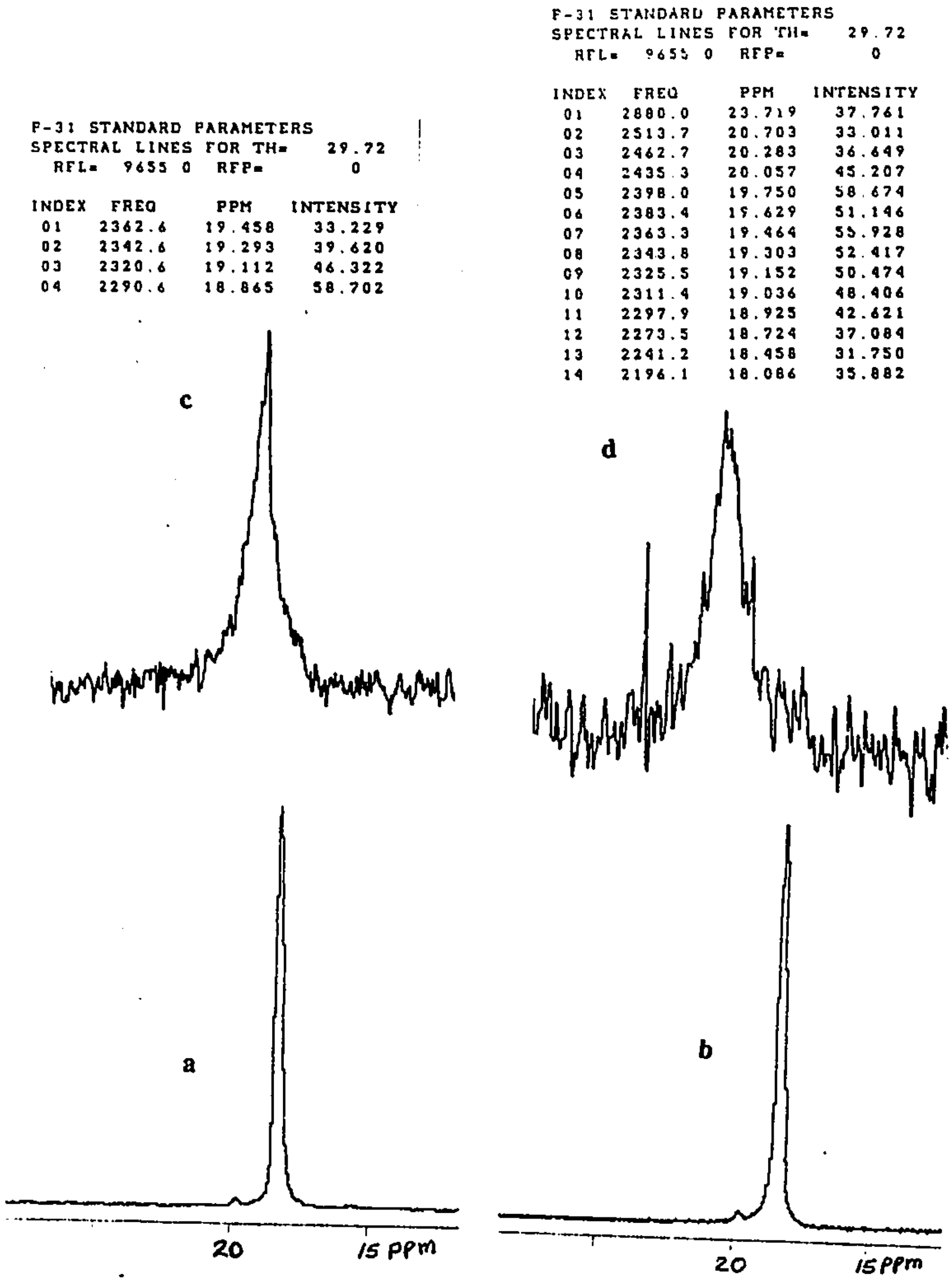
the n-hexane phase with water is seen from the chemical shifts of the free ligand (18.1 ppm) and when the same solution is contacted with an aqueous phase (18.3 ppm). At 0.5 M $HClO_4$ in n-hexane, no solid precipitated out; two peaks were obtained at 198K with chemical shifts at 18.6 and 14.2 ppm which can be assigned to the free ligand and the complex, respectively. The difference in the chemical shifts of the solid polymer and the complex in solution shows that the structure in the solid state differs from that in solution. The difference in the ^{31}P chemical shifts of solid $(NH_4)_3PO_4$ and 85% H_3PO_4 is not greater than 2 ppm [240]. Therefore, apart from suppling information about solubility and stability, investigation of the isolated solid complex by ^{31}P NMR spectroscopy substantiates the structural difference between the complex when pulled out and when left in solution. A gel is formed as a result of interaction between a dispersed phase and the solvent. Thus, the disparity between the chemical shifts of the gel, the solid polymer and the complex in solution can be explained as due to change in coordination. At higher acidities, only one peak corresponding to the free ligand was observed showing that no lanthanum is extracted. The chemical shifts for extractions without lanthanum are summarized in Table 7. Representative spectra are shown in Figure 17. The only peaks observed with just water and up to 6 M $HClO_4$ were that of the free ligand showing that no water molecules or acid were associated with the complex and/or ligand.

At 11.6 M acid however, the extraction system yielded three phases. HEHΦP has been shown to undergo protonation at concentrations higher than 6 M $HClO_4$, forming a molecular solvate of composition $(HEH\Phi P)_2.HClO_4$ which is sparingly soluble in aqueous and organic solvents and forms a separate phase [241]. The aqueous phase following extraction with 11.6M $HClO_4$ was evaporated to dryness under a heat lamp and the residue taken up in n-hexane. The chemical shifts of this

Table 7

^{31}P chemical shifts for extraction at different acidities without lanthanum into 0.1 M HEHΦP in n-hexane

Aqueous phase	Temperature (K)	^{31}P chemical shifts δ (ppm)
Water	198	18.3
0.5 M $HClO_4$	198	18.2
1.0 M $HClO_4$	198	18.3
6.0 M $HClO_4$	198	18.2
11.6 M $HClO_4$	200	20.8 upper layer
	200	19.8 middle layer
	199	18.9 aqueous layer



```
P-31 STANDARD PARAMETERS
SPECTRAL LINES FOR TH=   29.72
  RFL=  9655 0  RFP=        0

INDEX  FREQ      PPM     INTENSITY
 01    2362.6   19.458    33.229
 02    2342.6   19.293    39.620
 03    2320.6   19.112    46.322
 04    2290.6   18.865    58.702
```

```
P-31 STANDARD PARAMETERS
SPECTRAL LINES FOR TH=   29.72
  RFL=  9655 0  RFP=        0

INDEX  FREQ      PPM     INTENSITY
 01    2880.0   23.719    37.761
 02    2513.7   20.703    33.011
 03    2462.7   20.283    36.649
 04    2435.3   20.057    45.207
 05    2398.0   19.750    58.674
 06    2383.4   19.629    51.146
 07    2363.3   19.464    55.928
 08    2343.8   19.303    52.417
 09    2325.5   19.152    50.474
 10    2311.4   19.036    48.406
 11    2297.9   18.925    42.621
 12    2273.5   18.724    37.084
 13    2241.2   18.458    31.750
 14    2196.1   18.086    35.882
```

Fig. 17: ^{31}P NMR spectra for extractions without lanthanum from a) water,b) 6 M $HClO_4$ and c) and d) aqueous and middle layers, respectively from the 11.6 M $HClO_4$.

solution as well as of the middle and upper layers were recorded. At room temperature, a single peak, δ=21.2, 20.6, and 20.5 ppm was obtained for the upper, middle and aqueous layers, respectively. At 200K, a broad composite peak, δ=19.8 ppm, was observed for the middle layer whereas single peaks, δ=18.9 ppm characteristic of the free ligand and δ=23.5 ppm, were observed for the aqueous and upper layers, respectively. The broad signal for the middle layer could be explained by the existence of associated protonated species or the broadening could be due to viscosity as this layer was observed to freeze up a little more than the other samples.

The effect of increasing concentration of lanthanum for extractions with n-hexane HEHΦP organic phase solution was also studied and the results are summarized in Table 8 with the spectra shown in Figure 18. Increase and decrease of the intensities of the peaks due to the complex and ligand, respectively, are observed with increasing lanthanum concentration in the aqueous phase.

Studies of extraction systems with closely related extractants have established that the PO_2^- in organophosphorus compounds serves as the site for coordination to metal ions [239,242-245]. Based upon this and our results, i.e., elemental analysis and ^{31}P NMR spectroscopy we propose the structure shown in Figure 19 for the complex formed at saturation loading.

Table 8

^{31}P chemical shifts for the extraction of lanthanum at different acidities into 0.1 M HEHΦP solutions

Acidity (M)	Lanthanum concentration	^{31}P chemical shifts δ (ppm)
0.5	1.0	18.4, 14.0
	1.5	18.4, 13.9
	2.0	18.4, 14.0
	2.5	18.4, 14.0
1.0	1.0	18.3
	1.5	18.3, 14.1
	2.0	18.3, 14.0
	2.5	18.3, 14.1

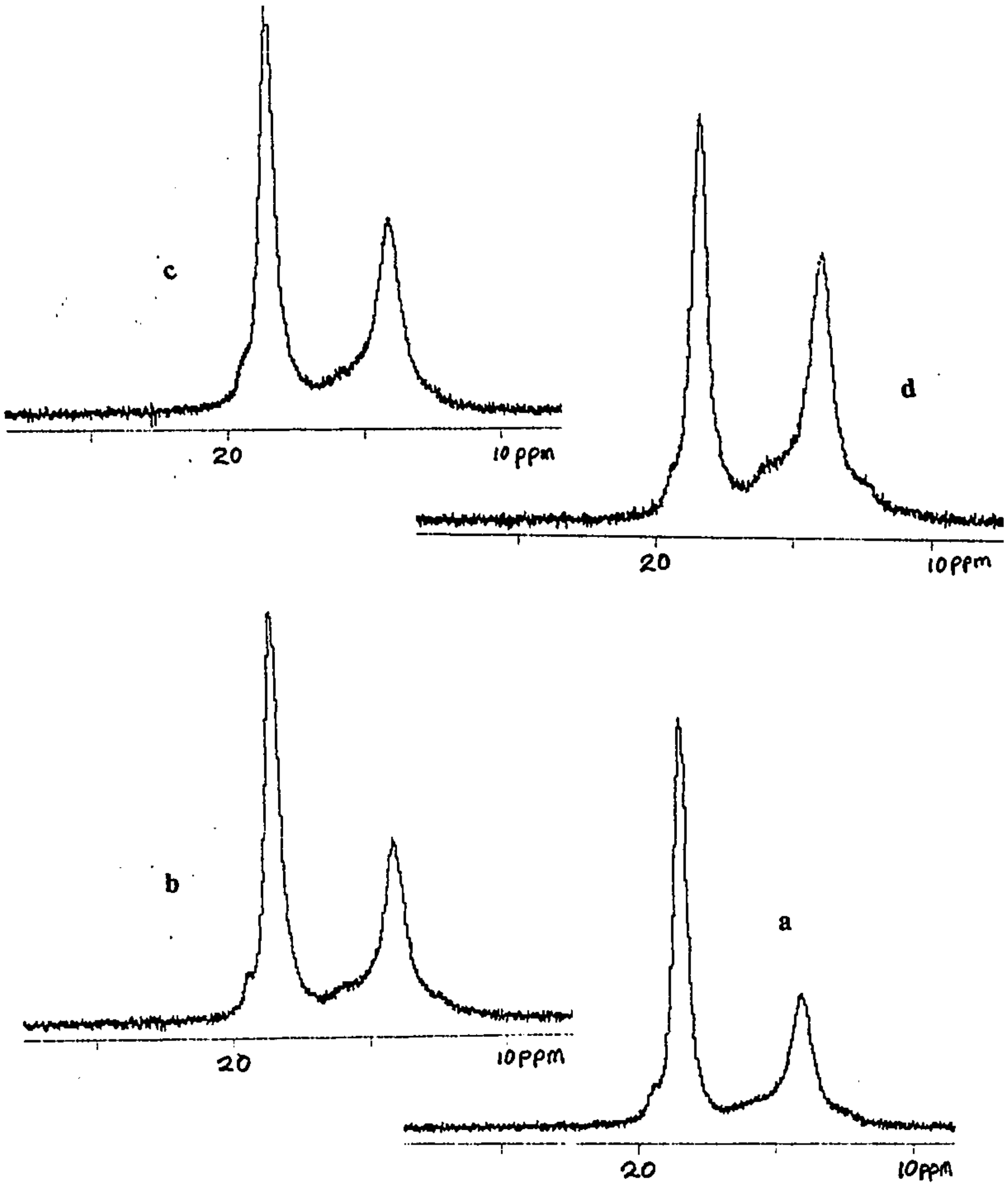


Fig. 18: ^{31}P NMR spectra for the extraction of a) 1, b) 1.5, c) 2.0, and d) 2.5 M lanthanum into 0.1 M HEHΦP in n-hexane at 198 K.

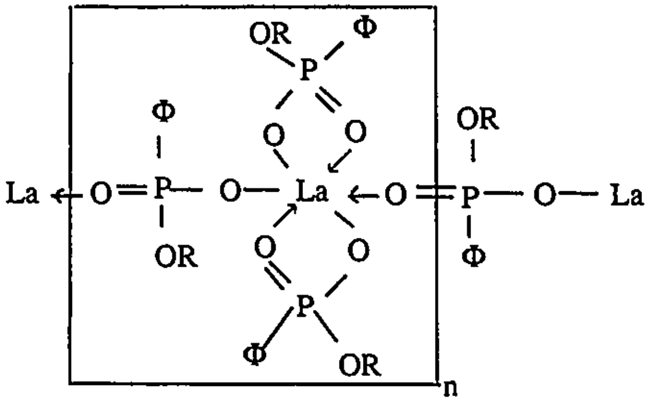


FIG. 19. Proposed structure for the polymeric lanthanum-HEHϕP species crystallized during saturation loading

Thermodynamics of extraction with DNNSA

It might be expected that the activities of metal ions in liquid extractants should be more nearly ideal than in solid ion exchange resins, provided that the stoichiometry of the complexes formed does not change with loading. Unfortunately, this is not the case at higher loadings and this is of importance in the engineering of many applications such as solvent extraction purification circuits or reversed-phase ion chromatography. With these applications in mind it became of interest to investigate the thermodynamics of the extraction process, particularly of the lanthanides. In the present work, the enthalpy and entropy terms for the extraction of a selection of ions at low concentrations were examined. Such studies should be of interest for application to trace analysis

Thermodynamic parameters for extractions with DNNSA in different diluents have been reported for lanthanide and actinide ions [43,246-248]. Studies at various temperatures are used to obtain ΔH^o and ΔS^o values for the extractions. However, previously obtained data are of relatively low accuracy. In the present study, measurements been have made over a wide range of temperatures, i.e. 15-85°C, and the resulting accuracy permits trends to be discerned across the lanthanide series. Comparisons were made with other M(III) ions and large differences in ΔS^o terms were found between extractions of M(III) and M(II) ions, repectively.

The temperature coefficient method which was employed here has the disadvantage when compared with the direct calorimetric method of providing approximate values of the enthalpy change of the extraction process. This is due firstly to the high accuracy required in the determination of the equilibrium constant and secondly to the fact that the heat capacity changes have finite but very small value in the temperature range of the experiments. However, the high concentration of metal ion required in the direct calorimetric method could result in a change of the extraction reaction stoichiometry. Consequently, it becomes imperative to use the temperature coefficient method when very small concentrations of metal ion which will yield small heat effects are involved.

In organic solvents of low dielectric constant, DNNSA and its complexes with metal ions are known to polymerize extensively [42-44,188]. The equation for extraction is therefore represented as follows:

$$M^{z+} + m(HD)_n \rightleftharpoons M(H_{mn-z}D_{mn}) + zH^+ \qquad 16$$

In the present work, HD represents DNNSA, z is the charge on the metal ion and n and m are the degree of polymerization and number of molecules of DNNSA, respectively. It has been shown [43,44,188] that a single $(HD)_n$ molecule reacts with metal ions, i.e. m is always one. Terms in the equation with charges refer to the aqueous phase, otherwise the organic phase is implied. It has been shown by various authors that the perchlorate ion does not complex the metal ion.

The K_d values are defined in terms of concentrations as is customary. It is not possible to derive absolute free energies and entropies of extraction for Al^{3+} and Bi^{3+} ions owing to the lack of published values of activity coefficients for their perchlorates but fairly reliable comparisons with the lanthanides are still possible. It is shown below how this comes about.

At constant concentration of acid and/or in a constant ionic medium, if the following assumptions are made, i.e., that

1). the temperature dependence of aqueous activity coefficients is, as usual, nearly negligible,

2). only a small concentration of the extracted metal-complex is present in the organic phase, 3). the standard enthalpy change, ΔH°, is constant in the temperature range i.e., the heat capacity change is negligible and

4). the activity coefficient for the neutral species is ca. unity,

then the integral of the derivative of the equilibrium constant with respect to temperature will yield the Van't Hoff equation in the following form;

$$\frac{\Delta \log K_d}{\Delta(1/T)} = -\frac{\Delta H^\circ}{2.303\,R} \tag{17}$$

which can be used to calculate the enthalpy change of the extraction process. The data given in Table 9 were used to calculate ΔH° from plots of $\log K_d$ vs $1/T$ using a linear regression computer programme at the 95% confidence level. The plots of $\log K_d$ vs $1/T$ in the temperature range studied are shown in Figures 20 and 21.

The ion exchange reaction for a z-valent ion (equation 16) is described by the following expression:

$$K_e = \frac{[M(H_{n-z}D_n)](\gamma_{H^+})^z[H^+]^z}{[(HD)_n]\gamma_{M^{z+}}[M^{z+}]} \tag{18}$$

providing assumptions 1 and 4 above hold, where K_e is the thermodynamic ion exchange constant and γ is the activity coefficient of the indicated species.

The following relationships will exist between the analytical concentration, C_{HD} and the polymerized extractant concentration, $[(HD)_n]$:

$$C_{HD} = [HD] + n[(HD)_n] \tag{19a}$$

which with the pronounced extent of polymerization reported for the sulphonic acids approximates to;

$$C_{HD} \cong n[(HD)_n] \tag{19b}$$

By defining

$$K_d = \frac{[M(H_{n-z}D_n)]}{[M^{z+}]} \tag{20}$$

Table 9

Variation of distribution coefficients (k_d) between $HClO_4$ and 0.01 M DNNSA in petroleum ether as a function of temperature

Metal ion	$[H^+]$	Distribution coefficient (K_d)							
		15	25	35	45	55	65	75	85°C
Zn^{2+}	0.02[a]	0.13	0.14	0.15	0.16	0.17	0.18	0.19	0.20
	0.1	1.66	1.69	1.78	1.83	1.86	1.92	2.08	2.27
Ca^{2+}	0.02[a]	-	0.47	0.47	0.45	0.46	0.48	0.48	0.49
	0.2	0.91	1.00	1.02	0.95	0.95	0.93	0.98	0.98
	0.2[a]	0.28	0.26	0.28	0.28	0.27	-	-	-
Al^{3+}	0.25	2.64	2.73	2.93	3.23	3.45	3.92	4.05	4.36
	0.25[a]	0.54	0.60	0.66	0.72	0.79	0.84	0.93	0.98
Bi^{3+}	0.5	2.95	3.24	3.58	3.94	4.29	4.83	5.25	-
La^{3+}	0.5	-	3.80	4.27	4.37	4.90	5.37	5.75	6.31[b]
Nd^{3+}	0.5	-	2.40	2.72	3.23	3.50	4.07	4.63	5.30
Gd^{3+}	0.5	-	2.34	2.55	2.88	3.06	3.60	4.19	4.43
Er^{3+}	0.25	13.06	14.16	15.07	16.89	19.36	22.88	25.39	28.08
	0.5	1.64	1.80	1.97	2.21	2.42	2.68	2.90	3.17

[a] Ionic strength made up to 0.5 M by addition of $NaClO_4$
[b] Temperature = 83°C

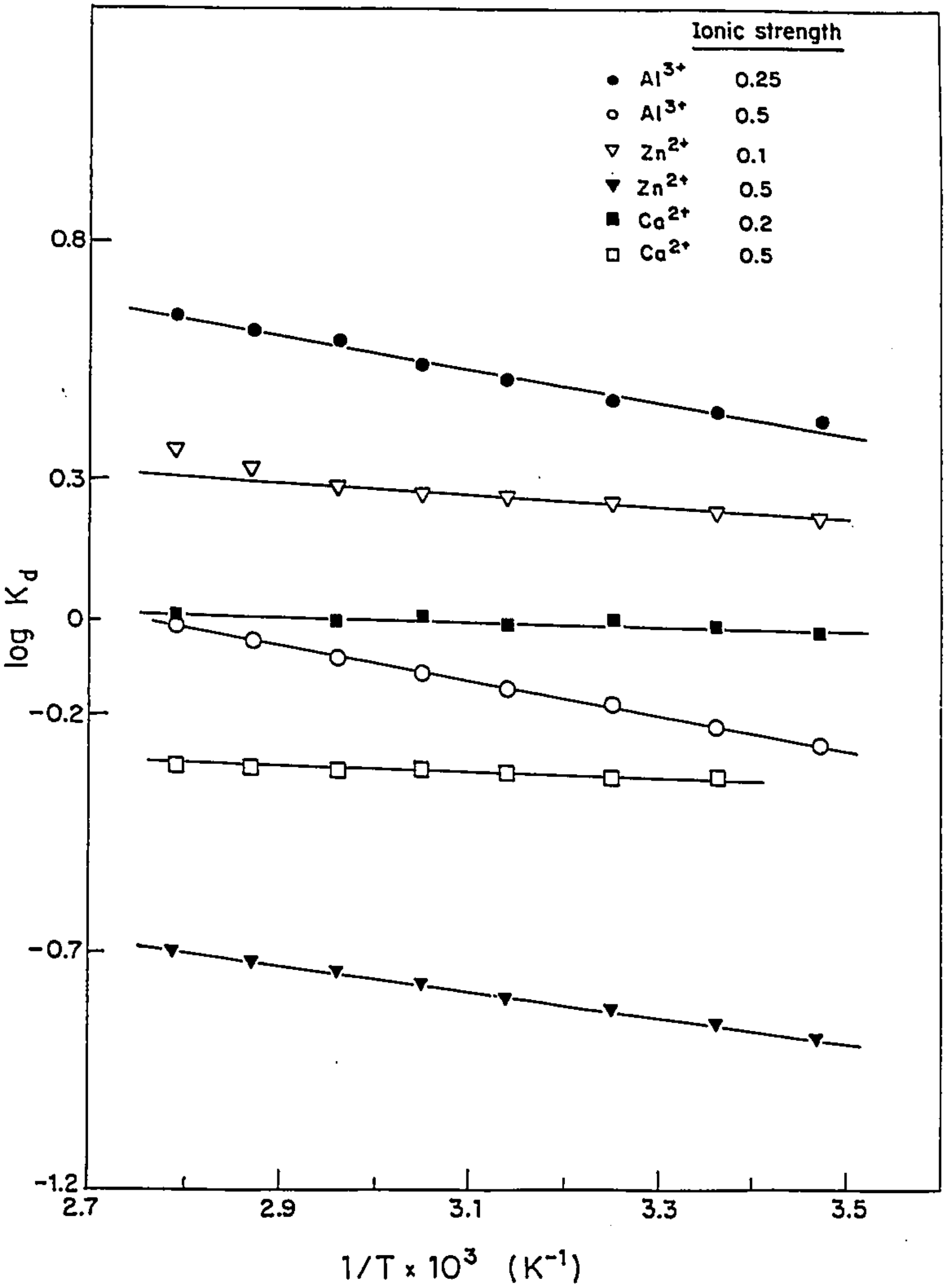


Fig. 20: Effect of temperature on the extraction of Al^{3+}, Zn^{2+} and Ca^{2+} into 0.01 M DNNSA in pet. ether.

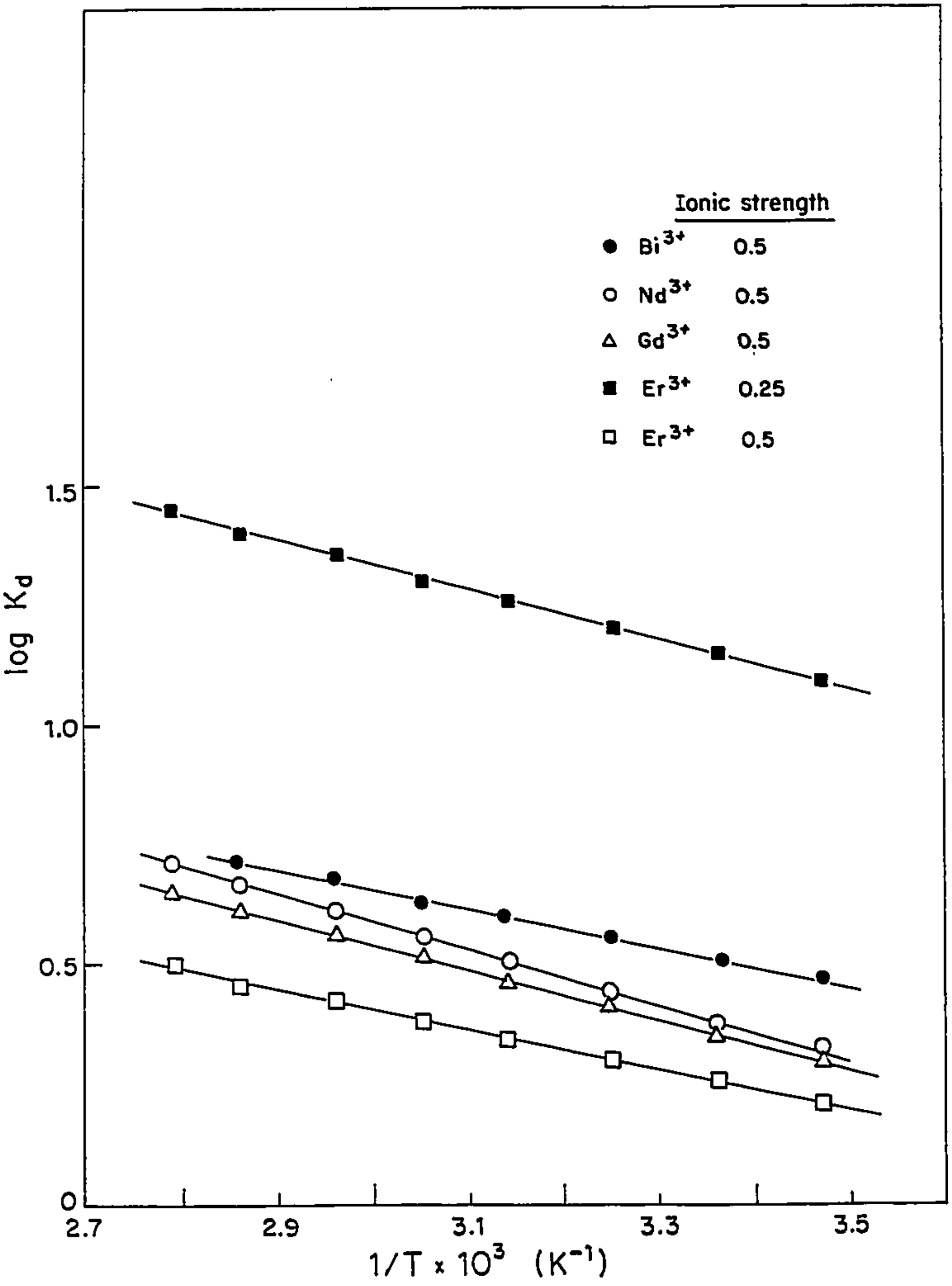


Fig. 21: Effect of temperature on the extraction of Bi^{3+}, Nd^{3+}, Gd^{3+} and Er^{3+} into 0.01 M DNNSA in pet. ether.

and for an electrolyte of stoichiometry $(\text{cation})_{\upsilon+}(\text{anion})_{\upsilon-}$, we have the mean activity coefficient

$$\gamma_{\pm}^{\upsilon} = \gamma_{+}^{\upsilon+}\gamma_{-}^{\upsilon-} \qquad \text{where } \upsilon = \upsilon_{+} + \upsilon_{-} \qquad 21$$

therefore

$$K_c/n = \frac{K_d[H^+]^z(\gamma_{\pm HClO_4})^{2z}}{[C_{HD}]\,\gamma_{\pm}{}^{\upsilon}{}_{M(ClO_4)_z}} \qquad 22$$

The mean activity coefficients, $\gamma_{\pm}$, were taken from published values [249,250]. Individual activity coefficients can also be calculated for sufficiently dilute ($\mu \leq 0.1$) solutions from the extended Debye-Hückel equation

$$-\log \gamma_i = \frac{0.5115\, z^2 \sqrt{\mu}}{1 + 0.0033\, \alpha_i \sqrt{\mu}} \text{ (at 25°C)} \qquad 23$$

where α_i is the effective radius of the *i*th ion. Values published by Kielland [251] were employed to calculate mean activity coefficients.

The free energy of the extraction reaction is defined as follows:

$$\Delta G = -RT\log_e K_c/n = -RT \ln \frac{K_d[H^+]^z}{[C_{HD}]}\,\Gamma \qquad 24$$

where Γ is the collection of activity coefficients. These values may be regarded as standard free energies with a shifted zero of reference such that they are less negative than the true values. For the value of n=10 [43], the contribution of $RT\log_e n$ to ΔG in the above equation will be about +6 kJ mol^{-1} but it would be constant throughout the extractions.

For Al^{3+} and Bi^{3+} ions where the activity coefficient of their perchlorate is unavailable, we have a modified free energy

$$\Delta G' = \Delta G + RT\ln\Gamma \qquad 25$$

However, use of $\gamma_{\pm}$ for $AlCl_3$, which admittedly is not likely to be equal to that of the perchlorate, suggests that the $\Delta G'$ value is estimated to be about 5 kJ mol^{-1} less than ΔG, a discrepancy that is small and can still permit conclusions to be drawn about other factors involved in the reactions. The free energy values appear in Table 10. Comparison of the extractions of lanthanides conducted at constant ionic strength should be valid. It should be possible to compare data for other trivalent ions but comparison of these with data for divalent ions, whose activity coefficients are closer to 1.0, should merely be regarded as suggestive rather than definitive.

The enthalpy values, ΔH°, given by the relation

$$\frac{d}{dT}\frac{(\Delta G)}{T} = -\frac{\Delta H^\circ}{T^2} \qquad 26$$

are independent of the activity coefficients, i.e. they are correct, provided that $\ln\gamma$ terms are essentially independent of temperature [252]. It has been shown that n, the aggregation number, does not change significantly with temperature [190].

Entropies have been calculated from the equation,

$$T\Delta S = \Delta H^\circ - \Delta G \qquad 27a$$

and for the instances where the mean activity coefficients are unavailable by

$$T\Delta S' = \Delta H^\circ - \Delta G' \qquad 27b$$

For these latter instances, the entropies, like free energies, are uncertain by an amount $R\log_e n\Gamma$ that is uncertain. Therefore,

$$\Delta S' = \Delta S - R\log_e n\Gamma \qquad 28$$

The contribution for n=10 is about 19 J K^{-1} mol^{-1} and should again be constant through out the extractions. The entropy values are tabulated in Table 10.

If data obtained with the ionic strength fixed at 0.5 are compared, it is seen that DNNSA does not exhibit any selectivity for the lanthanides (no significant differences in ΔG values) with increasing atomic number. The series of ΔH° and ΔS values do not exhibit the same non-selectivity, however. Lanthanum stands apart

Table 10

Thermodynamic values for the extraction
of selected metal ions with DNNSA at 25°C

Ion	Crystal Radius Pm[a]	$HClO_4$ concentration M	ΔG kJ mol^{-1}	ΔH° kJ mol^{-1}	ΔS J K^{-1} mol^{-1}
La^{3+}	117.2	0.5	-15.03 ± 0.16	7.31 ± 0.31	74.9 ± 1.2
Nd^{3+}	112.3	0.5	-13.79 ± 0.15	10.17 ± 0.26	80.5 ± 1.0
Gd^{3+}	107.8	0.5	-13.72 ± 0.20	8.51 ± 0.39	74.7 ± 1.5
Er^{3+}	103.0	0.5	-13.03 ± 0.13	7.50 ± 0.17	79.2 ± 0.7
		0.25	-10.64 ± 0.22	9.28 ± 0.58	66.9 ± 2.1
Bi^{3+}	117	0.5	-9.17 ± 0.11[c]	6.97 ± 0.22	54.1 ± 0.8[d]
Al^{3+}	67.5	0.25	-3.56 ± 0.14[c]	5.90 ± 0.31	31.8 ± 1.2[d]
		0.25[b]	-4.16 ± 0.12[c]	6.44 ± 0.20	35.6 ± 0.8[d]
Ca^{2+}	114	0.2	-4.33 ± 0.23	0.10 ± 0.52	14.9 ± 1.9
		0.2[b]	-7.27 ± 0.17	0.21 ± 0.74	23.3 ± 2.6
		0.1	-2.75 ± 0.30		
Zn^{2+}	88.0	0.1	-1.84 ± 0.11	3.13 ± 0.18	16.7 ± 0.7

[a] Values from R. D. Shannon [74] for coordination number = 6

[b] Ionic strength made up to 0.5 M by addition of $NaClO_4$

[c] $\Delta G'$; [d] $\Delta S'$

from the other members of the series.

The extraction is less favoured as the atomic number of the lanthanide increases. The reason for this is a slightly decreasing entropy of extraction. There is also a decrease in enthalpy which tends to favour extraction of the heavier lanthanides but fails to compensate for the entropy effect.

Danesi *et al.* have noted the relative importance of entropy in ion exchange processes [248].

The extraction represented by

$$M^{z+}(aq) + DNNSA \rightarrow M(complexed) + nH_2O \tag{29}$$

can be regarded as the sum of two processes

$$M^{z+}(aq) \rightarrow M^{z+}(g) + nH_2O \tag{30a}$$

$$M^{z+}(g) + DNNSA \rightarrow M(complexed) \tag{30b}$$

for which the entropies are $-\Delta S_h^o$ and ΔS_c^o, respectively. Therefore the entropy of reaction 29 is

$$\Delta S = \Delta S_c^o - \Delta S_h^o \tag{31}$$

Values of ΔS_h^o for the lanthanides taken from Bertha and Choppin have been employed [253]. By combining equations 27a,b and 31, our extraction enthalpies lead to the entropy, ΔS_c^o, and the shifted values of entropy for the complexing of the gaseous ions, $\Delta S' = \Delta S_c^o - \Delta S_h^o$, that are recorded in Table 11. The quantity ΔS_c^o becomes more negative for the lanthanides with greater atomic number. The logarithmic term should subtract less from ΔS with increasing atomic number as $\gamma_{M^{z+}}$ should increase with decreasing crystal radius*.

The hydrated radii *increase* with decreasing crystal radius.

Table 11

Entropies of hydration and entropies of complexing the gaseous ions with DNNSA,

Ion	$HClO_4$ Concentration M	ΔS_h^o J K^{-1} mol^{-1}	ΔS_c^o J K^{-1} mol^{-1}
La^{3+}	0.5	-341	-266
Nd^{3+}	0.5	-355	-274
Gd^{3+}	0.5	-390	-315
Er^{3+}	0.5	-399	-320
	0.25	-399	-332
Al^{3+}	0.25	-468[b]	-436[c]
	0.25[a]	-468[b]	-432[c]
Ca^{2+}	0.2[a]	-208[b]	-185
	0.2	-208[b]	-193
Zn^{2+}	0.1	-269[b]	-252

[a] Ionic strength made up to 0.5 M by addition of $NaClO_4$

[b] Values taken from ref. 254

[c] Shifted values ($\Delta S_c^o = \Delta S' + \Delta S_h^o$)

A study of the extraction of ions such as Mg^{2+}, Ca^{2+} and Ba^{2+} with a sulphonate ion exchanger has shown that the polymer micelle of $(HD)_n$ bonded to these ions undergoes electrostriction and decreases in volume with increasing electric field about the metal ion [43]. The authors' suggestion is that the lanthanide contraction leads to the same effect and that the more compact micelles possess less entropy.

The changes in ΔS_c^o and ΔS_h^o encountered in proceeding along the lanthanide series roughly compensate each other with ΔS_c^o being somewhat the more important term. If large separation factors for the lanthanides are to be achieved, it is likely that this could best be accomplished by either enhancing or suppressing the ΔS_c^o term. This could perhaps be done by reducing the size of the complex micelles. Morabbi et al. have influenced micelle size by the addition of alkali salts [193]. It is probable that a change of the nature of the extractant would be more effective.

In order to lend support to the idea of micelle electrostriction, some further ions of various size and charge were examined. Bismuth ion resembles La^{3+} very closely in size and charge. Both ions are free from crystal field effects, thus their thermodynamic data should be very similar, but activity of bismuth perchlorate is not available. This similarity becomes obvious if the $\Delta G'$ for La^{3+} is evaluated. The behaviour of Al^{3+} is of interest because it is a much smaller ion. It is extracted less readily despite a more favourable enthalpy of extraction. The data at ionic strength 0.25 may be compared with that for Er^{3+}. The reaction entropy for Al^{3+} is much less important than the entropy for Er^{3+}.

In another experiment, Al^{3+} was extracted from a 0.25 M acid solution in which the ionic strength had been adjusted to 0.5 M by the addition of $NaClO_4$. Some sodium was extracted and this had the effect of reducing the concentration of free

DNNSA in the organic phase. An attempt has been made to interprete the results obtained with sodium present by calculating the amount of sodium extracted and thereby correcting the concentration of free DNNSA that was employed in the calculation of K_e for Al^{3+}. The extraction coefficient K_e/n for Na^+ was reported to be 0.5 by Markovits and Choppin [43]. The same workers have reported that n, the aggregation number for the extractant in a micelle of the sodium complex is 10. In the simple case that one mole of $(HD)_n$ reacts with one mole of Na^+,

$$(HD)_n + Na^+ \rightleftharpoons NaH_{n-1}D_n + H^+ \qquad 32$$

Thus, setting

$$K_e/n = 0.5 = \frac{[NaH_{n-1}D_n]\ [H^+]}{n\,[Na^+]\ [(HD)_n]} \qquad 33a$$

$$= \frac{0.25\ [NaH_{n-1}D_n]}{10 \times 0.25\ (0.01 - [NaH_{n-1}D_n]\ )} \qquad 33b$$

Upon solving for $[NaH_{n-1}D_n]$, the concentration of sodium in the organic phase, it was possible to calculate the bracketted quantity in the denominator, i.e. the concentration of unreacted DNNSA.

The resulting data given in Table 10 show that, as expected, the enthalpy was but little affected by the change in ionic strength while the entropy increased somewhat. Although these data are estimates, they serve to show that the chief difference between the behaviour of the smaller Al^{3+} ion and the lanthanides is to be attributed to the entropy term. The loss of the large hydration shell upon the extraction of the lanthanides is felt to be a predominant factor.

The question now is whether the modified entropies of complexing in Table 11 may be compared for ions as different as Ln^{3+} and Al^{3+} in spite of the uncertainty in the logarithmic term for the latter ion. With values of γ taken from Kielland [251] for μ=0.1, one obtains for $R\ln\Gamma$ a value of 6 J K^{-1} mol^{-1} for Al^{3+}, which indicates a small difference only. Although μ was 0.25 at least in these experiments, it seems probable that the comparison of the data in Table 11 is valid to 10-20 J K^{-1} mol^{-1}. Therefore the low value recorded for Al^{3+} is outside the range of uncertainty and indicates a very strong electrostriction of the extractant by that ion.

Calcium resembles the lanthanide ions in size but its electrical field is one-third less strong. It is much less easily extracted so that the acidity was decreased to 0.2 M in one series of experiments and 0.1 M in one other case in order to achieve a good distribution between the phases. Both the enthalpy and entropy terms are small relative to the corresponding values for the trivalent ions but the decrease in entropy outweighs the reduced enthalpy. In one series the ionic strength was adjusted to 0.5 M and the effect of sodium extraction was taken into account as before. The three results for ΔG are influenced slightly by ionic strength as are the results for Al^{3+}. The value of ΔS_c^o in Table 11 is quite high as was expected for a large, divalent ion. There is relatively little electrostriction of the extractant.

The electric field strength at the ionic radial distance of $2e/r_{Zn}$=0.027e coulombs pm^{-1} for Zn^{2+} is comparable with the field about Nd^{3+}, $3e/r_{Nd}$=0.027e coulombs pm^{-1}. It was necessary to reduce the acid concentration to 0.1 M, therefore the entropy and free energy data can be compared precisely only with that for Ca^{2+} run in 0.1 M acid. The enthalpy, ΔH^o, is greater than that for Ca^{2+} but is still less than that obtained for the trivalent ions.

The enthalpy is marginally more important than the entropy in the comparison of Ca^{2+} and Zn^{2+}. The entropy of complexing for Zn^{2+} in Table 11 is considerably more negative than that for Ca^{2+} as expected. It is still not comparable with that for Nd^{3+}, however, so the conclusion is that the electric field strength is not a defining parameter of the thermodynamics.

As thermal entropies are roughly proportional to enthalpies, it may be assumed that ΔS (or $\Delta S'$) should be proportional to the Born charging energy, viz. $-(ze)^2(1-1/\epsilon)(1/2r_+)$ where ze is the ion charge, ϵ is the dielectric constant of the medium and r_+ is the cation radius. The second power dependence on ze would account for the relative effectiveness of the trivalent ions in bringing about electrostriction of the solvent.

In contrast to this, the solution enthalpy is given approximately by the expression $ze\mu\cos\theta/(r_+ + r_w)^2$ where μ is the dipole moment of a solvent molecule, r_w (=138 pm) the radius of water molecule and θ is the angle of orientation of that molecule to the radial direction [255]. Here the dependence is first power in ze. It follows that entropy effects will predominate over enthalpies with ions of high charge.

An ionic strength of 0.5 M is quite high in experiments of a thermodynamic nature. Apart from making it impossible to obtain activity coefficients for Al^{3+} and Bi^{3+}, the chief fault associated with the high ionic strength is the effect it would have on the individual ΔS_h° values, all of which would be diminished in magnitude by the field of counter-ions about any given cation. Thus the use of the standard state values, ΔS_h°, ignores the distinction. The data obtained with solutions that had somewhat less ionic strength support that obtained with μ=0.5 so there is no doubt of the general concept of micelle electrostriction.

Thermodynamics of extraction with HEHΦP

Liquid extractants that contain the phosphate or phosphonate functionality are superior in many applications to sulphonates, especially for the extraction of higher valent metal ions. Bis(2-ethylyhexyl)phosphoric acid (HDEHP) is widely used in metal extraction circuits. However, for separations of the greatest difficulty such as those involving lanthanides or actinides, it is claimed that 2-ethylhexyl phenylphosphonic acid (HEHΦP) is superior [20f,167].

Fidelis and Siekierski [256] studied the thermodynamics of the partition of the lanthanides between HEHΦP in hexane and aqueous nitric acid solution. They assumed that the extraction proceeded according to the equation

$$Ln_A + x(HY)_{2,O} \rightleftharpoons Ln(HY)_{2x,O} + xH_A \qquad 34$$

where Ln is a lanthanide ion, x = 2.30 and $(HY)_2$ is the extractant which is dimeric in solvents of low dielectric constant. It has been shown in the course of this work that the stoichiometry is not correctly represented by this equation for the majority of the ions studied in extraction from perchloric acid media [228]. Instead, one must use the general equation

$$M_A^{z+} + n(HY)_{2,O} \rightleftharpoons M(H_{2n-z}Y_{2n})_O + zH^+_A \qquad 35$$

In investigations involving this extractant, it was therefore necessary to repeat the thermodynamic study of the extraction of selected lanthanide ions and to compare them with some other ions of various sizes and charges. Particularly, the interest was in discovering what thermodynamic feature of the extractions causes HEHΦP to be unusually efficient in extracting large polyvalent ions. The results can be compared with those of dinonylnaphthalene sulphonic acid (DNNSA). In the latter case, it was found that the enthalpy of extraction with DNNSA did not vary significantly from one lanthanide ion to another, although the entropy decreases slightly across the series.

The entropy of hydration and the entropy of complexing with DNNSA largely cancelled and it was concluded that the trend observed in the net entropy was governed chiefly by the electrostriction of the water on the one hand and micelles of DNNSA on the other.

It can be argued that if the extractant polymerizes to a micelle, binding to an ion with a high charge to size ratio causes electrostriction and a resulting decrease in entropy. If, on the other hand, the extractant serves as a monomeric ligand, or as in the present situation, a dimeric ligand, the opportunity for electrostriction of an extended micelle is lost. In such a case, the entropy change on complexing should be more purely configurational, i.e., dependent primarily upon the numbers of particles engaged in the reaction and therefore less dependent upon the charge to size ratio.

A high charge density of the cation will reduce the thermal entropy of the complex but the author believes that this effect is less pronounced than the effect of electrostriction on a micelle, if one is present. The entropy of hydration remains strongly affected by the nature of the ion and therefore the net entropy should vary more strongly across the lanthanide series. The present study supports these ideas.

In the previous studies of Fidelis and Siekierski referred to above, the ionic strength was not held constant. In view of our own experience with both HEHΦP and DNNSA, it was necessary to determine the thermodynamic parameters at constant ionic strength and also ascertain the influence of the effect of $NaClO_4$ on the extractions.

The present study entailed extracting selected metal ions from $HClO_4/NaClO_4$ solutions into a solution of HEHΦP in petroleum ether. Enthalpy and free energy of extraction was determined over the range of temperature, 15 - 85°C, and the entropies calculated from data at 25°C.

Representative $\log K_d$ vs 1/T plots of the K_d data tabulated in Table 12, obtained in the temperature range are shown in Figures 22 and 23. Enthalpies were calculated by treating the $\log K_d$ / 1/T data by a linear regression computer programme at 95% confidence level and employing the Van't Hoff equation.

Extracts were analyzed for alkali ion and its concentration was found to be of the order of 1 µg per ml.

HEHΦP is dimeric in most organic diluents of low dielectric constant and thus the extraction equation must be written as above (eq. 35) with a known value for n if the thermodynamic parameters are to be obtained in a particular case.

The equilibrium constant for the extraction is defined by the expression

$$K_c = \frac{[M(H_{2n-z}Y_{2n})]_O\,[H^+]^z\,(\gamma_{\pm HClO_4})^{2z}}{[M^{z+}]_A\,[(HY)_2]^n\,\gamma_{\pm}{}^{\upsilon}{}_{M(ClO_4)_z}} \qquad 36$$

where again the activity coefficient of the neutral species are assumed to be ca. unity. By defning an extraction coefficient

$$K_d = \frac{[M(H_{2n-z}Y_{2n}]_O}{[M^{z+}]_A} \qquad 37$$

we obtain

$$K_e = K_d\,\frac{[H^+]^z}{[(HY)_2]}\,\Gamma \qquad 38$$

where Γ is defined as previously. The standard free energy of reaction is

$$\Delta G^o = -RT\ln\ K_d\,\frac{[H^+]^z}{[(HY)_2]}\,\Gamma \qquad 39$$

provided that the activity coefficients for the neutral species can be assumed to be ca. 1.0. As before (cf equation 25), a relative free energy

$$\Delta G' = \Delta G^o + RT\ln\Gamma \qquad 40$$

is defined in those cases where the activity coefficient of the perchlorate is not

Table 12

Variation of distribution coefficients (k_d) between $HClO_4$ and 0.025 M HEHΦP in petroleum ether as a function of temperature

Metal ion	$[H^+]$	Distribution coefficient (K_d)							
		15	25	35	45	55	65	75	85°C
Zn^{2+}	0.01	3.11	3.61	3.93	4.38	4.80	5.17	5.51	6.00
Ca^{2+}	0.01	0.11	0.08	0.05	0.04	0.03	0.02	-	-
Al^{3+}	0.05	-	-	0.04	0.10	0.27	0.45	1.15	2.19[b]
	0.05[a]	-	-	0.03	0.07	0.10	0.21	0.24	0.48
Bi^{3+}	1.0	6.70	3.63	2.47	1.67	1.18	0.79	0.54	0.37
La^{3+}	0.01	177.88	126.05	107.33	79.94	63.55	50.12	-	-
	0.025	21.38	15.53	12.41	8.53	6.55	5.25	4.53	3.47
	0.025[a]	7.21	4.72	3.04	2.28	1.62	1.24	-	-
Nd^{3+}	0.05	40.46	31.62	28.08	22.51	19.06	17.45	14.68	12.44
	0.05[a]	12.93	8.97	6.84	5.30	4.49	3.29	-	-
	0.10	3.43	2.70	2.40	1.82	1.59	1.34	1.08	-
	0.10[a]	1.57	1.16	0.87	0.79	0.54	0.48	-	-
Gd^{3+}	0.25	10.26	7.77	5.86	4.26	3.10	2.61	2.18	1.45
	0.25[a]	5.42	3.94	2.83	2.03	1.53	1.21	0.86	-
Dy^{3+}	0.5	16.55	11.48	8.45	5.96	4.27	3.13	2.59	-
	0.5[a]	10.03	7.11	4.97	3.49	2.52	1.74	1.24	1.07
Er^{3+}	1.0	9.57	6.76	4.43	2.82	1.92	1.45	0.96	-

[a] Ionic strength made up to 1.0 M by addition of $NaClO_4$

[b] Temperature = 84°C

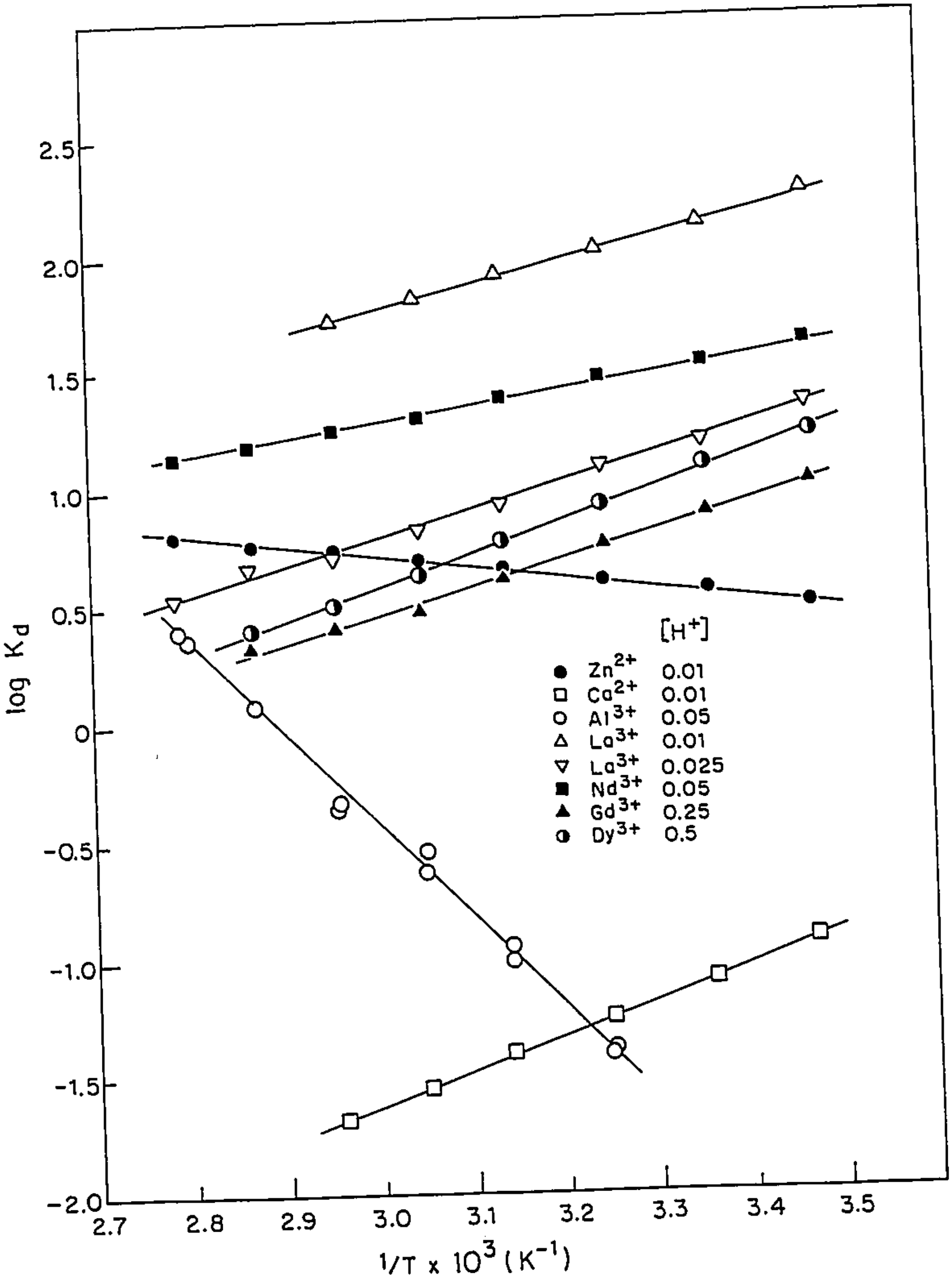


Fig. 22: Effect of temperature on the extraction of Zn^{2+}, Ca^{2+}, Al^{3+}, La^{3+}, Nd^{3+}, Gd^{3+},and Dy^{3+} at varying acidity into 0.025 M HEHΦP in pet. ether.

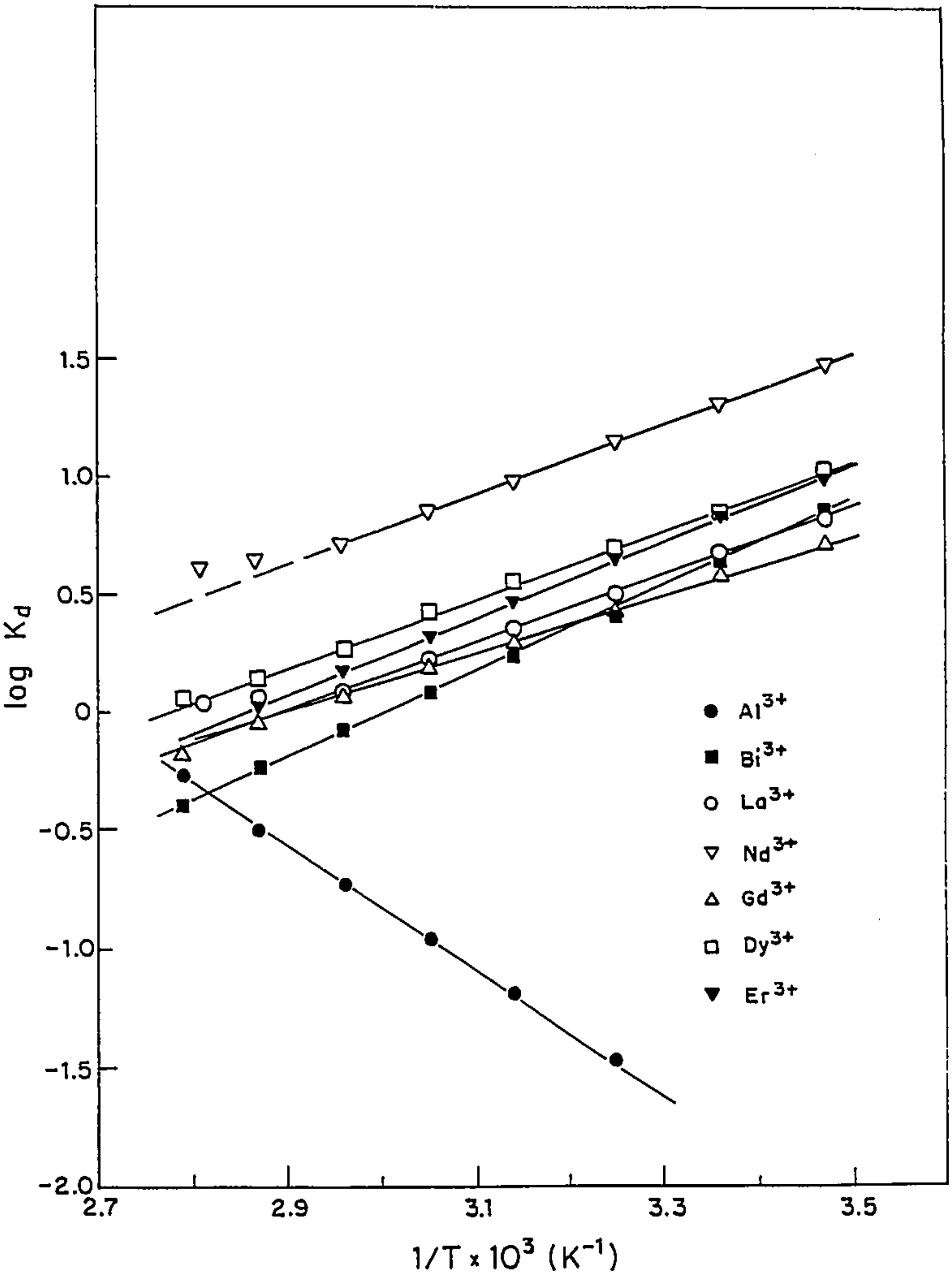


Fig. 23: Effect of temperature on the extraction of Al^{3+}, Bi^{3+}, La^{3+}, Nd^{3+}, Gd^{3+}, Dy^{3+} and Er^{3+} at varying acidity but ionic strength, $\mu(HClO_4+NaClO_4)$,

available

As stated previously, we may derive ΔH^o values from data measured at various temperatures because activity coefficients are essentially independent of temperature. Again, modified (shifted) entropies are defined by

$$\Delta S' = \Delta S^o - R\ln\Gamma \qquad 41$$

when the mean activity coefficients are not available. The values of $\Delta S'$ would be more positive than the standard values, ΔS^o, by about 10 J K^{-1} mol^{-1} at an ionic strength of 0.1 and the difference may be somewhat greater still in those experiments carried out at an ionic strength of unity because the $\gamma_{\pm}$ values generally go through a minimum (at about μ=1.0 M) with increasing concentration in dilute solution.

Comparison of thermodynamic parameters

The values of ΔG, ΔH^o and ΔS are given in Tables 13 and 14. The data in Table 13 refer to experiments carried out at relatively low ionic strength, i.e., in solutions of dilute $HClO_4$ at the concentrations shown. The results of experiments carried out in solutions of $HClO_4$ and $NaClO_4$ with an ionic strength of 1.0 M appear in Table 14.

For a given pair of ions, the difference in free energy of extraction is much greater when HEHΦP is the extractant rather than DNNSA. There is also a reversal in trends in the free energy. Thus Zn^{2+} is more readily extracted than Ca^{2+} by HEHΦP but the reverse is true for DNNSA. Throughout the series of lanthanides the trend in HEHΦP extraction is favoured by both enthalpy and entropy whereas the entropy differences oppose and out-weigh the effects of enthalpy in extractions with DNNSA. It was of particular interest to examine the significance of individual enthalpy and entropy terms in the reaction of various ions so it was necessary to

Table 13

Thermodynamic parameters for extractions of cations with HEHΦP from dilute perchloric acid media[a]

Ion	Crystal Radius pm[b]	Acid Conc, M	ΔG° kJ mol^{-1}	ΔH° kJ mol^{-1}	ΔS° J K^{-1} mol^{-1}
La^{3+}	117.2	0.01	-5.76 ± 0.30	-20.0 ± 0.6	-47.8 ± 2.3
La^{3+}	117.2	0.025	-7.34 ± 0.22	-20.9 ± 1.0	-45.5 ± 2.1
Nd^{3+}	112.3	0.05	-12.92 ± 0.22	-15.3 ± 0.6	-8.1 ± 2.2
Nd^{3+}	112.3	0.10	-12.57 ± 0.17	-15.6 ± 0.4	-10.3 ± 1.5
Gd^{3+}	107.8	0.25	-20.62 ± 0.30	-23.1 ± 0.8	-8.5 ± 3.0
Dy^{3+}	105.2	0.5	-29.03 ± 0.16	-26.3 ± 0.6	+9.5 ± 1.9
Al^{3+}	67.5	0.05	+16.51 ± 0.46[c]	+73.2 ± 2.3	+184.1 ± 7.5[c]
Ca^{2+}	114	0.01	+1.60 ± 0.25	-28.1 ± 0.6	-99.8 ± 1.1
Zn^{2+}	88.0	0.01	+5.83 ± 0.19	+7.8 ± 0.3	+6.7 ± 1.1

[a] Data refer to 25°C except where otherwise noted

[b] Values taken from ref. 74 for 6-coordination

[c] Calculated from data at 35°C

Table 14

Thermodynamic parameters for extractions of cations with HEHΦP from solutions of $HClO_4$ and $NaClO_4$ at an ionic strength of unity

Ion	Crystal Radius pm[a]	Acid Conc, M	ΔG° kJ mol^{-1}	ΔH° kJ mol^{-1}	ΔS° J K^{-1} mol^{-1}
La^{3+}	117.2	0.025	-10.92 ± 0.27	-28.7 ± 0.9	-59.7 ± 3.0
Nd^{3+}	112.3	0.05	-15.78 ± 0.28	-19.9 ± 1.0	-13.9 ± 3.4
Nd^{3+}	112.3	0.10	-15.79 ± 0.37	-19.4 ± 1.4	-12.0 ± 5.0
Gd^{3+}	107.8	0.25	-22.89 ± 0.16	-25.1 ± 0.4	-7.5 ± 1.4
Dy^{3+}	105.2	0.5	-30.37 ± 0.28	-28.4 ± 0.6	+3.4 ±2.4
Er^{3+}	103.0	1.0	-34.56 ± 0.23	-32.5 ± 0.7	+7.0 ± 2.5
Al^{3+}	67.5	0.05	+17.81 ± 0.73[b,c]	+47.4 ± 3.4	+96.1 ± 11.4[b,c]
Bi^{3+}	117	1.0	-30.62 ± 0.35[c]	-34.2 ± 0.9	-12.0 ± 3.3[d]

[a] Values taken from ref. 74 for 6-coordination

[b] Calculated from data at 35°C

[c] ΔG′ ; [d] ΔS′

compare experiments in which the ionic strength was equal.

Lanthanum appears to behave in a singular way although the data show a uniform trend from Nd^{3+} to Er^{3+}. The same uniqueness of lanthanum was observed in DNNSA extractions but to a lesser extent.

The enthalpy of extraction becomes increasingly favourable with increasing atomic number of the lanthanides. With DNNSA, however, the trend was slight and the enthalpies were positive. The stronger Brønsted basicity of the phosphate and phosphonate functionality is accompanied by a stronger affinity for higher-valent cations.

The comparison of ΔS^o values for HEHΦP with corresponding entropy data for DNNSA is revealing. In the case of the latter, it was shown that there was a decrease in entropy across the lanthanide series but with HEHΦP there is an increase. This conforms with the suggestion outlined earlier in the last section where it was argued that the effect of electrostriction of DNNSA micelles outweighs the effect on the solvent water. No comparable effect occurs with HEHΦP so that the trend in hydration energy dominates strongly. The data in Table 15 illustrates this conclusion in a quantitative way. As explained previously, the entropy of the complexing process

$$M_g^{z+} + n(HY)_2 \rightarrow M(\text{complexed}) + zH^+_A \qquad 42$$

is

$$\Delta S^o_c = \Delta S^o + \Delta S^o_h \qquad 43$$

where ΔS^o_h is the entropy of hydration of the gaseous ion. Again we employ a modified form of this for those metal ions where $\gamma_\pm$ of the perchlorate is unavailable, namely

$$\Delta S' = \Delta S_c^o - \Delta S_h^o \qquad 44$$

Again values of ΔS^o_h for the lanthanides taken from reference [253] have been

Table 15

Entropies of hydration and entropies of complexing the gaseous ions with HEHΦP

Ion	ΔS_h^o J K^{-1} mol^{-1}	ΔS_c^o J K^{-1} mol^{-1}
La^{3+}	-341	-401
Nd^{3+}	-355	-369
Gd^{3+}	-390	-398
Dy^{3+}	-397	-394
Er^{3+}	-399	-392
Al^{3+}	-468[a]	-372[b]
Ca^{2+}	-208[a]	-308
Zn^{2+}	-269[a]	-262

[a] Values taken from ref. 253

[b] Shifted values ($\Delta S_c^o = \Delta S' + \Delta S_h^o$)

employed and the value for Al^{3+} should be more positive by about 25 J K^{-1} mol^{-1}.

Whereas the values of ΔS_c^o decreased considerably in extractions with DNNSA as a result of the lanthanide contraction, the values reported in Table 15 for HEHΦP show little, if any, trend across the lanthanide series. It follows that the downward trend in ΔS_h^o is not compensated or more than compensated by a similar trend in ΔS_c^o. The entropy of extraction and hence the free energy can therefore display more pronounced differences between ions in extractions with HEHΦP. The derivation of ΔS_c^o supposes that the lanthanide ions are completely desolvated upon complexing. This is not necessarily the case as the work of Fourest, et al. suggests [257]. The qualitative conclusions are not dependent upon this point, however.

It is widely understood that the chelate effect can be ascribed to the increase in entropy that accompanies desolvation. In the present systems, the large ions do not seem to experience this effect, instead the results indicate a greater decrease in entropy when the gaseous ion is complexed with HEHΦP than when it is hydrated. The reason for this is not clear; perhaps it can be attributed to the dimeric nature of the HY_2 ligand.

Aluminium ion has a much higher charge density than the lanthanides. The large gain in ΔH^o upon extraction is attributed to the loss of hydration which is not compensated by the complexing step. The entropy is also large and positive. These two factors do not nearly compensate one another with the result that the free energy is quite positive. Whereas in extractions with DNNSA, the behaviour of Al^{3+} was similar to that of the lanthanides, in the case of HEHΦP extractions, Al^{3+} complexes with only 1.5 molecules of $(HY)_2$. This results in ΔS_c^o being much less negative. Thus, in this further respect, HEHΦP is capable of providing enhanced separation ability.

The divalent ions demonstrate this effect once again. Calcium ion is comparable in size to the lanthanides and, like the larger lanthanides, it binds three $(HY)_2$ molecules. However, because of the ion's lower charge, it deprotonates only two of the extractant molecules and the complex is written: $Ca(HY_2)_2(HY)_2$. The entropy of complexing is consequently less negative. Zinc ion, however, has a high charge density and this results in the formation of a simpler complex, $ZnY(HY_2)$. Fewer molecules being bound, ΔS_c^o is again, less negative. The individual enthalpy and entropy values for Ca^{2+} and Zn^{2+} differ greatly but there is a large measure of cancellation so that the free energies are not greatly different. However, in extractions with DNNSA, there is so little difference between Ca^{2+} and Zn^{2+} that they are difficult to separate with that extractant.

Reversed-phase chromatographic separation of the lanthanides

In a modification of the solvent extraction technique, a column packed with a solid support which is coated with the extractant was employed to separate the lanthanides. Therefore, in addition to the extractant, choice of the solid material should be critical as well. Among others, the solid support material should meet the following requirements; it should

a) be chemically inert, not swell, dissolve, or undergo any chemical change (for example, hydrolysis of the hydroxyl group in silica gel at low pH) in the extractant and/or the mobile phase.

b) show good wettability by the stationary phase and exhibit a sufficiently strong capillary binding force with the stationary phase.

c) possess a large surface area

d) be hydrophobic or should be made to be, e.g., by exposure to vapours of dimethyldichlorosilane.

In the present work we have used phenylated Kel-F powder which was prepared by the method of Siergiej and Danielson [258] who applied this type of support for the separation of organic mixtures. This technique referred to as reversed-phase extraction chromatography (or supported-phase solvent extraction) is actually a multistage separation process and could accomplish separation of pairs of ions that are difficult to separate by simple solvent extraction. Braun and Ghersini [259] have written an excellent review on the principles and application of this technique.

The raising of this technique to a position competitive with ion exchange for the separation of such related groups as the lanthanides and actinides can be credited to the development of acidic organophosphorus extractants, anionic long chain tertiary and quarternary amines and the first successful application of the technique itself by Siekierski et al. [167,260].

Previous work done in this laboratory and by other workers have employed gradient elution with concentrated acid solutions for the heavier lanthanides. In the present work, we have sought to keep the aqueous mobile phase acidity low by fractionating the lanthanide series into two groups, the first by eluting with an aqueous acid solution (< 1 M) and the second by stripping with a polar organic solvent. We however ran into the problem of low recovery upon wet-ashing the resulting residue after evaporation of the organic eluent. Quantitative recovery of La, Nd and Gd was obtained with 200 ml of 0.9 M HNO_3. Chemical interference that might be due to the resulting phosphate (as in AAS for say, calcium) after ashing is not known to occur in DCP. The support was found to dissolve in the organic eluent. Upon ashing though, even for blanks, the residue was not completely soluble in the aqueous acid solution ($\cong$ 1 M) that was presented to the DCP.

In order to account for the low recoveries obtained when the elements are stripped with 99% ethanol, synthetic samples containing approximately 50 μg per ml of the analyte and varying amounts of phosphate with either H_3PO_4 or KH_2PO_4 as the matrix were prepared. The percent recovery of some elements versus the concentration of phosphate added are shown in Figure 24.

The expectation, especially for the dc plasma of excitation temperatures ca 6000 K, is that atomization should occur efficiently. Whether or not it does even in the presence of such high concentrations of the concomitant salt is uncertain. The speculation, which may not seem plausible given the temperature regime attainable in the plasma and the amount of information from the study thus far, is the formation of hollow solid aerosols which can encapsulate smaller spheres as observed in atomic

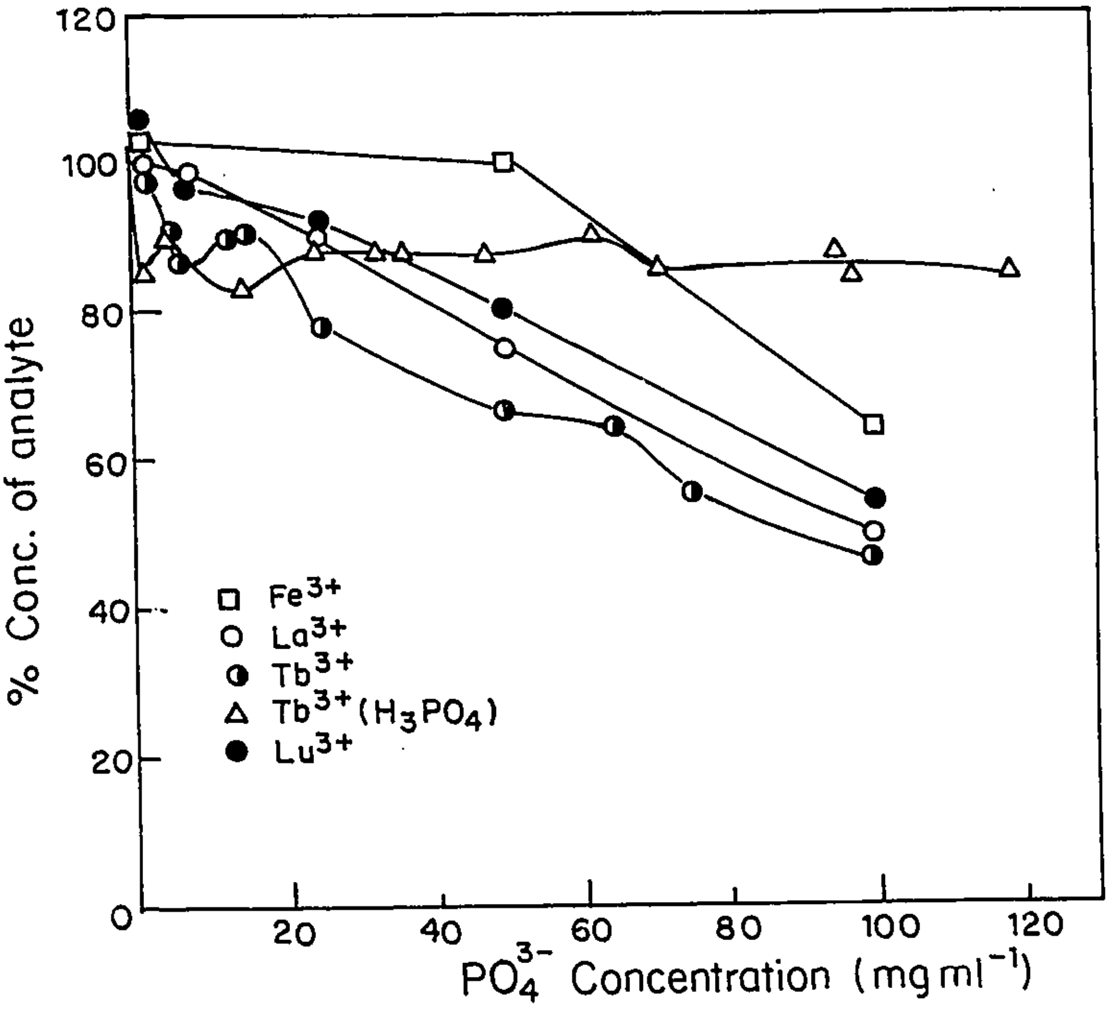


Fig. 24: Percent concentration of Fe^{3+}, La^{3+}, Tb^{3+}, and Lu^{3+} determined in the presence of phosphate.

absorption spectrometry [261]. These authors and others have established that solution composition causes shifts in aerosol size distribution. The latter increases with increase in the concentration of the concomitant salt. Larger aerosol size will and have been observed to result in decreased transport efficiency and a consequent reduction in the analytical signal in atomic absorption [262] and microwave-induced plasma [263] spectrometry.

Consonant with increase in aerosol size distribution is the fact that a longer time will be required to vaporize a larger aerosol and delay the production of atoms such that the analytical signal observed will be reduced.

The effect of KH_2PO_4 is understandable and could be linked to the loss of water from the salt when aspirated into the plasma. The resulting metaphosphate aerosol scavenges for the lanthanides and could be said to be doing that just well, given that recovery becomes poorer for the later lanthanides. This also is expected considering their (i.e., REE) affinity for phosphate ligands. Reproducibility was found to deteriorate for the same sample containing a specfic concentration of KH_2PO_4.

Wet ashing the organophosphonate is most likely to produce the metaphosphate.

The effect observed for H_3PO_4 may be attributed to a poor nebulization due to viscosity [264]. The acid is likely to form metaphosphoric acid in the plasma.

For a definite interpretation of the suppositions made above in trying to explain the results obtained when the concomitant salt is KH_2PO_4, a far more detailed study (such as aerosol size, production and transport processes) of solution composition and behaviour in the plasma is required.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The expectation is that the stabilizing influence that should result upon complexing three dimers to a lanthanide ion should lead to the exclusive formation of the species, $M(HY_2)_3$, in the organic phase but this has been shown not to always be the case, especially for extractants containing a phosphorus-carbon linkage as our results demonstrate. The number of molecules of the extractant that reacts with a given ion decreases with the electric field around the ion. The metal-extractant dimer complexes are monomeric in solution in the presence of excess extractant and polymeric solids crystallize at high (saturation) loading of the organic phase.

Strongly acidic sulphonic acid cation exchange resins have played a central role in metal recovery processes. Their ability to separate the lanthanides is low as is manifested by the narrow range of the free energy (only ca 2.0 kJ mol^{-1} from La^{3+} - Er^{3+}). For the phosphonic acid cation exchanger, our results of about 23 kJ mol^{-1} difference in the free energy of extraction from La^{3+} - Er^{3+} clearly shows that there is certainly an effective alternative to the sulphonic acid resins and the historical notion that the REE are very similar (surely!) is somewhat weakened.

The selective complexation of a strategic metal ions by a given ligand is an important objective for many applications including catalytic [265], chromatographic [266] and metal ion recovery [267] processes. The inherent coordinative ability of phosphoryl containing extractants (due to the strong Brønsted basicity of the phosphoryl oxygen) is responsible for their display of a good deal of selectivity relative to the sulphonyl extractants. The inability of sulphonyl extractants to differentiate among ions can also be seen from the narrow range in the free energy of the ion-exchange and also the change in enthalpy of the reaction with, for example, the lanthanides. This inability can certainly obviate their use for practical recovery processes of valuable or toxic metal ions in a background of innocuous ions present at much higher concentrations.

The superior selectivity exhibited by HEHΦP over DNNSA is manifested by the separation factor, K_β ($K_\beta^{A/B} = K_d^A/K_d^B$), data summarized in Tables 16 and 17. A proper choice of temperature can be employed in order to optimize selectivity of HEHΦP systems whereas a similar option would produce little or no effect for DNNSA systems. If the La^{3+}/Ca^{2+} pair is taken, for example, one notices that the entropy effect leads to a one-stage separation of the two ions in the case of HEHΦP while a multi-stage process would be required with DNNSA to achieve the same separation. One finds that in the case of the La^{3+}/Al^{3+} pair, the difference in extraction mechanism with HEHΦP really accounts for the still better and quantitative separation obtained. The Zn^{2+}/Ca^{2+} pair certainly does not fit into the preferential extraction of the larger ion, but is as a result of differences in extraction mechanism. There is little difference between Er^{3+} and Bi^{3+}, thus these are difficult to separate by either system. Extractability by organophosphorus acid extractants is strongly dependent on acidity so that for the lanthanide series, K_β has been estimated by extrapolating the lines in Figure 12 to $[H^+] = 0.01$ M.

Defining $\Delta S_c^o = \Delta S$ (or ΔS^o) $+ \Delta S_h^o$ was in an attempt to separate the components of the entropy due to complexing apart from the (de)hydration. The results in Tables 11 and 15 certainly do show that changes in entropy of complexing of the free metal ions with HEHΦP plays a major role in contributing to the separability of the metal ions. Thus, the superiority exhibited by HEHΦP over DNNSA is a result of two factors, viz; entropy effects and differing extraction mechanisms.

Table 16

Variation of separation factor (K_β) with temperature in extractions with DNNSA

Pair of ions	K_β at different temperatures			
	25	35	45	65°C
Al^{3+}/Ca^{2+}	2.70	2.87	3.40	4.22
$Al^{3+}/Ca^{2+, a}$	2.31	2.36	2.57	-
Al^{3+}/Zn^{2+}	1.62	1.65	1.77	2.04
Al^{3+}/Bi^{3+}	0.84	0.82	0.82	0.81
Bi^{3+}/Ca^{2+}	3.24	3.51	4.15	5.19
Bi^{3+}/Zn^{2+}	1.92	2.01	2.15	2.52
Er^{3+}/Bi^{3+}	0.56	0.55	0.56	0.55
Er^{3+}/Al^{3+}	5.19	5.14	5.23	5.84
La^{3+}/Al^{3+}	1.39	1.46	1.35	1.42
La^{3+}/Ca^{2+}	3.80	4.19	4.60	5.77
La^{3+}/Zn^{2+}	2.25	2.40	2.39	2.80
Nd^{3+}/Al^{3+}	0.88	0.93	1.00	1.40
Zn^{2+}/Ca^{2+}	1.69	1.75	1.93	2.06
$Zn^{2+}/Ca^{2+, a}$	0.30	0.32	0.36	0.38
Nd^{3+}/La^{3+}	0.63	0.64	0.74	0.76
Gd^{3+}/Nd^{3+}	0.93	0.94	0.89	0.88
Er^{3+}/Gd^{3+}	0.77	0.77	0.77	0.74

[a] Ionic strength adjusted to 0.5 M by addition of $NaClO_4$

Table 17

Variation of separation factor (K_β) with temperature in extractions with HEHΦP

Pair of ions	K_β at different temperatures			
	25	35	45	65°C
Al^{3+}/Ca^{2+}	-	0.8	2.5	22.5
Al^{3+}/Zn^{2+}	-	0.0_1	0.0_2	0.0_9
Al^{3+}/Bi^{3+}	-	0.0_1	0.0_4	0.2_7
Bi^{3+}/Ca^{2+}	43.4	49.4	41.8	39.5
Bi^{3+}/Zn^{2+}	1.0_1	0.6_3	0.3_8	0.1_5
Er^{3+}/Bi^{3+}	1.8_6	1.7_9	1.6_9	1.7_8
Er^{3+}/Al^{3+}	-	148	40.3	6.9
$La^{3+}/Al^{3+, a}$	-	101.3	32.6	5.9
La^{3+}/Ca^{2+}	1576	-	1999	2506
La^{3+}/Zn^{2+}	34.9	27.3	18.3	9.7
Nd^{3+}/Al^{3+}	-	702	225	38.8
$Nd^{3+}/Al^{3+, a}$	-	228	75.7	15.7
Zn^{2+}/Ca^{2+}	45.1	78.6	109.5	259
Nd^{3+}/La^{3+}	16.2^b	-	-	-
Gd^{3+}/Nd^{3+}	33.3^b	-	-	-
Dy^{3+}/Gd^{3+}	50.1^b	-	-	-
Er^{3+}/Gd^{3+}	114.8^b	-	-	-

[a] Ionic strength adjusted to 1.0 M by addition of $NaClO_4$

[b] K_d estimated by extrapolating the lines in Fig. 12 to $[H^+] = 0.01$ M

In order to maximize the separation factor for pairs of similar ions, such as the lanthanides, with DNNSA it is apparent that the best results would probably be achieved by considerably reducing the size of the complex micelle. The HEHΦP extraction system has the ability of differentiating between large polyvalent cations and common sample matrix elements, like calcium and aluminium.

Investigation of extraction processes from the thermodynamic point of view can be used in the determination of the factors influencing the efficiency of extraction. Such data can be used to ascertain what modifications should be made to improve the efficiency and selectivity of extraction systems. In addition, knowledge of the extraction behaviour as a function of temperature can be used in the optimization of conditions (i.e., temperature, concentration of acid and extractant) and the designing of extractants with high extractability and selectivity for the extraction of one metal in the presence of others.

With the intent of reducing and/or eliminating data processing corrections for interelement interference effects between lanthanides as is currently practised, this work pursued their fractionation into at least two sub-groups. Recoveries observed in this effort may not be entirely due to the presence of phosphate; poor nebulization effects may be implicated. The question I ask now is whether phosphate containing matrices are actually dissociated (atomized) in the temperature regime obtainable in the DC plasma. Firm conclusions must await further investigation.

Some of the initial objectives of this work on chromatography are not conclusive. The goal was to be able to employ materials containing the phosphonate functionality in ion exchange (or precisely, extraction chromatography) circuits. The research should continue in terms of finding a reasonably organic insoluble back bone for this particular extractant, polymerization of this mixture which should lead to the application of the resulting resin to the fast fractionation of such chemically similar group of elements like the lanthanides and actinides. Existing separation methods for these elements take a long time. The potential time and cost advantages for the separation of the REE by our proposed method as opposed to gradient elution are obvious.

CLAIMS TO ORIGINAL RESEARCH

1. It was shown by slope analysis method that log-log plots of distribution coefficients versus acid concentrations vary inversely to the charge of the particular metal ion. Due to the dimeric nature of the extractant either integral or half integral dependencies on the extractant concentration were obtained; the number of molecules being dependent on the electric field around the ion.
2. The low temperature ^{31}P NMR study of species forming in the organic phase following extraction of lanthanum in addition to providing information about solubility and stability, revealed structural differences between the isolated solid complex and the complex in solution.
3. The entropy of complexation was shown to be the most important factor in extraction of trivalent ions with the sulphonic acid. As the extracted species is micellar, its entropy of formation from the free ion is numerically large and subject to large variations with change of field about the cation. In the case of the two divalent ions studied, the entropy of hydration dominated marginally.
4. The enthalpy change of the extraction process was shown to be the determining factor in extractions with HEHΦP that exhibit a negative standard free energy of extraction.
5. Also, it was shown that the singular behaviour exhibited by lanthanum in relation to the other REE may be attributed to some structural changes in extractions with HEHΦP as was observed in terms of how many dimers were involved in its complex and the micelle size in the case of DNNSA, respectively.
6. It was shown that the varied mechanism of extraction by HEHΦP makes this

reagent much more selective than DNNSA for metal ion separations.

7. This work established that the presence of an alkali salt ($NaClO_4$ in our case) affects the thermodynamic parameters, especially the free energy and entropy change and emphasizes the importance of maintaining a constant ionic strength in such studies. As well as making the chemistry of the systems comparable, this made generalizations and comparisons based on ΔH^o, ΔG^o (ΔG) and ΔS^o (ΔS) values meaningful.

Parts of the work in this thesis have appeared in a scientific journal while others are awaiting publication.

E. O. Otu and A. D. Westland, Polyhedron 8, 1307-13 (1989)

REFERENCES

1. R. C. Mallett, in *"Analytical Chemistry in the Exploration, Mining and Processing of Materials"*, L. R. P. Butler (ed.), 2nd Inter. Symp., Pretoria, South Africa, April 1985 p.101.
2. P. C. Stevenson and H. G. Hicks, *Ann. Rev. Nucl. Sci.*, 3, 221 (1953).
3. M. Berthelot and E. Jungfleisch, *Ann. Chim. Phys.*, 4, 26,396 (1872).
4. W. Nernst, *Z. Phyzik Chem.*, 8, 110 (1891).
5. J. G. Kirkwood, *J.Chem. Phys.*, 2, 351 1934).
6. R. P. Bell, *Trans. Faraday Soc.*, 27, 797 (1937).
7. H. H. Uhlig, *J. Phys. Chem.*, 41, 1215 (1937).
8. D. D. Eley, *Trans. Faraday Soc.*, 35, 1281,1421 (1939).
9. J. H. Hildebrand and R. L. Scott, *"The Solubility of Non-Electrolytes"*, Dover Publ. Inc., New York, 1964 pp.205-209.
10. G. H. Morrison and H. Freiser, *"Solvent Extraction in Analytical Chemistry"*, John Wiley, New York, 1957.
11. J. Stary, *"The Solvent Extraction of Metal Chelates"*, Pergamon, Oxford, 1964.
12. Y. Marcus and A. S. Kertes, *"Ion Exchange and Solvent Extraction of Metal Complexes"*, John Wiley, New York, 1969.
13. R. M. Diamond and D. G. Tuck, in *"Progress in Inorganic Chemistry", vol.2*, Interscience Publ. Co., New York, 1960, p.109.
14. J. Minczewski, J. Chwastowska and R. Dybczyński, *"Separation and Preconcentration Methods in Inorganic Trace Analysis"*, Ellis Horwood Publ., Chichester, 1982.
15. G. M. Ritchey and A. W. Ashbrook, *"Solvent Extraction" Part 1*, Elsevier,

New York 1984.

16. M. Born, *Z. Phyzik,* 1, 45 (1920).

17. N. Bjerrum, *Kgl. Danske Vidensk. Selskab* 7(9), 1 (1926).

18. R. M. Fuoss and C. A. Kraus, *J. Amer. Chem. Soc.*, 55, 1019,2387 (1933).

19. R. L. Moore, in *USAEC Report HW-15453* (1949).

20a. D. F. Peppard, G. W. Mason, J. L. Maier and W. J. Driscoll, *J. Inorg. Nucl. Chem.*, 4, 334 (1957).

b. D. F. Peppard, J. R. Ferraro and G. W. Mason, *ibid* 4, 371 (1957).

c. D. F. Peppard, G. W. Mason, W. J. Driscoll and R. J. Sironen, *ibid* 7, 276 (1959).

d. D. F. Peppard, G. W. Mason and R. J. Sironen, *ibid* 10, 117 (1959).

e. D. F. Peppard, G. W. Mason W. J. Driscoll and R. J. Sironen, *ibid* 12, 141 (1959).

f. D. F. Peppard, G. W. Mason and I. Hucher, *ibid* 18, 245 (1961).

g. J. R. Ferraro, G. W. Mason and D. F. Peppard, *ibid* 22, 285 (1961).

h. G. W. Mason, S. McCarty and D. F. Peppard, *ibid* 24, 967 (1962).

i. D. F. Peppard, G. W. Mason and C. M. Anderjasich, *ibid* 25, 1175 (1963).

j. D. F. Peppard and G. W. Mason, *Nucl. Sci. Eng.*, 17, 247 (1963).

k. D. F. Peppard, *"Advances in Inorganic Chemistry and Radiochemistry"*, H. J. Emeléus and A. G. Sharpe (eds.), 9, 1 (1966)

21. G. M. Kosolapoff and J. S. Powell, *J. Chem. Soc.*, 3535 (1950).

22. D. Dyrssen, *Acta Chem. Scand.*, 11, 1771 (1958).

23. C. J. Hardy and D. J. Scargill, *J. Inorg. Nucl. Chem.*, 11, 128 (1959).

24. R. D. Baybarz and R. E. Leuze, *Nucl. Sci. Eng.*, 11, 90 (1963).

25. D. Dyrssen, S. Ekberg and D. H. Liem, *Acta Chem. Scand.*, 18, 135

(1964).

26. I. S. Levin, *Zh. Analit. Khim.*, 23, 673 (1968).

27. E. V. Komarov, N. N. Komarov and M. F. Pushlenkov, *Radiokhimiya* 12, 455 (1970).

28. J. Barnes, J. H. Setchfield and G. O. .R. Williams, *J. Inorg. Nucl. Chem.*, 38, 1065 (1976).

29. V. A. Tarasova, I. S. Levin and T. F. Rodina, *Zh. Analit. Khim.*, 32, 719 (1977)

30. O. Navrátil, *Collect. Czech. Chem. Commun.*, 42, 2778 (1977).

31. J. Rydberg, *Arkiv Kemi*, 8, 101 (1955).

32. I. M. Kolthoff and E. B. Sandell, *J. Amer. Chem. Soc.*, 63, 1906 (1941).

33. R. W. Geiger and E. B. Sandell, *Anal. Chim. Acta* 8, 197 (1953).

34. D. Dyrssen, M. Dyrssen and E. Johansson, *Acta Chem. Scand.*, 10, 341 (1956).

35. H. Irving, F. J. C. Rossotti and R. P. J. Williams, *J. Chem. Soc.*, 1906 (1955).

36. S. Siekierski, *J. Radioanal. Chem.*, 31, 355 (1976).

37. M. Oosting, *Anal. Chim. Acta*, 21, 301,397,505 (1959)

38. G. R. Choppin and P. J. Unrein, *J. Inorg. Nucl. Chem.*, 25, 387 (1963).

39. M. J. Jaycock and A. D. Jone in *"Solvent Extraction Chemistry"*, D. Dyrssen, J. -O. Liljenzin and J. Rydberg (eds.), North-holland, Amsterdam, 1967, p.160.

40. J. M. White, P. Kelly and N. C. Li, *J. Inorg. Nucl. Chem.*, 16, 337 (1961).

41. J. Stary and V. Balek, *Collect. Czech. Chem. Commun.*, 27, 809 (1962).

42. S. Kaufmann and C. R. Singleterry, *J. Colloid Sci.*, (a) 10, 139 (1955); (b)

12, 465 (1959)

43. G. Y. Markovits and G. R. Choppin, in *"Ion Exchange and Solvent Extraction", vol.3,* J. A. Marinsky and Y. Marcus (eds.), Marcel Dekker, New York, 1973, p.51 and references therein.

44. R. Chiarizia, P. R. Danesi, M. A. Raieh and G. Scibona, *J. Inorg. Nucl. Chem.,* 37, 1495 (1975)

45. P. Y. Chen, C. L. Tseng, S. Y. Yeh and P. S. Weng, *J. Radioanal. Chem.,* 37, 801 (1977)

46. E. Högfeldt, R. Chiarizia, P. R. Danesi and V. S. Soldatov, *Chemica Scripta* 18, 13 (1981) and references therein.

47. N. H. Nachtrieb and R. E. Fryxell, *J. Amer. Chem. Soc.,* 74, 897 (1952).

48. J. B. Hasted, D. M. Ritson and C. H. Collier, *J. Chem. Phys.,* 16, 1 (1948)

49. A. Aue, L. Skjutare, G. Bjorling, H. Reinhdart and J. Rydberg, *Proc.- Int. Solv. Extr. Conf., Publ. Soc. Chem. Ind., London,* 1971, p.447.

50. V. S. Archer and F. G. Doolittle, *Anal. Chem.,* 39, 371 (1967); *Talanta* 14, 921 (1967).

51. D. W. Margerum and C. V. Banks, *Anal. Chem.,* 26, 200 (1954).

52. F. Vydra and R. Pribil, *Talanta* 3, 72 (1959).

53. Yu. A. Zolotov, *Koord. Khim.,* 5, 23 (1979).

54. O. M. Petrukhin, *Zh. Neorg. Khim.,* 24, 3155 (1979).

55. C. Yuan, S. Li and S. Hu, *Proc.- Int. Solv. Extr. Conf.,* 1986 p.487

56. Y. Marcus, E. Yanir and A. S. Kertes, *"Equilibrium Constants of Liquid-liquid Distribution Reactions"* IUPAC Chemical Data Series No. 15 (1977) Pergamon.

57. Y. Marcus, *Solv. Extr. Ion Exch.,* 7, 567 (1989) and references therein.

58a. J. R. Ferraro and D. F. Peppard, *Nucl. Sci. Eng.*, 16, 389 (1963).

b. D. F. Peppard, G. W. Mason, and C. Andrejasich, *J. Inorg. Nucl. Chem.*, 28, 2347 (1966).

c. G. S. Rao, G. W. Mason and D. F. Peppard, *ibid* 28, 887 (1966)

d. D. F. Peppard, G. W. Mason and G. Griffin, *ibid* 27, 1683 (1975)

e. Ref. 39 p.264

f. D. C. Stewart and H. W. Crandell, *J. Amer. Chem. Soc.*, 73, 1377 (1951)

59a. K. Bange and J. W. Smith, *J. Chem. Soc.*, 4244 (1964)

b. E. Högfeldt and F. Fredlund, *Acta Chem. Scand.*, 18, 543 (1964)

c. W. Smułek and S. Siekierski, *J. Inorg. Nucl. Chem.*, 24, 1651 (1962)

d. R. M. Diamond, *Proc.- Int. Conf., Gottenberg (1966)*, 349 (see ref. 39)

e. Ref. 39 p.383.

f. Ref. 39 p.390

60. E. V. Komarov and V. N. Komarov, *Radiokhimiya* 12, 297 (1970)

61. A. P. Samedelov, *Zh. Neorg. Khim.*, 10, 1723 (1965)

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

63. A. W. Ashbrook and G. M. Ritchey, *"The Eldorado Process for the Separation of Cobalt and Nickel"*, Presented at the 5th Conf. Metallurgists, Toronto, August 1966.

64. G. M. Ritchey and B. H. Lucas, *Proc.- Int. Solv. Extr. Conf., Lyon,* Sept.1974, pp.2437-2481, Publ. Soc. Chem. Ind., London, 1974

65. R. D. Baybarz, *Nucl. Sci. Eng.*, 17, 463 (1963).

66. M. A. Hughes and P. D. Middle-brook, *Hydrometallurgy* 4, 125 (1979)

67. Ref. 15 pp.195-199

68. A. A. Beus, *Geochemistry* 4, 388 (1958)

69. D. A. Mineyev, Yu. P. Dikov, B. P. Sobolev and V. L. Borutskaya, *Geokhimiya* 469 (1966)

70. R. F. Martin, J. E. Whitley and A. R. Woolley, *Contrib. Mineral. Petrol.*, 66, 69 (1978)

71. P. L. Hellman, R. E. Smith and P. Henderson, *Contrib. Mineral. Petrol.*, 71, 23 (1978)

72. H. W. Nesbitt, *Nature* 270, 206 (1979)

73. L. H. Ahrens, in *"Progress in the Science and Technology of the Rare Earths", vol.1*, L. Eyring (ed.), MacMilliam Co., New York, 1964, p.1-29

74. R. D. Shannon, *Acta Crystallogr.*, 32(A), 751 (1976)

75. A. F. Wells, *"Structural Inorganic Chemistry"*, Clarendon Press, Oxford, 4th ed., 1984, pp.1248-1250

76. L. B. Asprey and B. B. Cunningham, in *"Progress in Inorganic Chemistry", vol.2*, Intrescience Publ., New York, 1960, pp.267-302.

77. P. N. Yocom, in *"Lanthanide/Actinide Chemistry", vol.71, Advances in Chemistry Series, Amer. Chem. Soc.*, Washington D. C., 1967, pp51-55.

78. G. R. Machlan, C. T. Stubblefield and L. Eyring, *J. Amer. Chem. Soc.*, 77, 2975 (1955)

79. C. T. Stubblefield and L. Eyring, *ibid* 3004

80. T. Moeller, *"The chemistry of the Lanthanides"*, Reinhold Book Corp., New York, 1963, Chap.2

81. P. B. Venuto, and E. T. Habib, *"Fluid Catalytic Cracking with Zeolite Catalysts"*, Marcel Dekker, Inc., New York 1979

82a. J. E. Otterstedt, and J. Sterte, *Appl. Catal.*, 38, 131 (1988).

b. J. E. Otterstedt, Y. M. Zhu and J. Sterte, *ibid* 143.

83. L. L. Hegedus and J. J. Gumbleton, *Chemtech*, 10, 630 (1980)

84. RIC News 6(4) December 4, 1971. *Rare Earth Information Centre, Institute for Atomic Research*, Iowa State University, Ames Iowa, 50010, U.S.A.

85. F. L. Kennard III, in *"Industrial Applications of the Rare Earth Elements"*, K. A. Gschneider, Jr. (ed.), ACS Symposium Series, Amer. Chem. Soc., Washington D. C., 1981, Chap.15.

86. F. L. Harding, *"Introduction to Glass Science"*, L. D. Pye, H. J. Stevens and W. C. LaCourse (eds.), Pleunum Press, New York, 1972 pp.417-423

87. N. J. Kreidl and J. R. Hensler, *J. Amer. Chem. Soc.*, 38(12), 423 (1955)

88. T. C. Schutt and G. Barlow, *Amer. Ceram. Soc. Bull.*, 51, 155 (1972)

89. H. J. Weinmann, *Am. J. Radiol.*, 142, 619 (1984).

90. F. Conti, M. Delfini, F. Scopinaro and U. Croatto, *Inorg. Chim. Acta.*, 140, 335 (1987).

91. Ph. Poirier, *Proceedinds of the 4th Industrial Minerals Inter. Congr.*, Atlanta, Ga. (1981). *Metal. Bull. PLC(London)*, 205-209 (1981).

92. K. A. Wickersheim and R. A. Lefever, *J. Electrochem. Soc.*, 111, 47 (1964)

93. A. E. Hardy, *IEEE Trans. Electron Devices* ED15, 868 (1968).

94. A. K. Levine and F. C. Papilla, *Appl. Phys. Lett.*, 5, 118 (1964)

95. J. G. Rabatin, ref. 82, Chap. 12.

96. M. J. Lammers, G. Blasse, D. R. Terrell and L. B. Alaerts, *Euro. Pat. Appl. EP* 257,138. *CA* 108 P213616r.

97. A. Lempicki and H. Samelson, *Sci. Am.*, 216, 81 (1967)

98. E. Snitzer, *J. Amer. Ceram. Soc.*, 52, 516 (1973)

99. T. M. Baer and M. S. Keirstead, **Ger. Offen. DE 3,643,648.** *CA* 108

P176862v

100. Roskill Information Services Ltd., *"The Economics of the Rare Earths and Yttrium"*, Roskill, London, 4th ed., 1980

101. J. Lindmayer, **U.S.** *US* **4,705,952.** *CA* 108 P176858

102. C. M. Moore, *U. S. Bureau of Mines* (1979) 11pp.

103. A. L. Robinson, *Science*, 233, 920 (1984).

104. K. H. J. Buschow, *Mater. Sci. Rep.*, 1, 1 (1986)

105. J. Chavanne, J. Laforest and R. Pauthenet, *Mater. Res. Soc. Symp. Proc.*, 96, 307 (1987)

106. J. W. Nielsen, ref. 82, Chap. 13

107. W. K. Anderson, in *"The Rare Earth"*, F. H. Spedding and A. H. Daane (eds.), John Wiley, New York, 1961 p.522

108. A. Raman, *Z. Metallkd.*, 67, 780 (1976)

109. R. G. Wells, in *" The Rare Earths in Modern Science and Technology"*, G. J. McCarthy and J. J. Rhyne (eds.), Plenum Press, New York, 1978 pp.341-346

110. I. N. Ross, *Metals Mater.*, October 1975 pp.42-45

111. A. Raman, *Z. Metalkd.*, 68, 163 (1977)

112: T.Murai and Y. Hashimoto, **Jpn. Kokai Tokkyo Koho JP 62,202,056 [87,202,056].** *CA* 108 P116767h.

113. W. Hoskins, *J. Chem. Educ.*, 54, 128 (1977)

114. H. H. van Mal, K. H. J. Buschow and A. R. Miedema, *J. Less-Common Metals*, 49, 473 (1976).

115. K. Soga, J. Imamura and S. Ikeda, *J. Phys. Chem.*, 81, 1762 (1977)

116. B. Ceccaroli, L. Alstad and M. J. F. Leroy, *Polyhedron* 1, 257 (1982).

117. D. Li, Z. Wang, Y. Xie, C. Shen, C. Zhung and S. Le, *New Front. Rare Earth Sci. Appl., Proc.- Int. Conf. Rare Earth Dev. Appl.*, 1, 463 (1985)

118. G. Xie and G. Chen, *Jinan Liyi Xuebao* 3, 60 (1986)

119. D. F. Peppard, G. W. Mason and I. Hucher, *Radioisotopes in the Physical Sciences and Industry, Proc.- Conf. Use., Copenhagen*, 1960, 2, 541 (publ.1962)

120. B. Weaver and R. R. Shoun, *J. Inorg. Nucl. Chem.*, 33, 1909 (1971)

121. G. Ghersini, *J. Chromatogr.*, 102, 299 (1974)

122. K. S. Math, Q. Fernando and H. Freiser, *Anal. Chem.*, 36, 1762 (1964)

123. Z. Kolarík, S. Dražanová and V. Chotívka, *J. Inorg. Nucl. Chem.*, 33, 1125 (1971)

124. P. R. Danesi, L. Reichley-Yinger, G. W. Mason, L. Kaplan, E. P. Horwitz and H. Diamond, *Solv. Extr. Ion Exch.*, 3, 435 (1985)

125. M. A. Davis, *J. Org. Chem.*, 32, 1161 (1967)

126. S. Fisel, T. Ungurenasu and Gh. Grosu, *CA* 68 26662w

127. J. Preston, *Hydrometallurgy* 9, 115 (1982)

128. Z. Kolarík and H. Pánková, *J. Inorg. Nucl. Chem.*, 28, 2325 (1966)

129. Z. Kolarík, J. Hejná and H. Pánková, *ibid* 30, 253,2795 (1968)

130. C. Yuan, H. Long, E. Ma, W. Cheng and X. Yan, *New Front. Rare Earth Sci. Appl., Proc.- Int. Conf. Rare Earth Dev. Appl.*, Beijing, Sept., 10-14, 1985, vol.1, p.457

131. C. Yuan, W. Ye, H. Long, E. Ma, J. Yan, F. Wu, X. Yan and P. Jing, *Proc.- Int. Solv. Extr. Conf.*, Munchen, FRG., 1986 p.495

132. C. Yuan, J. Yan, H. Feng, H. Long, F. Wu and P. Jing, *Sci. Sin., Ser. B*, 30, 681 (1987). *CA* 107 184677h

133. T. Sato, *J. Radioanal. Nucl. Chem.,* 101, 77 (1986)

134. C. Bao, *Huaxue Xuebo* 42, 1210 (1984). *CA* 102 101357b

135. K. Inoue, Y. Baba and K. Yoshizuka, *Hydrometallurgy* 19, 393 (1988).

136. T. Sato, S. Ishii and K. Sato, *Proc.- Symp. Solv. Extr.,* 1987 p.137

137. T. Sato, J. Horie and T. Nishimura, *Proc.- Symp. Solv. Extr.,* 1987 p.131.

138. M. Tanaka, M. Niiane and M. Ichijo, *Kogai Shigen Kenkyusho Iho* 15, 15 (1985). *CA* 104 228094k

139. Y. Sato, F. Valenzuela, T. Tsuneyuki, K. Kondo and F. Nakashio, *J. Chem. Engng. Japan* 20, 317 (1987).

140. *Extraction of Molybdenum.* Nippon Mining Co. Ltd, Japan, **Kokai Tokkyo Koho JP 58,120,523 [83,120,523].**

141. K. Inoue and Y. Baba, *Solv. Extr. Ion Exch.,* 5(6), 1031 (1987)

142. D. Liu, R. Li, R. Zhang and G. Chen, *Congr. Int. Mineralurgie, 15th,* 2, 459 (1985). GEDIM: St Etienne, Fr.

143. D. Pearson, *Proc.- Int. Conf. Cobalt: Metall. Uses* 1, 139 (1981)

144. D. B. Dreisinger and W. C. Cooper, *Hydrometallurgy* 12, 1 (1984).

145. A. Fujimoto, I. Miura and K. Noguchi, **Japan Patent 53-1141176** (1978)

146. I. Komasawa, T. Otake and I. Hottori, *J. Chem. Eng. Japan* 16, 210 (1983); idem, *ibid* 16, 384 (1983)

147. I. Komasawa and T. Otake, *J. Chem. Eng. Japan* 17, 416 (1984)

148. F. Nakashio, K. Kondo, A. Murakami and Y. Akiyoshi, *J. Chem. Eng. Japan,* 15, 274 (1982).

149. D. F. Peppard, M. N. Namboodiri and G. W. Mason, *J. Inorg. Nucl. Chem.,* 24, 979 (1962)

150. A. Fujimoto, I. Miura and K. Noguchi, **Japan Patent 54-38273** (1979)

151. Y. Mori, H. Ohya, H. Ono and W. Eguchi, *J. Chem. Eng. Japan* 21, 86 (1988)

152. E. Ma, X. Ya, W. Sanyi, H. Long and C. Yuan, *Proc.- Int. Solv. Extr. Conf.*, Liege, paper 80-147, Sept. 1980

153. D. F. Peppard, G. W. Mason, I. Hucher and F. A. J. A. Brandao, *J. Inorg. Nucl. Chem.*, 42, 1387 (1962)

154. L. Cheng, Y. Yang, M. Luo and D. Zhang, *Inorg. Chim. Acta* 130, 119 (1987)

155. G. Wang, Z. Hu and M. Liu, *Sepu* 5, 377 (1987). *CA* 108 105419r

156. Q. Lai and C. Yuan, *Huaxe Xuebao* 40, 563 (1982). *CA* 97 229250g.

157. W. Ya, N. Wang and Z. Jin, *New Front. Rare Earth Sci. Appl., Proc.- Int. Conf. Rare Earth Dev. Appl.*, Beijing, Sept., 10-14, 1985 vol.1 p.423

158. X. Luo and N. Ye, *Yanshi Kuangwu Ji Ceshi* 3, 179 (1984). *CA* 102 55312h

159. *INIS Atomindex* 8 1977; Abstr. No. 295162. *CA* 87 145198

160. H. Hubicka and H. Hubicki, *Mater. Sci.*, 3, 101 (1977)

161. Y. Zhai, X. Chen, Z. Su and M. Tan, *Lanzhou Daxue Xuebo, Ziran Kexueban*, 20, 126 (1984). *CA* 102 89126r

162. S. Ohashi, S. Shigeto and K. Akiba, *Kakuirkan Kenkyu Hokoku (Tohoku Daigaku)*, 20, 52 (1987). *CA* 108 98356s

163. H. Matsuyama, Y. Katayama, A. Kojima, I. Washijima, Y. Miyake and M. Teramoto, *J. Chem. Eng. Japan* 20, 21 (1987).

164. W. Murayama, Y. Kobayashi, Y. Kosuye, H. Yano, Y. Nunogaki and K. Nunogaki, *J. Chromatogr.*, 239, 643 (1982)

165. S. Sawai, S. Nakamura, K. Akiba and W. Murayama, *Proc.- Symp. Solv.*

Extr., 1987 p.37

166. T. Araki, Y. Kubo, T. Toda, M. Takata, T. Yamashita, W. Murayama and Y. Nunogaki, *Analyst* 110, 913 (1985)

167. I. Fidelis and S. Siekierski, *J. Chromatogr.*, 17, 542 (1965).

168. D. F. Peppard, E. P. Horwitz and G. W. Mason, *J. Inorg. Nucl. Chem.*, 24, 429 (1962)

169. R. E. Leuze, R. D. Baybarz and B. Weaver, *Nucl. Sci. Eng.*, 17, 252 (1963)

170. B. Weaver, *J. Inorg. Nucl. Chem.*, 30, 2233 (1968)

171. G. A. Yagodin, O. A. Sinegribova and N. A. Plesskaja, *CIM Spec. vol.* 1979 21 *Pro.- Int. Solv. Extr. Conf.*, 1977 p.645

172. S. V. Shmidt. A. V. Afanas'ev, O. A. Simegribova and G. A. Yagodin, *Zh. Neorg. Khim.*, 30, 443 (1985). *CA* 102 138568x

173. R. G. W. Schulze and H. H. Y. Schulez, **Ger. Offen. 2,614,356.**

174. R. D. Baybarz, *J. Inorg. Nucl. Chem.*, 27, 1813 (1965).

175. C. J. Kantipuly, *PhD Thesis*, University of Ottawa, 1984

176. J. Alstad, B. Ceccaroli, J. P. Brunnette and M. J. F. Leroy, *Proc.- Int. Solv. Extr. Conf.*, 1980 paper 80-48.

177. M. J. Herak and V. Jagodić, *Croat. Chem. Acta*, 36, 51 (1964). *CA* 62 2462h

178. V. Jagodić, M. J. Herak and J. Radošević, *J. Less-Common Metals*, 15, 371 (1968); idem, *J. Inorg. Nucl. Chem.*, 39, 2053 (1977)

179. V. Jagodić and M. Herak, *J. Inorg. Nucl. Chem.*, 32, 1323 (1970)

180. C. G. Warren, *ibid* 23, 103 (1961)

181. D. F. Peppard, G. W. Mason, S. McCarty and F. D. Johnson, *ibid* 24, 321 (1962)

182. A. Fujimoto and I. Miura, (Daihachi Chemical Ind. Co. Ltd.), **Japan Kokai Tokkyo Koho JP 79,38,273.** *CA* 90 140541k; 91 77365j

183. O. Navrátil and R. Kolouchi, *Hydrometallurgy* 7, 289 (1981)

184. M. J. Puga, G. Ndip, H. K. Lee, I. Yang and R. A. Bartsch, *Anal. Chem.*, 58, 2723 (1986)

185. V. S. Soldatov, Z. I. Kuvaeva and A. W. Popov, *Solv. Extr. Ion Exch.*, 4, 361 (1986).

186. R. C. Little and C. R. Singleterry, *J. Phys. Chem.*, 68 3453 (1968).

187. V. S. Soldatov, L. V. Yurevich and E. Högfeldt, *J. Inorg. Nucl. Chem.*, 39, 2069 (1977)

188. D. F. C. Morris, *Chem. Ind.*, 624 (1973)

189. A. van Dalen, K. W. Gerritsma and J. Wijkstra, *J. Colloid Sci.*, 48, 122 (1974)

190. D. F. C. Morris, *J. Colloid Interface Sci.*, 51, 52 (1975)

191. G. G. David, D. F. C. Morris and E. L. Short, *J. Colloid Interface Sci.*, 82, 226 (1981)

192. A. S. Kertes and H. Gutmann, *"Surface and Colloid Science"*, E. Matijević (ed.), vol.8, Interscience, New York, 1974

193. M. H. Morabbi, D. F. C. Morris and E. L. Short, *Radiochim. Acta* 29, 41 (1981).

194. D. F. C. Morris, A. I. McLeod and T. J. McNicholas, unpublished work cited in ref. 181

195. S. A. Bryan, W. J. McDowell, B. A. Moyer. C. F. Baes, Jr., and G. N. Case, *Solv. Extr. Ion Exch.*, 5, 717 (1987).

196. F. M. Fowkes, *"Solvent Properties of Surfactant Solutions"*, K. Shinoda

(ed.), Marcel Dekker, 1967, p.65

197. N. M. Patel and J. R. Thornback, *Solv. Extr. Ion Exch.*, 5, 633 (1987)

198. M. A. Khan and D. F. C. Morris, *J. Less-Common Metals* 13, 53 (1967)

199. S. W. Wang, M. N. Chen, C. L. Tseng and P. S. Weng, *Radioisotopes* 22, 493 (1973)

200. S. W. Wang, C. L. Tseng, C. N. Hsu and P. S. Weng, *ibid* 22, 497 (1973).

201. F. Ore and J. Brandford, Paper presented at the ACS Meeting, Chicago, Aug. 1975

202. V. K. Rao, G. R. Mahajan and P. R. Natarajan, *Inorg. Chim. Acta* 128, 131 (1987)

203. *CA* 92 153830v

204. C. S. Brooks, *Proc.- Ind. Waste Conf., 1986 (Publ.1987). 41st pp.647-51.* *CA* 107 100178k

205. C. S. Brooks, *Met. Finish.*, 85, 55 (1987). *CA* 106 199638z

206. W. F. Kinard, W. J. McDowell and R. R. Shoun, *Sep. Sci. Technol.*, 15, 1013 (1980)

207. W. F. Kinard and W. J. McDowell, *J. Inorg. Nucl. Chem.*, 43, 2947 (1981)

208. I. H. Gerow, J. E. Smith, Jr., and M. W. Davis, Jr., *Sep. Sci. Technol.*, 16, 519 (1981)

209. W. J. McDowell, G. N. Case and D. W. Aldrup, *Sep. Sci. Technol.*, 18, 1483 (1983)

210. R. G. Schuler, C. B. Bowers, Jr., J. E. Smith, Jr., V. van Brunt and M. W. Davis, Jr., *Solv. Extr. Ion Exch.*, 3, 567 (1985)

211. W. J. McDowell, B. A. Moyer, G, N, Case and F. I. Case, *Solv. Extr. Ion Exch.*, 4, 217 (1986)

212. D. D. Ensor, G. R. McDonald and C. G. Pippin, *Anal. Chem.*, 58, 1814 (1986)

213. M. W. Davis, Jr., and C. B. Bowers, Jr., **Eur. Pat. Appl. EP216,473.** *CA* 107 185702z

214. W. J. McDowell, B. Moyer, S. A. Bryan, R. B. Chadwick and G. N. Case, *Proc.- Int. Solv. Extr. Conf.*, Munchen, FRG., 1, 477 (1986).

215. Ref. 12, p.164

216. A. van Dalen and K. W. Gerritsma, *Proc.- Int. Solv. Extr. Conf.*, (1971), 2, 1096.

217. A. van Dalen, K. W. Gerritsma and J. Wijkstra, *J. Colloid Interface Sci.*, 48, 127 (1974)

218. idem, *J. Inorg. Nucl. Chem.*, 40, 875 (1978)

219. R. Swarup, A. G. Godbole and S. K. Patil, *Radiochem. Radioanal. Lett.*, 54, 183 (1983).

220. M. H. West, *Report* 1983, DOE/ER/10489-14. *CA* 103 93769r

221. K. Osseo-Asare and M. E. Kenney, *Sep. Sci. Technol.*, 15, 999 (1980)

222. A. Ramadan and P. R. Danesi, *Solv. Extr. Ion Exch.*, 6, 157 (1988)

223. D. N. Muraviev and E. Högfeldt, *React. Poly., Ion Exch., Sorbents* 8, 97 (1988).

224. P. R. Danesi, R. Chiarizia and G. Scibona, *J. Inorg. Nucl. Chem.*, 37, 3926 (1973)

225. E. B. Sandell, *"Colorimetric Determination of Traces of Metals"*, 2nd ed., Interscience, New York, 1950 p.216

226. K. Govindaraju, G. Mevelle and C. Chouard, *Anal. Chem.*, 48, 1325 (1976)

227. I. Kojima, J. Fukuta and M. Tanaka, *J. Inorg. Nucl. Chem.*, 31, 1875 (1969).

228. E. O. Otu and A. D. Westland, *Polyhedron* 8, 1307 (1989)

229. L. A. Ajawin, J. Demetriou, E. S. Perez de Ortiz and H. Sawistowski, *Extraction'84; Symp. Liquid-Liquid Extr. Sci., Int. Chem. Engng. Symp. Ser.* No.88, p.183

230. D. F. Peppard, J. R. Ferraro and G. W. Mason, *J. Inorg. Nucl. Chem.*, 12, 60 (1959)

231. Ref. 43 p.83 and references therein.

232. Y. Egozy and S. Weiss, *J. Inorg. Nucl. Chem.*, 33, 1451 (1971).

233. A. Vashman, T. Vereschagina and I. S. Pronin, *Zh. Neorg. Khim.*, 17, 471 (1972); 18, 2897 (1973)

234. R. von Ammon, *Proc.- Inter. Solv. Extr. Conf.*, Lyon, Sept. 1974. Publ. Soc. Chem. Ind., London, 1974 p.2512.

235. A. E. Lemire, A. F. Janzen and K. Marat, *Inorg. Chim. Acta* 110, 237 (1985); 114, 211 (1986).

236. D. G. Kalina, *Solv. Extr. Ion Exch.*, 2, 381 (1984)

237. Ref. 12 pp.543-544 and references therein

238. C. J. Hardy, *J. Inorg. Nucl. Chem.*, 21, 348 (1961)

239. T. Sato, *J. Inorg. Nucl. Chem.*, 37, 1485 (1975)

240. J. Ripmeester, NRC, Ottawa, *Private communication.*

241. N. A. Adaikin, É. S. Barketov and A. A. Zaitsev, *Radiokhimiya* 16, 187 (1974); 18, 351 (1976).

242. D. F. Peppard and J. R. Ferraro, *J. Inorg. Nucl. Chem.*, 10, 275 (1959).

243. L. C. Thomas, *"Interpretation of the IR Spectra of Organophosphorus*

Compounds", Heyden, London 1974.

244. L. J. Bellamy, *"The Infrared Spectra of Complex Molecules"*, 3rd ed. (1975); *"Advances in Infrared Group Frequencies"*, Chapman and Hall, London (1975)

245. L. I. Katzin, G. W. Mason and D. F. Peppard, *Spectrochim. Acta* 34A, 51 (1978).

246. D. F. C. Morris and S. D. Hammond, *Electrochim. Acta* 13, 545 (1968).

247. G. R. Choppin and J. K. Schneider, *J. Inorg. Nucl. Chem.*, 32, 3283 (1970)

248. P. R. Danesi, R. Chiarizia, M. A. Raieh and G. Scibona, *J. Inorg.Nucl. Chem.*, 37, 1489 (1975).

249. J. A. Rard, H. O. Weber and F. H. Spedding, *J. Chem. Eng. Data* 22, 187 (1977)

250. J. Torrent, F. Sanz and J. Virgili, *J. Solution Chem.*, 15, 363 (1986)

251. J. Kielland, *J. Am. Chem. Soc.*, 59, 1675 (1937).

252. B. E. Conway, *"Electrochemical Data"* Amsterdam, Elsevier, 1952.

253. S. L. Bertha and G. R. Choppin, *Inorg. Chem.*, 8, 613 (1969).

254. W. J. Moore, *"Physical Chemistry"*, 1972, 4th ed., Prentice-Hall, Englewood Cliffs, p.539

255. D. D. Eley and M. G. Evans, *Trans. Faraday Soc.*, 34, 1093 (1938)

256. I. Fidelis and S. Siekierski, *J. Inorg. Nucl. Chem.*, 29, 2629 (1967)

257. B. Fourest, J. Duplessis and F. David, *Radiochim. Acta* 36, 191 (1984)

258. R. W Siergiej and N. D. Danielson, *Anal. Chem.*, 55, 17 (1983)

259. T. Braun and G. Ghersini (eds.), *"Extraction Chromatography", J. of Chromatography Library, vol. 2*, Akademiai, Kiado

260. R. J. Sochaka and S. Siekierski, *J. Chromatogr.*, 16, 376 (1964)

261. R. K. Skogerboe and S. J. Freeland, *Appl. Spectrosc.*, 36, 925 (1985)

262. J. B. Willis, *Spectrochim. Acta* 23A, 811 (1967).

263. R. K. Skogerboe and K. W. Olson, *Appl. Spectrosc.*, 32, 181 (1978).

264. S. Greenfield, H. D. McGeachin and P. B. Smith, *Anal. Chim. Acta* 84, 67 (1976).

265. H. Hirai and N. Toshima, In *"Tailored Metal Catalysts"*, Y. Iwasawa (ed.), Reidel: Dordrect, 1986

266. F. Helfferich, *J. Am. Chem. Soc.*, 84, 3237 (1962)

267. M. Marhol, *"Ion Exchangers in Analytical Chemistry"*, G. Svehla (ed.), Elsevier: Amsterdam, 1982, *Compr. Anal. Chem., Chap. 14*