

SOLVENT EXTRACTION OF BUTYL PHOSPHATES FROM
AQUEOUS SOLUTIONS

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of the University of London.

by

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ABSTRACT

Studies have been made of the solvent extraction of di-n-butyl phosphate (HDBP), mono-n-butyl phosphate (H_2MBP) and phosphoric acid from aqueous nitrate solutions by 2-ethylhexan-1-ol. Distribution coefficients of 120, 2.2 and 1.7×10^{-2} were obtained for the extraction of HDBP, H_2MBP and H_3PO_4 respectively from 3M HNO_3 solution by the solvent. The distribution coefficients were found to be independent of the phosphate compounds concentrations which implies that the phosphates exist as monomers in the organic phase. The distribution coefficients varied with HNO_3 concentration: this effect has been explained in terms of the distribution constant of monomer phosphates (K_D) and the dissociation constant of the acids (K_a) and model equations containing these constants have also been derived to fit the distribution data. The kinetics of the extraction, the stripping of the phosphates from the solvent, the extraction of mixtures of phosphate compounds and the use of a diluent, i.e. kerosene, in conjunction with the solvent have also been studied.

The effects of certain metal ions namely U, Fe, Ce, Cs, Mo and Zr on the extraction of the phosphate compounds from 3M HNO_3 solutions by 2-ethylhexan-1-ol have been examined. Results showed that only Zr affected the extraction of phosphates and that this metal ion reduced the transfer of HDBP into the organic phase at low HDBP concentrations. At higher HDBP concentrations a solid third phase which contained most of HDBP was formed in the organic phase. In the case of H_2MBP , reduction of the distribution coefficient values was caused by the formation of the solid phase in the solvent. H_3PO_4 formed insoluble complexes in the aqueous phase with Zr which reduced the extraction of H_3PO_4 by the

solvent. The distribution of Zr between the phases in the presence of HDBP and H_2MBP was also studied.

Finally, 2-ethylhexan-1-ol and 30% mixtures of 2-ethylhexan-1-ol, kerosene in contact with 3M HNO_3 were irradiated in the cobalt source. The solvent showed signs of degradation which resulted in the reduction of its extracting power for HDBP and H_2MBP .

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LIST OF SYMBOLS AND ABBREVIATION

A	Radioactivity
a	Activity
C	Concentration
C^*	Equilibrium concentration
c.p.m.	Unit of radioactivity - counts per minute
d	Optical density (absorbance)
D	Distribution coefficient
EOH	2-Ethylhexan-1-ol
F	Interfacial area
HDBP	Di-n-butyl phosphate
H_2MBP	Mono-n-butyl phosphate
HAR	Highly active raffinate
Hexone	4-Methylpentan-2-One
I	Ionic strength
K_a	Acid dissociation constant - K_{a1} , K_{a2} and K_{a3} refer to the first, second and third dissociation constant respectively
K_2	Dimerisation constant
K_D	Distribution constant
K_N	Equilibrium constant for the reactions involving nitric acid
K_p	Polymerisation constant
K_{01}	Overall mass transfer coefficient based on phase 1
L.W.R.	Light water reactor
M	Unit of concentration - mol dm^{-3}
N	Number of polymeric H_2MBP
pK_a	$-\log K_a$
pK_a^T	Thermodynamic value of pK_a
TBP	Tri-n-butyl phosphate
t	Time

V	Volume
x	Number of HNO_3 molecules in HDBP - HNO_3 complex
y	Number of HNO_3 molecules in H_2MBP - HNO_3 complex
z	Number of HNO_3 molecules in H_3PO_4 - HNO_3 complex
γ	Activity coefficient
γ_r	Gamma radiation
[]	Refers to concentration
Subscripts :	org - organic phase
	aq - aqueous phase
	u - undissociated
	i - initial
	f - final

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To my parents

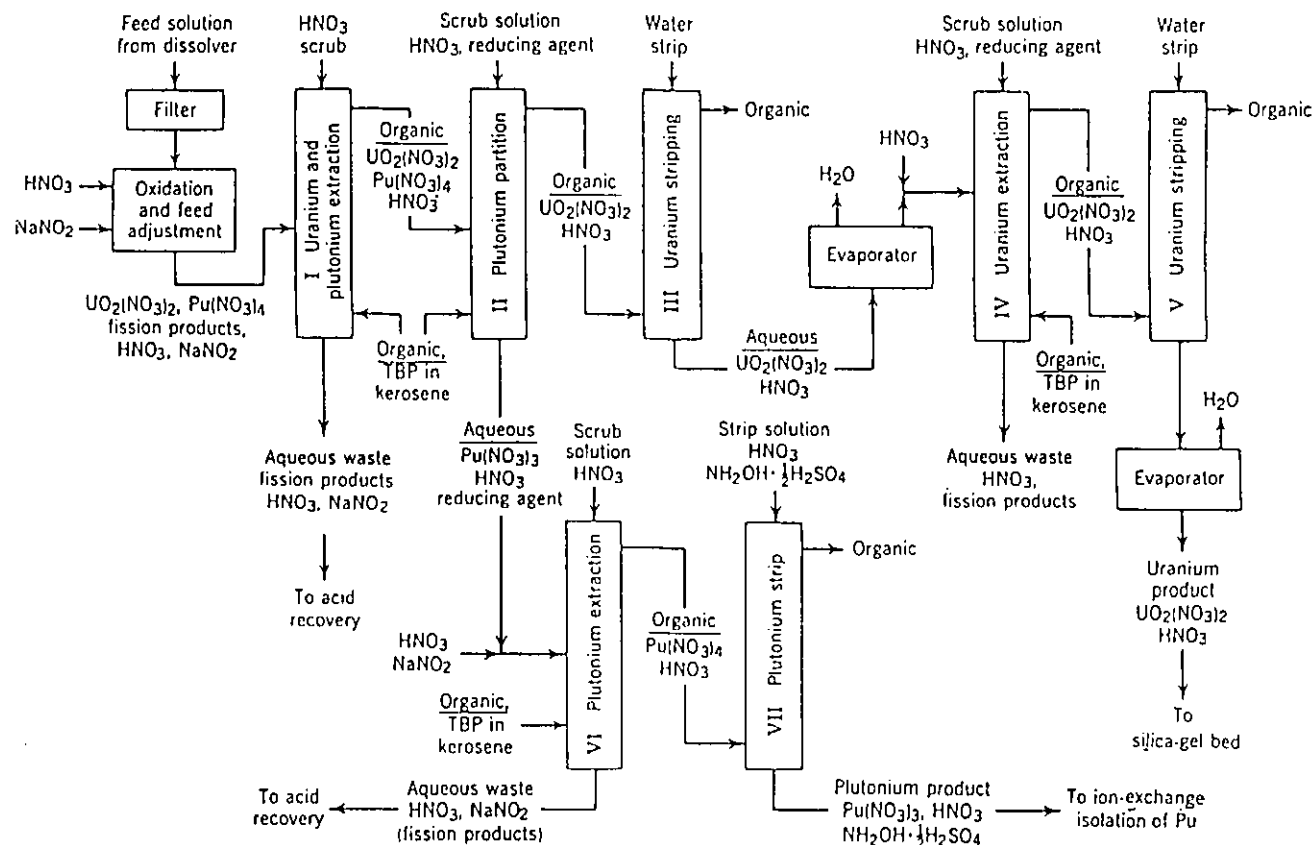
C H A P T E R 1

INTRODUCTION

The irradiated fuel rods from the nuclear reactors are normally reprocessed to recover the uranium and the plutonium by using a process known as the Purex process, Figure (1.1). In such a process, uranium and plutonium are first extracted from the fission products in column I by contacting the aqueous feed with TBP dissolved in an inert solvent, such as kerosene. Fission products are scrubbed from the extract with a nitric acid scrub solution, and practically all the fission products present in the feed leave in the aqueous raffinate, known as the highly active raffinate (HAR), from column I. HAR mainly consists of fission products in about 3M HNO_3 . It will also contain small amounts of phosphates: TBP and the acids HDBP, H_2MBP and H_3PO_4 . The acids are the degradation products of TBP.

Under the influence of water, acids,alkalis or radiation, TBP degrades to give successively HDBP, H_2MBP and H_3PO_4 ^[1-5]. The formation of the acidic phosphates from TBP occurs in three ways^[6]:

- (a) By hydrolysis (a splitting of the P-O bond) in an alkaline aqueous phase containing TBP.
- (b) By hydrolysis and de-alkylation (a splitting of the O-Bu bond) which takes place both in an acidic aqueous phase containing TBP and in the organic phase itself.
- (c) By radiolysis which also occurs both in the aqueous and the organic phases.



Figure(1.1) Flowsheet of Purex process for separation of uranium,plutonium and fission products by solvent extraction with TBP.

No information could be obtained on the amount of individual acidic phosphates in HAR, but Kubota^[7] has estimated the total amount of phosphates to be $2.5 \times 10^{-3} \text{M}$. This value corresponds to a HAR, of which composition was calculated on the assumption that L.W.R. fuel burned up to 28,000 MWd/Mt at a specific power of 30 MW/Mt was processed by the Purex method.

Under reprocessing plant conditions most of the TBP and the HDBP produced are in the organic phase which is separated. The aqueous raffinate then passes to a steam stripper to remove the dissolved TBP and HDBP, but this does not reduce the TBP level below 25 p.p.m.. Sometimes after storage this solution is fed batchwise to an evaporator and under ideal conditions only H_2MBP and H_3PO_4 should reach this stage, but in practice some TBP and consequently some HDBP gets through.

Thus significant amounts of HDBP, H_2MBP and H_3PO_4 can be present in waste storage tanks, and since these compounds, and possibly some of the flocculent metal complexes formed from them, cause foaming of the tank liquor, their presence can render difficult the use of air lift circulators for agitation or limit the transfer of HAR from the storage tanks in case of emergencies. Higher concentrations of HDBP, H_2MBP and H_3PO_4 may be expected in future when fast breeder reactor fuels are reprocessed. Such high concentrations of phosphate species in HAR may even cause the precipitation of metal complexes in the evaporator. In these circumstances more complete removal of the phosphate species from HAR may be necessary and a different phosphate separation process will then be required. The most likely candidate processes are solvent extraction, precipitation or absorption on a solid. Of these, solvent extraction is probably the best to use for the following reasons:

1. Solvent extraction is a well developed process for treating solutions of high activity.
2. Precipitation and absorption involve the formation or use of solids having high surface area, with the following disadvantages:
 - (a) the processing of solid-liquid systems under highly active conditions is not well developed
 - (b) solids having high interfacial area are likely to adsorb fission products which may prove difficult to remove.
 - (c) any solids entrained in the HAR could deposit on the heat transfer surfaces in the evaporator and act as nucleation sites for further precipitation in the evaporator or in the storage tanks.

The purpose of this project is to select a suitable solvent and study the separation of HDBP, H_2MBP and H_3PO_4 by the chosen solvent under the conditions appropriate to HAR. Information is also required to enable a decision to be made on three possible flow-sheets for the treatment of HAR namely;

- (i) Steam strip the TBP as quickly as possible after leaving column I, followed by solvent extraction of the remaining phosphate species.

- (ii) Allow the TBP to degrade and then remove all the phosphates by solvent extraction.
- (iii) Immediate treatment of HAR by solvent extraction after leaving column I, to remove all the phosphate species including the TBP.

C H A P T E R 2

SOLVENT SELECTION

2.1 General Requirements

A solvent suitable for separation of phosphate species from HAR should meet the following requirements:

- (a) It should be selective; i.e. the ratio of distribution coefficients should be high.
- (b) It should have good capacity for extraction; i.e. distribution coefficients in the extracting section should be of the order of unity or higher.
- (c) It should be readily stripped; i.e. distribution coefficients in the stripping section should be no greater than unity and also the equilibration time should be short.
- (d) It should be relatively immiscible with water, to reduce solubility losses.
- (e) Its density should be appreciably different from water, and it should have low viscosity and fairly high interfacial tension. These physical properties are important in promoting separation of phases following contact.

- (f) For safety reasons it should be relatively nonvolatile, nonflammable, and nontoxic.
- (g) It should be readily purified.
- (h) It should be stable in the presence of chemical agents used in the process, such as nitric acid.
- (i) It should have a high degree of stability in the presence of radiation and any degradation products should be innocuous to any subsequent treatment of HAR. Also degradation products should not interfere with the efficiency of the separation.
- (j) It should be cheap.

The first step in selecting the most suitable solvent for the desired separation process has been to draw up from the literature a list of solvents used for the extraction studies of the phosphate compounds.

2.2 Literature Survey

The distribution of HDBP in various systems has been widely studied by a number of authors^[8-14] and the results have been published mainly in terms of the distribution coefficient. The distribution coefficient of HDBP for most of the solvents studied varies with the HDBP concentration and it is also affected by the nature and the acid concentration of the aqueous phase. Hence the comparability of these results is limited. However most of the authors have also expressed their results in terms of a constant called the distribution

constant, K_D , which is defined as the ratio of the concentration of the HDBP monomer in the organic phase to the concentration of HDBP monomer in the aqueous phase. Theoretically K_D should be independent of the HDBP concentration and the acidic condition of the aqueous phase and therefore it is possible to compare the extraction power of the solvents by comparing their K_D values irrespective of the acidity of the aqueous phase or the HDBP concentration. Table (2.1) is a summary of the distribution of HDBP between various organic and aqueous systems and their K_D values.

Considerably less information is available on the extraction of H_2MBP as it is completely miscible with the aqueous phase which makes it rather difficult to separate. However H_2MBP does appear to form an association complex with TBP and this has the effect of increasing the extraction of H_2MBP when a substantial amount of TBP is present in the organic phase. These works have not been included in this review of solvent selection because the presence of TBP would merely resaturate the aqueous phase with phosphate. The extraction of H_2MBP from water in the absence of TBP has been studied by Stewart and Crandall^[8] and the values of the distribution coefficient reported are 0.66, 2.9 and 2.1 for dibutyl ether, n-primary amly alcohol and dibutyl digol respectively.

Although phosphoric acid is strongly aquophilic, solvent extraction is to some extent effective under certain conditions such as high concentrations of H_3PO_4 or in the presence of an extracting strong acid^[15] where presumably high concentrations of unionised acid prevail. The summary of the solvent extraction of phosphoric acid has been reported by Blumberg^[16,17], who has concluded that alcohols are the best solvents for the extraction of H_3PO_4 . Extraction of phosphoric acid with ethers^[18,19], ketones^[20,21] and carboxylic esters^[18,22,23] has been studied and reported not to be effective.

Table (2.1) Summary of distribution constants for HDBP
in various two phase systems

AQUEOUS PHASE	ORGANIC PHASE	K_D	REFERENCE
Water	n-primary amyl alcohol	$D > 1000$	8
0.1M HClO_4 - NaClO_4	Hexone	22.91	9
	Chloroform	2.187	9
0.1M HNO_3 - 0.9M NaNO_3	Cyclohexane	0.0195	13
"	Carbon tetrachloride	0.0708	"
"	O-Xylene	0.2188	"
"	Toluene	0.257	"
"	Chlorobenzene	0.282	"
"	Benzene	0.813	"
"	Chloroform	4.786	"
"	Bromoform	0.724	"
"	Nitrobenzene	1.380	"
"	Butyl ether	1.778	"
"	Methyl isobutyl ketone	35.48	"
0.1M HNO_3	Methyl isobutyl carbinol	162.18	11
"	TBP	93.32	"
"	Isopropyl ether	3.311	"
"	Chloroform	1.738	"
"	Carbon tetrachloride	0.0363	"
"	n-Hexane	0.0045	"
"	1-octanol	144.54	14
"	1-decanol	141.25	"
"	1-octanoic acid	63.10	"
"	2-ethyl-1-hexanoic acid	57.54	"
"	p-diisopropyl benzene	0.0436	"

Table (2.1) continued/...

AQUEOUS PHASE	ORGANIC PHASE	K _D	REFERENCE
0.1M HNO ₃	2-ethyl-1-hexanol	177.82	14
1M HNO ₃	Odourless kerosene	0.0109	10
"	Carbon tetrachloride	0.123	"
"	Benzene	0.380	"
"	Chloroform	1.905	"
"	Nitrobenzene	0.724	"
"	Carbon tetrachloride	0.0513	12
1M HClO ₄	Carbon tetrachloride	0.0616	"
6M HNO ₃	Carbon tetrachloride	12.88	"

Extraction of phosphoric acid with alcohols has been extensively studied. Alcohols investigated include butyl alcohol^[11,17,18,19], isobutyl alcohol^[24,25], amyl alcohol^[24], isoamyl alcohol^[26] and other higher aliphatic alcohols^[18] and cyclohexanol^[27].

The extraction of phosphoric acid with alcohols increases with increasing acid concentration: with isoamyl alcohol, the distribution coefficient varies from 0.131 to 0.264 as the concentration changes from 5% to 31% H_3PO_4 . Also distribution coefficients of 0.15, 0.17, 0.072, 0.049 and 0.03 have been reported for the extraction of phosphoric acid at low concentration from 0.05M H_2SO_4 solutions with isobutyl alcohol, butyl alcohol, amyl alcohol, hexyl alcohol and heptyl alcohol respectively^[28]. TBP has also been examined as an extractant for phosphoric acid^[28-31] and a distribution coefficient of 0.087 has been reported^[28] for very low H_3PO_4 concentration. Various other organophosphorus extractants such as HDBP^[32] have been examined for the extraction of phosphoric acid.

2.5 The Best Group of Solvents

From the solvents which have so far been examined for the extraction studies of the phosphate species, alcohols seem to be the group which most meets the requirements of a suitable solvent. The most important factors are:

1. The highest values of K_D and the distribution coefficients for the extraction of phosphate compounds have been obtained by using alcohols as extractants.
2. There are several alcohols which possess the desired physical properties of a suitable solvent.

3. Longer chain alcohols are rather stable in the presence of acids.
4. Some work has been done on the radiolysis of some of the alcohols and the published results show that alcohols are of average radiolytic stability and the radiolysis products would not be expected to cause any immediate problem in the treatment of HAR^[35].
5. Generally polar solvents which include alcohols dramatically reduce the distribution coefficients of metal ions^[34, 35]. This means that alcohols will not effectively extract the fission products or other metal ions which may be present in HAR.

Dyrssen and Ekberg^[34] found that the distribution coefficient of Y(III) between a solution of 0.1M HDBP in chloroform and 0.1M HNO₃ could be reduced by four orders of magnitude by the addition of methyl isobutyl carbinol up to 2M in concentration. Mason et al.^[35] reported similar effects on the distribution coefficients of certain actinides and lanthanides using phosphoric acid esters in decyl alcohol.

Considering the physical properties, commercial availability and the cost^[36,37] (see below), the best alcohol for the proposed solvent extraction process appeared to be 2-ethylhexan-1-ol, abbreviated to EOH henceforth.

2.4 The Chosen Solvent, EOH

2.4.1 Physical Characteristics and Properties:

EOH, a colourless liquid with a characteristic odour and the molecular formula of $\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{OH}$, belongs to the octanol group. With respect to physical properties, Table (2.2), EOH meets most of the physical criteria required for use in the proposed solvent extraction process. It is also commercially available (99% pure) and compared with other alcohols it has an average price (£4/1, B.D.H. Chemicals' price). In a practical situation a diluent may have to be used as EOH has a rather high viscosity.

Table (2.2) Physical properties of 2-ethylhexan-1-ol^[37]

Molecular weight	130.23
Boiling point at 760 mm Hg	183.50°C
Melting point	-76°C
Flash point (closed cup)	86°C
Specific gravity at 20°C	834 kg m ⁻³
Refractive index at 20°	1.4328
Solubility at 20°C	
alcohol in water	0.1% w/w
water in alcohol	2.55%w/w
Coefficient of cubic expansion at 20°C	0.000875
Latent heat of evaporation	3.886 x 10 ² KJ kg ⁻¹
Specific heat at 25°C	2.361 KJ kg ⁻¹
Surface tension at 22°C	0.03 N m ⁻¹
Viscosity at 20°C	0.001 N s m ⁻²
Vapour pressure at 20°C	48.0 N m ⁻²
Evaporation rate (n-butyl acetate = 100):	<1

2.4.2 Physiological Properties:

Very little precise data is available, but the indications are that under normal conditions of industrial usage this solvent presents no appreciable hazard.

2.4.3 Storage and Handling:

EOH is not corrosive to metals and may be stored in iron, mild steel, copper or aluminium. It is combustible but not flammable.

2.4.4 Chemical Stability:

EOH was left in contact with HNO_3 solution in a range of concentrations from 1M to 10M at 25°C and 50°C and there were no visible signs of oxidation or other chemical reaction between the alcohol and the nitric acid.

2.4.5 Solubility in HNO_3 :

The solubility of EOH in H_2O and various nitric acid solutions at 25°C and 50°C is shown in Table (2.3). The solubility goes through a minimum around 0.3M HNO_3 as the concentration of nitric acid is increased. There is a slight increase in solubility with increasing temperature.

Table (2.3) Solubility of EOH in HNO_3 solutions [14]

HNO_3 concentration (M)	Solubility at 25°C (M)	Solubility at 50°C (M)
0.000	1.3×10^{-2}	1.1×10^{-2}
0.103	9.3×10^{-3}	9.5×10^{-3}
0.318	9.7×10^{-3}	8.9×10^{-3}
0.983	1.1×10^{-2}	1.1×10^{-2}
2.390	1.4×10^{-2}	1.4×10^{-2}
3.520	2.0×10^{-2}	2.0×10^{-2}
6.320	2.3×10^{-2}	2.6×10^{-2}
8.420	2.7×10^{-2}	3.0×10^{-2}

2.4.6 Radiolytic Stability

No work has yet been reported on the radiolysis of EOH, but McDonnell^[33] has studied the radiolysis of octan-1-ol when bombarded with alpha-particles. The studies include the identification of the degradation products, Table (2.4). It is probable that the radiolysis of EOH will be similar to that of octon-1-ol. Some of the carbonyl products may have extractive power for the fission products, actinides, etc. and there is no immediately obvious way of cleaning up the solvent comparable to the alkali wash for TBP.

Table (2.4) Yields of chemical products of the helium ion irradiation of n-octyl alcohol [33]

PRODUCT	MOLECULES OF PRODUCT per 100eV
H ₂	3.48
CO	0.052
CH ₄	0.022
n*	0.107
O*	0.036
Total Gas	3.68
Acid	0.011
H ₂ O	0.430
Carbonyl	0.870
Aldehyde	0.700
Vic-glycol	0.570

Note: n* = gaseous fraction volatile at dry ice temperature (-78°C), but non-volatile at liquid nitrogen temperature (-196°C)

O* = gaseous fraction non-volatile at dry ice temperature (-78°C), hydrocarbon from butane through heptanes and other unidentified products probably present.

2.4.7 Extraction of Metal Ions:

As previously mentioned, alcohols are not good extractants for metal ions, i.e. fission products, actinides, etc. which are present in HAR. The extraction of some actinides by EOH has been studied by Horwitz et al.^[14]. The values of the distribution coefficient reported are 6.5×10^{-2} and 2×10^{-2} for the extraction of U(VI) and Pu(IV) respectively by EOH in the presence of 10^{-4} M HDBP and a value of 2.5×10^{-4} for the extraction of Am(III) in the presence of 10^{-1} M HDBP in the organic phase. Normally the presence of HDBP in the organic phase increases the extraction of the metal ions and therefore in the absence of any HDBP or H₂MBP in the organic phase, the extraction of U, Pu or Am by EOH would be expected to be much less.

C H A P T E R 3

EXPERIMENTAL

3.1 Purification of HDBP and H₂MBP

3.1.1 Introduction

HDBP was obtained from Eastman Kodak and had the approximate specification of 55% HDBP and 45% H₂MBP. It is also reported^[38] that HDBP, H₂MBP mixtures normally contain the impurities TBP and H₃PO₄. For the purpose of the experiments in this project highly pure HDBP and H₂MBP were required in order to obtain the true distribution coefficient for each of these species. Therefore a method was required for the separation of HDBP and H₂MBP and also to obtain individual acids to a purity of more than 99%.

The separation and purification of mixtures of HDBP and H₂MBP has been achieved by a variety of methods:

- (i) Multiple batch or counter-current extraction with immiscible organic and aqueous phases^[38-41].
- (ii) Differential solubilities of the barium salts in water (the H₂MBP salt has the lower solubility), followed by repeated crystallization from aqueous alcoholic solution^[42].
- (iii) Precipitation of ferric mono- and di-butyl phosphates by the addition of ferric chloride solution, and partial separation of these by contact for ten hours with a certain exchange resin; the ferric mono-butyl

phosphate dissolves and the remaining dibutyl phosphate complex is decomposed with alkali and pure HDBP extracted from the solution^[43].

Apart from (i) the above methods are either lengthy if products of high purity are required, or only give moderately pure products and consequently the method of Hardy and Scargill^[38] was adopted. This method gave highly pure solutions of H_2MBP , but the HDBP solutions contained small but detectable amounts of H_2MBP . The Hardy and Scargill^[38] method uses carbon tetrachloride as the organic solvent. The use of this solvent is discouraged on safety grounds and a method of purification based on batch solvent extraction, using diethyl ether as the organic solvent was developed to produce highly pure HDBP and H_2MBP solutions.

3.1.2 Procedure

(a) separation of HDBP and H_2MBP :

One volume of the crude mixture was dissolved in four volumes of diethyl ether and more than 90% of the H_2MBP was extracted in to 3 x 5 volumes of water by stirring the phases together for two minutes. The first water wash which contains most of the H_2MBP is kept for H_2MBP recovery and the ether phase for HDBP recovery.

(b) purification of HDBP:

The ether phase from (a) is treated with one volume of 3M NaOH solution to form the water soluble sodium salt of HDBP. The ether phase is then discarded and the

alkaline solution is washed with 2 x 1 volume of ether, the non-acidic solvent-soluble impurities, e.g. TBP, are discarded with the ether phase. The alkaline solution is then acidified with one volume of 4M HNO_3 solution and the HDBP extracted with 2 x 2 volumes of ether. The ether phases are combined and washed with 2 x 1 volume of 4M HNO_3 solution followed by 5 x 3 volumes of water. The ether is removed on the water pump at about 50°C or less.

(c) purification of H_2MBP :

The first water wash from (a) contains most of the H_2MBP , small amount of HDBP and the H_3PO_4 impurity. This solution is washed with 3 x 1 volume of ether to extract the HDBP and discarded. The H_2MBP is then extracted from the solution with 10 x 4 volumes of ether. The ether phases are combined and washed with 2 x 1 volume of water. At this stage the ether can either be removed on the water pump at about 30°C or since for the purpose of this project H_2MBP solution is required, the H_2MBP is back extracted by washing the ether phase with 3 x 10 volumes of water and the ether dissolved in the H_2MBP solution is removed by leaving the solution in a fume-cupboard overnight.

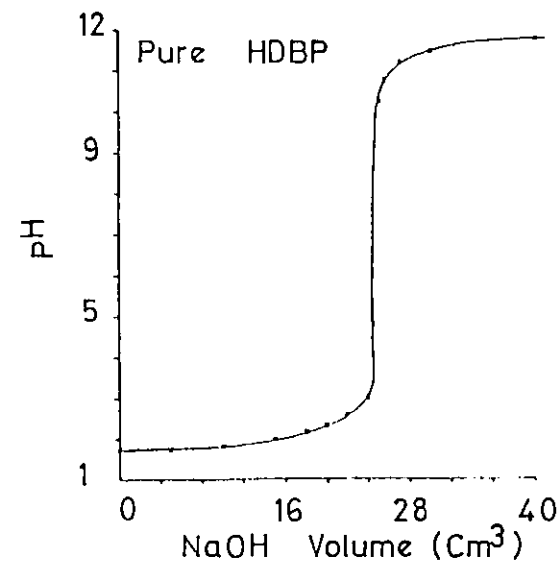
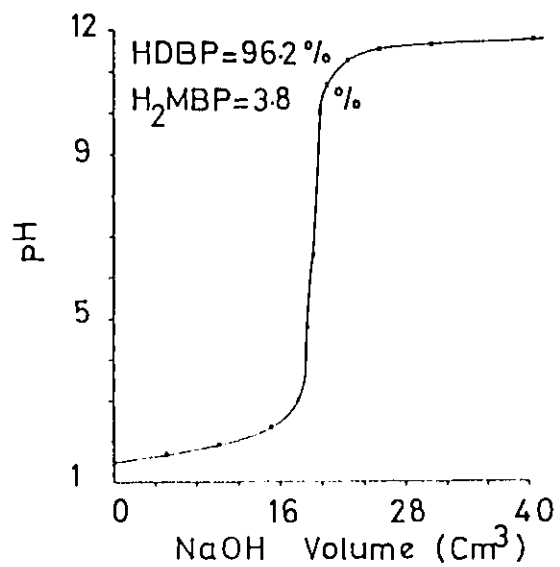
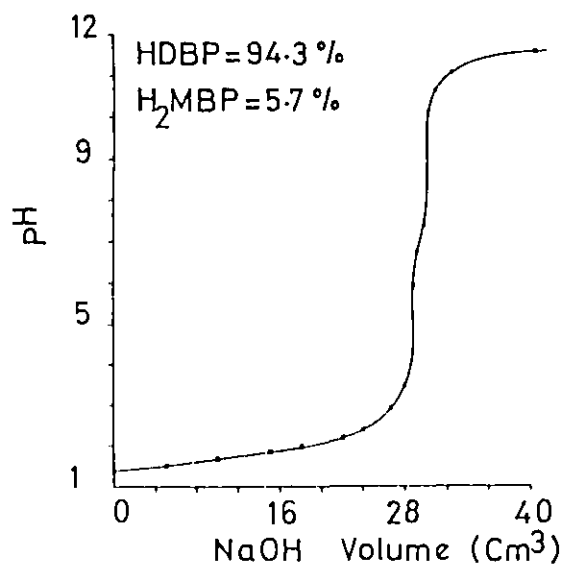
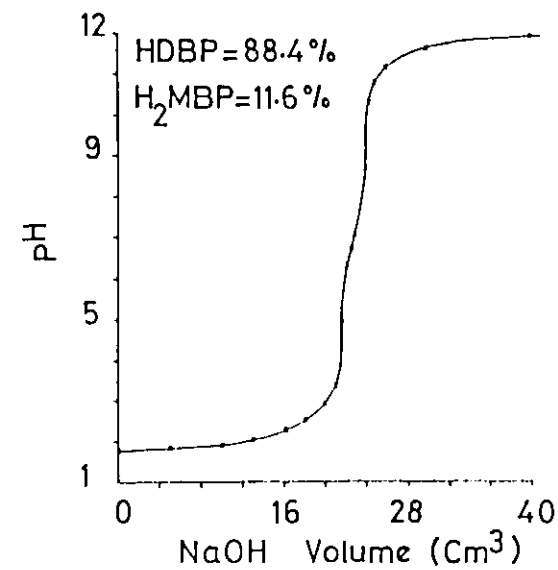
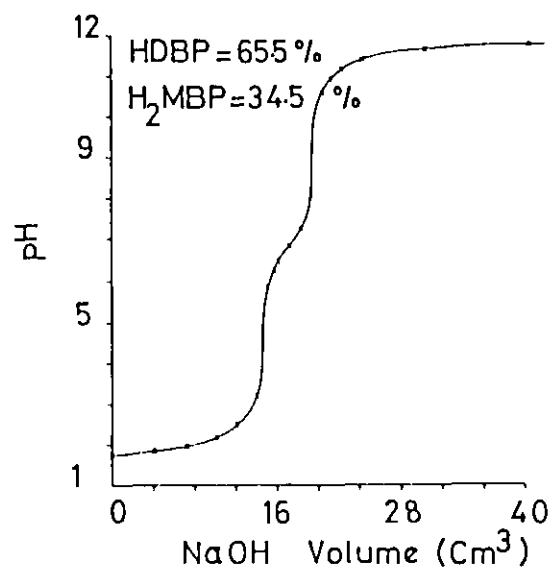
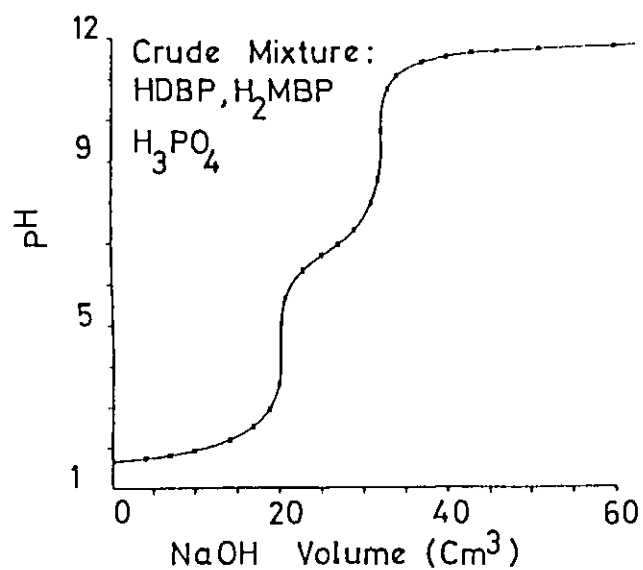
3.1.3 Yield and Purity Determination

20% and 40% of the HDBP and H_2MBP respectively were lost during the purification procedure. The yield of H_2MBP can be increased by increasing the number of ether wash to extract more of H_2MBP from the aqueous solution or increasing the ratio of the volume of ether to the aqueous phase.

The purities of HDBP and H_2MBP were determined by the pH titration method: samples of the acid were titrated with standard 0.1M NaOH and the pH of the solution measured after adding known volumes of the NaOH. HDBP is a monobasic acid and the titration curve (pH vs volume of NaOH added) of its pure solution should have only one break. Figure (3.2) shows the titration curve for the purified HDBP. No H_2MBP can be detected from the curve implying that the HDBP solution must be more than 99% pure.

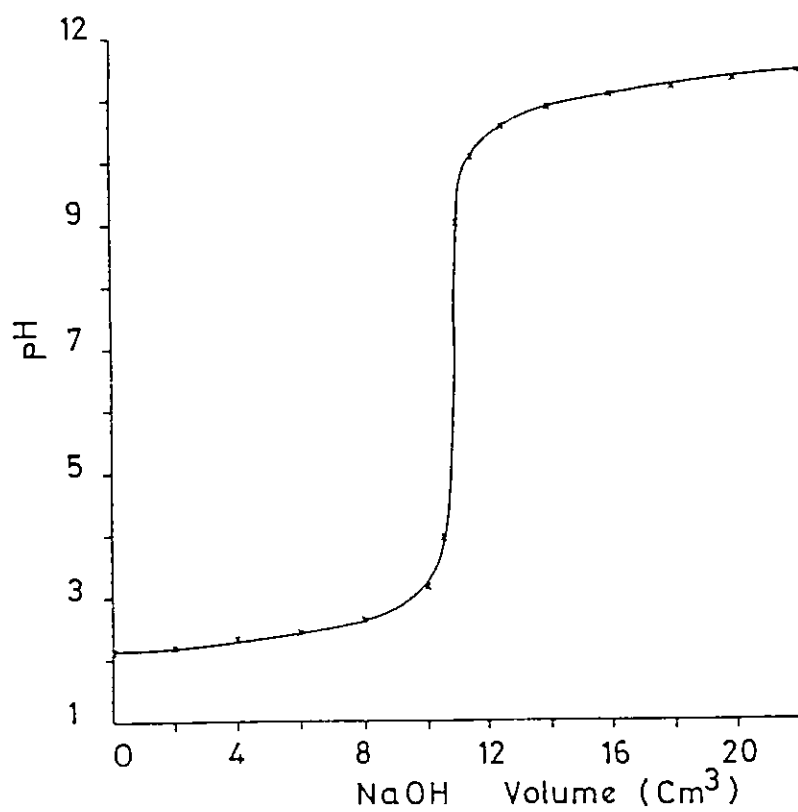
In developing the method for the purification of HDBP, the number of water washes were fixed by checking the purity of the HDBP solution by pH titration and increasing the number of water washes until no H_2MBP could be detected from the curve. This is illustrated in Figure (3.1) where the amount of HDBP and H_2MBP from each curve is calculated as follows^[8]; the difference in titre between the two breaks of the curve is taken to represent the amount of H_2MBP and the difference between this quantity and the titre to the first break represents the amount of HDBP.

In the case of H_2MBP a dibasic acid the pH titration curve should have two breaks and for a pure solution the volume of NaOH needed to reach the first break should be exactly half the volume needed to reach the second break. Figure (3.3) shows the titration curve for the purified H_2MBP solution which must be more than 99% pure.

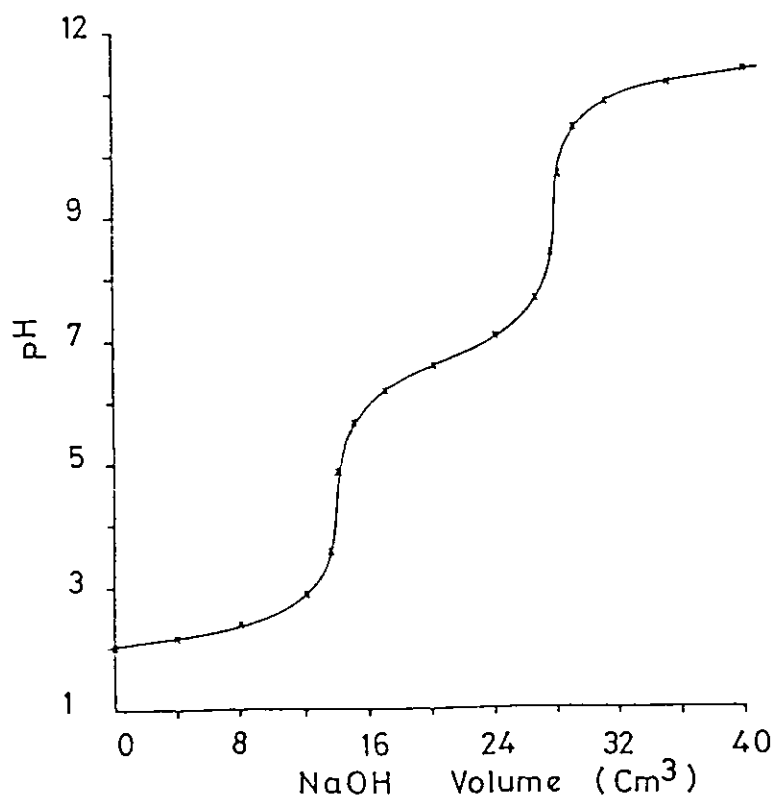


Figure(3.1) pH titration of mixtures of HDBP and H_2MBP .

Figure(3.2) pH titration of pure HDBP at 25 °C.



Figure(3.3) pH titration of pure H₂MBP at 25 °C.



3.2 Phosphate Analysis

3.2.1 Introduction:

Previous studies on HDBP, H_2MBP and H_3PO_4 were carried out using the ^{32}P labelled compounds which were then commercially available. Unfortunately the production of labelled HDBP and H_2MBP has long been stopped and as their preparation is rather tedious an alternative method for their analysis had to be adopted.

The spectrophotometric method for the analysis of the phosphate compounds was perhaps the most suitable method available with the disadvantage that this method can only be applied to inorganic phosphate compounds. Therefore the HDBP and H_2MBP must first be converted into inorganic phosphates before the method could be applied for their analysis.

3.2.2 Conversion of HDBP and H_2MBP :

The conversion of HDBP or H_2MBP into organic compounds were carried out by oxidation with a mixture of HNO_3 and H_2SO_4 .

10 cm³ of concentrated HNO_3 and 1 cm³ of concentrated H_2SO_4 were added to a known volume of HDBP or H_2MBP solution. The solution was left on a hot plate in a fume-cupboard until all the nitric acid had evaporated. The solution was then left to cool down and was made up to the original volume of HDBP or H_2MBP solution in a volumetric flask.

The temperature of the hot plate had to be so adjusted that the solution did not boil or otherwise some would have been lost.

3.2.3 Spectrophotometric Method:

There are several different methods available for the analysis of the phosphate compounds by spectrophotometry, the most sensitive being the phosphomolybdenum blue method^[44,45]. The principle of this method is the formation of the pale yellow molybdophosphoric acid by the phosphate compounds with excess molybdate in an acid medium. The molybdophosphoric acid is then reduced to phosphomolybdenum blue under mild conditions to prevent the reduction of the free molybdic acid. Reductants employed include hydrazine^[46], stannous chloride^[47-49], ascorbic acid^[50] and various other reagents^[51-53]. Molybdophosphoric acid may be reduced either in aqueous medium^[47-49] or in the organic phase after molybdophosphoric acid has been extracted^[48,52].

Having tried several of the above methods it was found that either the blue phosphomolybdenum colour was not stable or some of the reducing reagents e.g. stannous chloride in HCl, lost their reducing power over a short period of time. However the method described below is a combination of several of the above methods with some alterations to suit the range of concentration of the phosphate species used in this project.

3.2.4 Phosphomolybdenum Blue Method:

(i) Reagents:

1. Ammonium molybdate 10%: 25 grams of ammonium molybdate was dissolved in about 200 cm³ of distilled water at about 50°C. The solution was allowed to stand overnight, filtered and diluted with distilled water to the mark in a 250 cm³ volumetric flask.

2. Stannous chloride: 2.5 grams of stannous chloride was dissolved in 100 cm³ of glycerol. To ease the dissolution the glycerol was placed on a water bath and stirred with a glass rod.

8 cm³ of the above solution was diluted with 50 cm³ of fresh glycerol and used as the reducing reagent.

3. Perchloric acid 72%.

4. Hexone, A.R.

5. Standard phosphate solution: KH_2PO_4 was used as the standard solution for the calibration curve.

(ii) Procedure:

2 cm³ of the sample containing phosphate together with 5 cm³ of the perchloric acid were transferred into a 100 cm³ separating funnel and diluted with 30 cm³ of distilled water. 50 cm³ of hexone followed by 5 cm³ of the ammonium molybdate reagent were added to the solution in the separating funnel and the mixture was immediately shaken for not less than one minute. Any delay in shaking increases the amount of polyphosphates if present. The aqueous phase was drained off and the organic phase was shaken with about 10 drops (1 cm³) of the stannous chloride reagent for about one minute. The bottom phase was drained off and the optical density of the organic solution was measured after 10 minutes at the appropriate wavelength using 1 cm³ cells against a blank reagent solution prepared by the same procedure using distilled water in place of the phosphate solution.

Two calibration curves have been drawn, one for the concentration range of 1 to 10 p.p.m. KH_2PO_4 , Figure (3.4) and the other for 10 to 300 p.p.m., Figure (3.5). In the former case 10 cm^3 of the perchloric acid was first diluted with 30 cm^3 of distilled water and then 5 cm^3 of the diluted perchloric acid, 5 cm^3 of the phosphate solution and 20 cm^3 of hexone were used for the analysis.

(iii) The absorbance wavelength:

Figure (3.6), the optical density against the wavelength, shows two peaks, one at 725 nm and the other at 625 nm. In measuring the optical densities of the phosphate solutions the 725 nm wavelength was used as it gives a higher reading of the optical density than at 625 nm.

(iv) Minimum detectable concentration:

Using a Perkin-Elmer 554 U.V.-VIS spectrophotometer, the minimum detectable concentration was about 0.5 p.p.m. KH_2PO_4 .

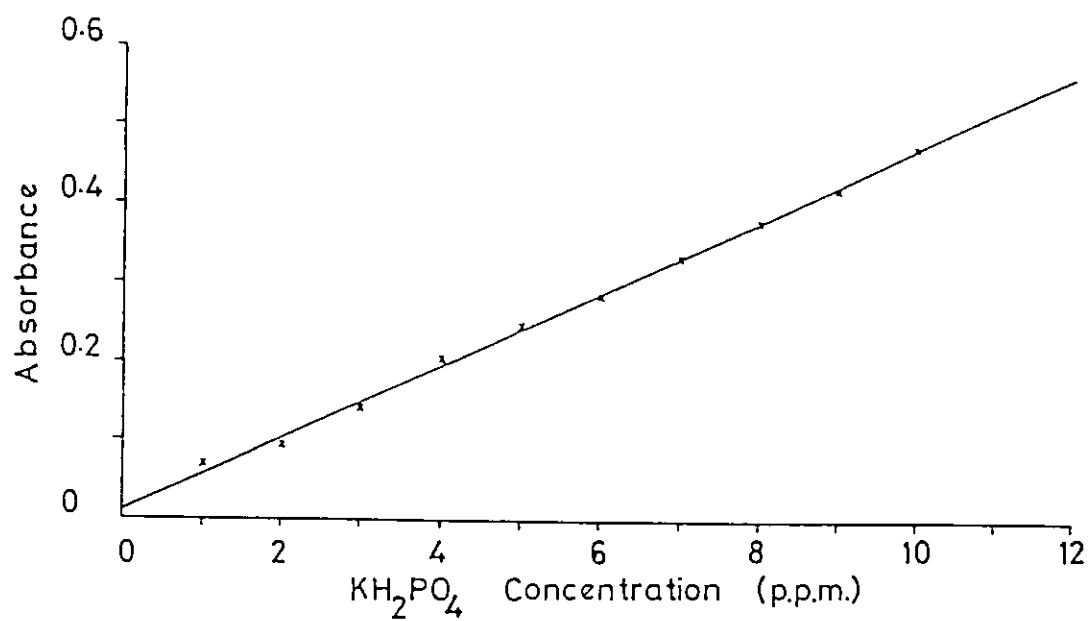
(v) Stability of blue colour:

The stability of the blue colour is shown in Figure (3.7), where there was a reduction of about 9% in the intensity of the colour after two hours.

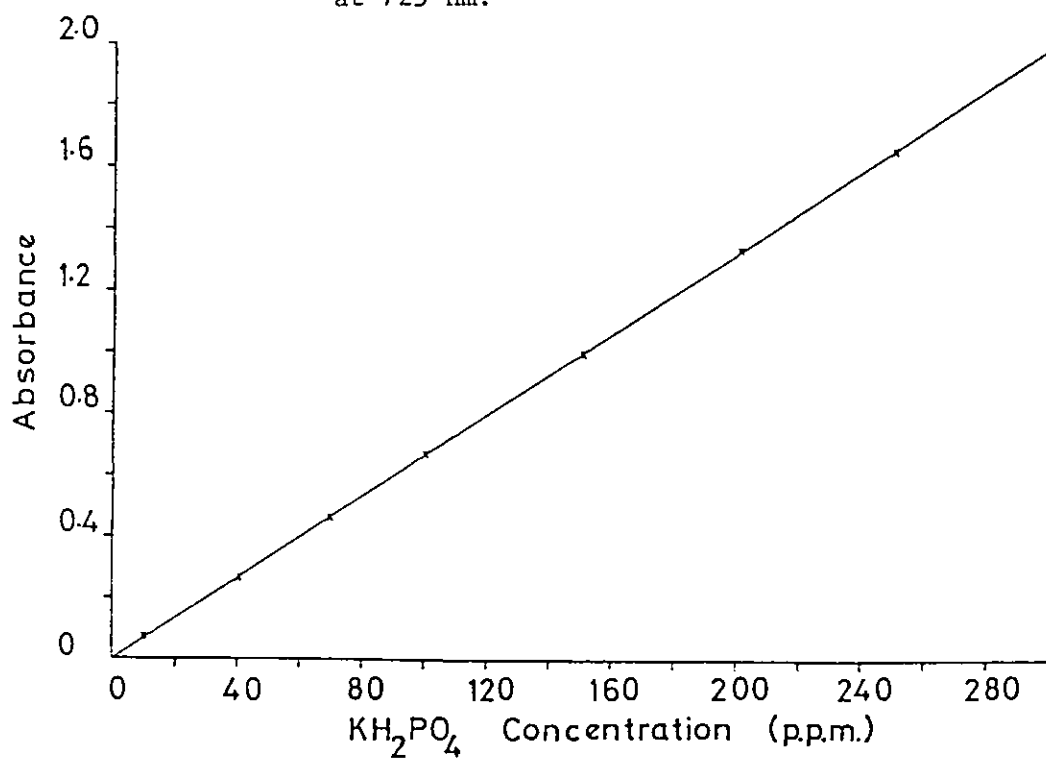
(vi) Interference:

Interference comes primarily from arsenic (V), silicon and germanium which also react with molybdate to form the corresponding acids.

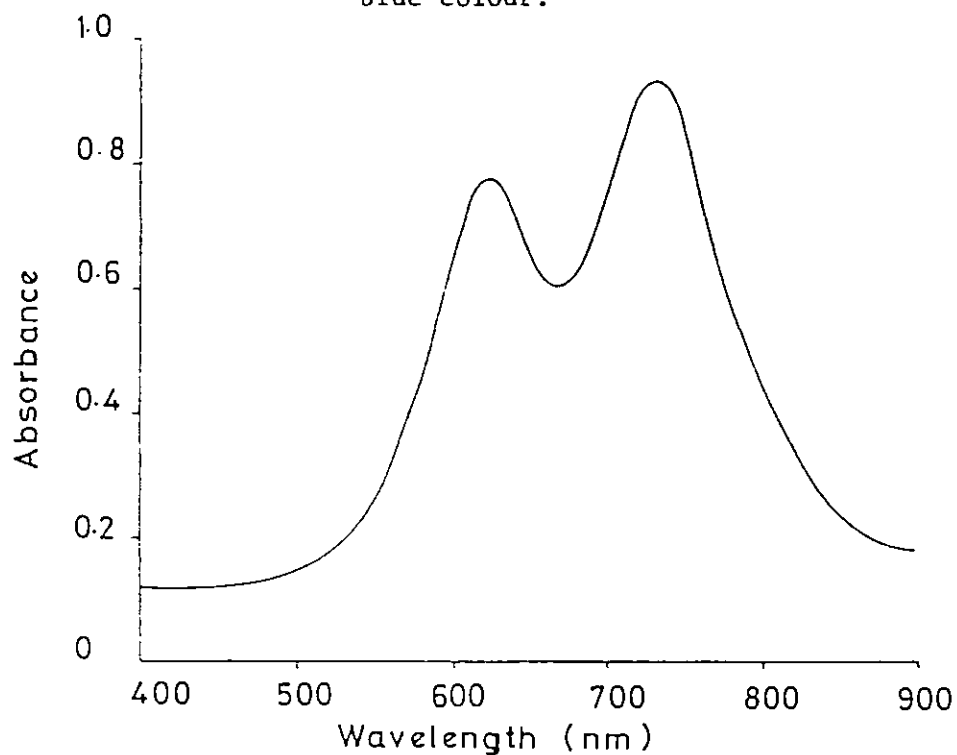
Figure(3.4) Phosphomolybdenum blue calibration curve at 725 nm.



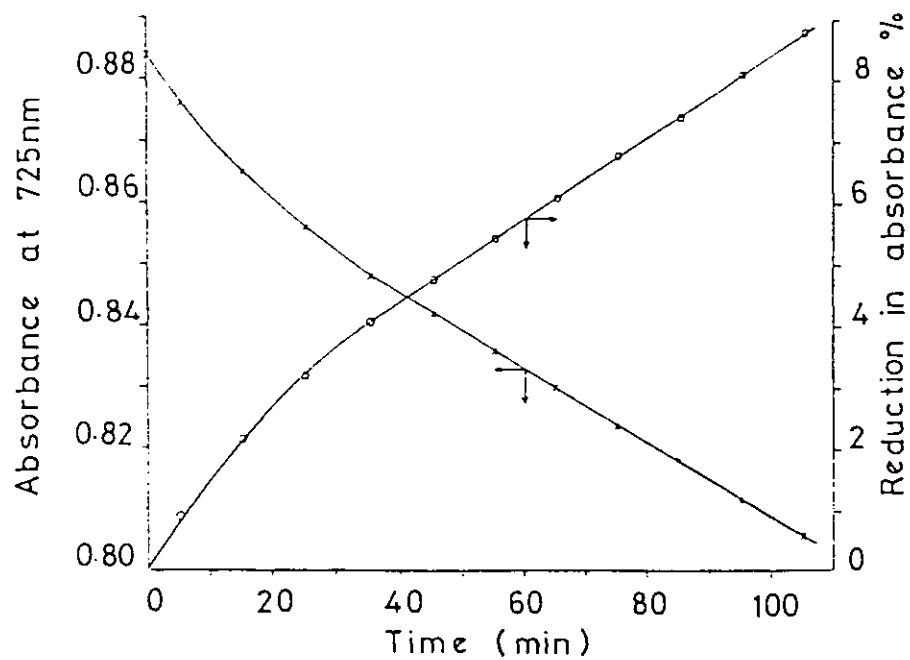
Figure(3.5) Phosphomolybdenum blue calibration curve at 725 nm.



Figure(3.6) Absorbance-wavelength for phosphomolybdenum blue colour.



Figure(3.7) Stability of phosphomolybdenum blue colour.



The interference from silicon makes it necessary for the molybdenum reagent to be stored in polythene containers unless the reagent is used up within around seven days.

(vii) The accuracy of the method:

The accuracy of the spectrophotometric method for the analysis of HDBP and H_2MBP was checked by comparing the concentration of solutions of HDBP and H_2MBP in water obtained by the spectrophotometric and the pH titration methods: close agreement was obtained.

3.3 Extraction of Nitric Acid by EOH

3.3.1 Volume Changes on Mixing:

To measure the volume changes in the organic and the aqueous phases, 10 cm^3 of the aqueous solution of known acid concentration was mixed with 10 cm^3 of the organic solution (EOH) in a 50 cm^3 conical flask and stirred in a water bath at 25°C until equilibrium was reached. The two phases were then separated and the volume of each phase measured separately in a measuring cylinder calibrated in 0.1 cm^3 divisions.

3.3.2 Amount of HNO_3 Extracted:

To measure the amount of the acid extracted, equal volumes of the nitric acid solution and the organic solvent were agitated together in a water bath at 25°C using a miniature stirrer. The phases were then separated, after reaching equilibrium, in a separating funnel and three 10 cm^3 samples of the aqueous phase were pipetted out and titrated with standard 1M NaOH solution using phenolphthalein as the indicator. For nitric acid solutions below 1M , 0.1M standard

NaOH solutions were used for the titration. The concentration of the nitric acid solution before contact with the organic solvent was measured in the same manner.

3.3.3 Calculation of the Distribution Coefficient

The distribution coefficient, D , is defined as the ratio of the concentration of HNO_3 in the organic phase to the aqueous phase. The following relationship was used to calculate D_{HNO_3} ;

$$D_{\text{HNO}_3} = \{(V_{\text{iaq}} C_{\text{iaq}}) - (V_{\text{faq}} C_{\text{faq}})\} / V_{\text{forg}} C_{\text{faq}}$$

where

V_{iaq} = initial volume of the aqueous phase.

V_{faq} = final volume of the aqueous phase.

V_{forg} = final volume of the organic phase.

C_{iaq} = initial HNO_3 concentration in aqueous phase.

C_{faq} = final HNO_3 concentration in aqueous phase.

3.4 Extraction of Phosphate Compounds by EOH

3.4.1 Amount of Phosphate Compounds Extracted:

50 cm³ of the phosphate solution was extracted with 50 cm³ of the organic extractant (EOH) in a 100 cm³ conical flask. The flask was placed in a constant temperature water bath at the desired temperature and the phases were agitated for about 30 minutes using a miniature stirrer. The flask was left in the water bath for a further 30 minutes without any agitation and then the phases were separated in a 100 cm³ separating funnel. Using a 10 cm³ pipette, 3 x 10 cm³ of the aqueous samples were taken for the analysis. Using

a centrifuge to separate the phases made no difference in the values of the distribution coefficients.

For kinetic measurements, the phases were stirred in a separating funnel at the desired temperature and the speed of the stirrer was kept the same for all the kinetic measurements. The aqueous phase was run off as soon as the stirrer was stopped and the samples were taken from the aqueous phase for the phosphate analysis. HDBP and H_2MBP samples were first oxidised, as described in 3.2.2, and then analysed by the spectrophotometric method.

In the case of H_3PO_4 , no oxidation was necessary, but during the course of these experiments it was found that the extraction of H_3PO_4 by the solvent was normally rather low and the spectrophotometric method was not sensitive enough to detect the changes in the concentration of H_3PO_4 solutions before and after the extraction. Hence ^{32}P labelled H_3PO_4 mixed with inactive phosphoric acid was used for the extraction studies of H_3PO_4 .

The activity of the phases, both the organic and the aqueous, were measured using an M6C liquid Geiger detector (20th Century Electronics Limited) and associated Harwell 2000 series counting equipment. The initial concentration of the phosphoric acid in the aqueous phase was measured by the chemical method.

3.4.2 Calculation of the Distribution Coefficient:

The distribution coefficient, D , is defined as the ratio of the total amount of phosphate in the organic phase to the total amount of phosphate in an equal volume of the aqueous phase. For HDBP and H_2MBP the values of the distribution coefficient are calculated as follows;

$$D = (C_{iaq} - C_{faq})/C_{faq}$$

where C_{iaq} = initial concentration of HDBP or H_2MBP
in the aqueous phase.

C_{faq} = final concentration of HDBP or H_2MBP in
the aqueous phase.

Since the calibration curves, optical density against concentration, Figures (3.4) and (3.5), are both straight lines, the above relationship for D can be rewritten in terms of the optical density of the solution;

$$D = (d_{iaq} - d_{faq}) / d_{faq}$$

where d is the optical density of the solution at the wavelength of measurement. The values of the distribution coefficient have to be corrected for the volume changes which occur both in the organic and the aqueous phases;

$$D = [(V_{iaq} d_{iaq}) - (V_{faq} d_{faq})] / V_{forg} d_{faq}$$

where

V_{iaq} = initial volume of the aqueous phase

V_{faq} = final volume of the aqueous phase

V_{forg} = final volume of the organic phase.

In the case of H_3PO_4 where the radioactivities of the solutions are measured instead of the optical densities, D is calculated as:

$$D = A_{forg} / (A_{iorg} - A_{forg})$$

where A is the activity of the solution and the subscripts org, aq, i and f refer to the organic phase, aqueous phase, initial and final

respectively. It is necessary to use $(A_{\text{iaq}} - A_{\text{forg}})$ instead of measuring the activity of the aqueous phase after extraction because only a small amount of H_3PO_4 is extracted by the solvent and no difference could be detected in the initial and final activities of the aqueous phase by direct counting.

In the above expression, to calculate $D_{\text{H}_3\text{PO}_4}$, the activities have to be corrected for the dead time of the counter, the difference between the densities of the organic and the aqueous phases and the volume changes. A sample of the calculation is shown in Appendix A.

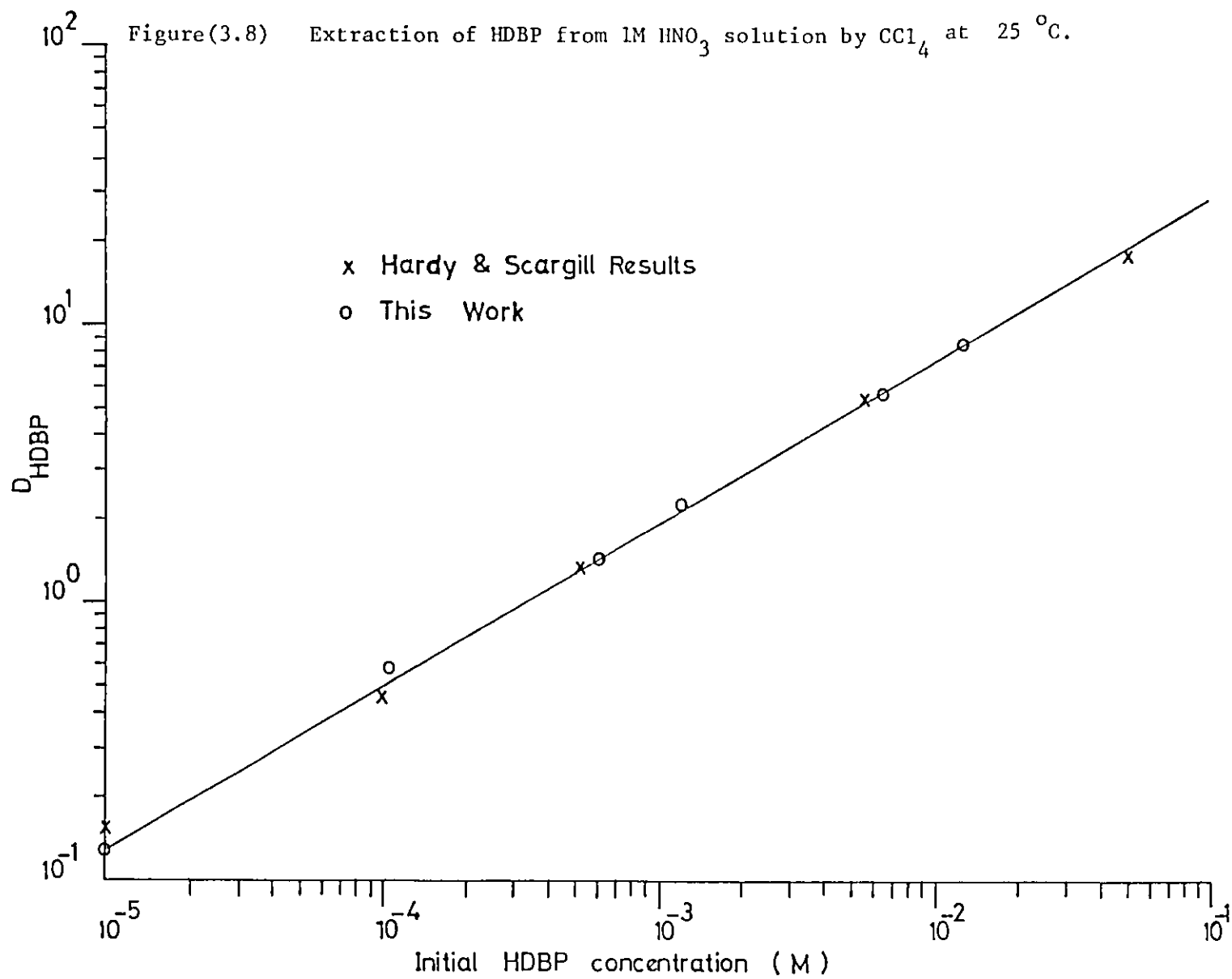
3.5 Credibility of the Distribution Coefficient Values of Phosphate Compounds

A check was carried out on the accuracy and the credibility of the method used to measure the distribution coefficient values for HDBP and H_2MBP by studying the extraction of HDBP from 1M HNO_3 into carbon tetrachloride.

The distribution coefficients of HDBP for this system have been obtained previously by Hardy and Scargill^[10] using ^{32}P labelled HDBP and comparison with the values obtained in the present work offers a useful check on the validity of the chemical method which has been used for the analysis of the phosphate compounds (fig. 3.8).

3.6 Extraction of Phosphate Compounds in the Presence of Metal Ions

Some changes had to be made to the experimental procedure in studying the extraction of phosphate compounds in the presence of metal ions. Since some metal ions form insoluble complexes with the phosphate compounds, HDBP and H_2MBP were dissolved in the organic



phase and contacted with the aqueous phase containing the metal ion in 3M HNO₃. The initial concentration of HDBP or H₂MBP was measured by washing the organic phase with an equal volume of 0.1M Na₂CO₃ and then following the phosphate analysis procedure.

In the case of H₃PO₄, the solution containing the metal ion was added to the H₃PO₄ solution already in contact with the organic phase.

In studying the extraction of HDBP and H₂MBP in the presence of zirconium, solid was formed in the organic phase at certain concentrations of zirconium and the phosphate compounds. In such cases, the organic phase was first centrifuged to separate the solid and then was washed with water followed by 0.1M Na₂CO₃ to measure the amount of HDBP or H₂MBP. In the case of H₃PO₄, solid was formed in the aqueous phase which was separated by centrifuge.

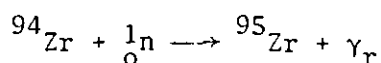
3.7 Extraction of Zirconium

3.7.1 Zirconium Determination:

There are two principal methods for the zirconium determination. These are the chemical methods, i.e. atomic absorption or U.V. spectrophotometry, and radiochemical methods. An atomic absorption method using nitrous oxide flame did not give satisfactory results as the readings were unstable. This may have been due to the presence of nitrate in the test solutions.

U.V. spectrophotometry using arsenazo (II) as the reagent [45] failed to produce a stable colour and this method was also not proceeded with.

Labelled zirconium is produced by the reaction:



This reaction is brought about by the irradiation of zirconium metal or zirconium compounds in the reactor. Most zirconium compounds and also zirconium metal are only soluble in concentrated solution of HF. However because fluoride ion forms strong complex with zirconium, the presence of HF is not desirable in the solutions and hence such compounds could not be used. For the purpose of this work, the only soluble zirconium compounds are zirconyl nitrate, which could not be irradiated in the reactor because of local safety regulations, and zirconium sulphate which was, in consequence, used.

3.7.2 Conversion of Zirconium Sulphate to Zirconium Nitrate:

- (i) 1 gram of irradiated zirconium sulphate was dissolved in 20 cm^3 of water
- (ii) 5 cm^3 of solution (i) was made up to 3M HNO_3 in a 100 cm^3 volumetric flask
- (iii) 5 cm^3 of solution (i) was mixed with 5 cm^3 of $\text{Ba}(\text{NO}_3)_2$ solution (same concentration as $\text{Zr}(\text{SO}_4)_2$) and the precipitate was separated by centrifuge. The solution was made up to 3M HNO_3 in a 100 cm^3 volumetric flask.

Solutions (ii) and (iii) were contacted with HDBP in EOH and no significant difference was found between the zirconium distribution coefficient obtained for the two solutions. Similar values for the HDBP distribution coefficient was also obtained. Therefore it was decided that $\text{Zr}(\text{SO}_4)_2$ dissolved in 3M HNO_3 could be used in place of zirconyl nitrate in 3M HNO_3 .

3.7.3 Experimental Procedure:

A known amount of zirconium sulphate was irradiated in the core tube of the university reactor for eight hours. The irradiated zirconium sulphate was then dissolved in water and made up to 3M HNO_3 in a volumetric flask. Note that zirconium sulphate was very difficult to dissolve in 3M HNO_3 and it had to be dissolved in water first. The zirconium solution was then contacted with HDBP or H_2MBP dissolved in EOH. The phases were separated, centrifuged and their gamma activity measured by a gamma-detector. The main isotope of zirconium is ^{95}Zr which has two decay energies, 0.724 and 0.756 MeV. The gamma spectrum of the solutions were analysed using a germanium crystal detector and an Elscient multichannel analyser which automatically calculated the area under the peaks at 0.724 and 0.756 MeV energies. The sum of the areas after correction for the background were taken as the total gamma activity of the solution. The distribution coefficient for zirconium, D_{Zr} , is defined as:

$$D_{\text{Zr}} = \frac{\text{Total gamma activity in the organic phase}}{\text{Total gamma activity in an equal volume of aqueous phase}}$$

C H A P T E R 4

EXTRACTION OF HNO_3 BY EOH

4.1 Introduction

In the solvent extraction of the phosphate compounds from nitric acid solutions by EOH some nitric acid is also extracted with a consequent acidity change of the aqueous phase. Also, due to the mutual solubilities of the extractant and the aqueous phase, volume changes occur in both the phases. These two phenomena are important in the study of the extraction of the phosphate compounds from nitric acid solutions.

In this chapter studies of the volume changes and the extraction of nitric acid by EOH for various nitric acid concentrations have been made and the results will be used in the determination of the distribution coefficients for the extraction of the phosphate compounds from nitric acid solutions by EOH in the following chapters.

Extraction of nitric acid with various solvents has been extensively studied and compared with the extraction of other strong acids such as perchloric acid, sulphuric acid etc. This comparison has shown that nitric acid and perchloric acid are usually extracted by oxygen containing polar solvents much better than other acids^[54]. Extraction studies of nitric acid with solvents such as ethers^[55-59], esters^[56,57], ketones^[58,60-63], alcohols^[56,59,64] and TBP^[65-78] has been reported. The extraction studies include the investigation of the main extracted species which have been suggested to be monosolvated

acid containing several water molecules, i.e. with TBP; $\text{HNO}_3 \cdot \text{TBP} \cdot x\text{H}_2\text{O}$, but disolvates and trisolvates have also been suggested. Some of these studies have been carried out to investigate special subjects such as the effect of temperature on the distribution coefficient values, viscosity of the organic phase and kinetics of the extraction of the acid.

When an acid in aqueous solution is contacted with an organic solvent the mutual solubilities of the phases and the extraction of the acid may result in volume changes in both the aqueous and the organic phases. The factors affecting these changes are concentration of the acid, nature of the acid and the nature of the organic solvent. Normally the volume changes increase with increasing acid concentration as both the mutual solubilities and the extraction of the acid by the solvent will increase with the acid concentration. However in diethyl ether-hydrohalic acid systems, with the exception of hydrofluoric acid, it has been reported that the volume ratio $V_{\text{org}}/V_{\text{aq}}$ decreases as the concentration of the acid in the aqueous phase increases [79]. It has also been reported that the extraction of hydrochloric acid decreases the $V_{\text{org}}/V_{\text{aq}}$ ratio when the solvents are other ethers [79,80] and ketones [79], but it increases the ratio when the solvents are alcohols [79]. The extraction of nitric acid with ethers, ketones, or alcohols, on the other hand, increases the $V_{\text{org}}/V_{\text{aq}}$ ratio, and the increase is larger when the acid concentration is higher [81,82].

Generally, non-polar solvents result in much smaller volume changes than polar solvents because non-polar solvents have lower mutual solubility with aqueous solutions and also because of their lower extracting power for strong acids.

4.2 Results and Discussion

4.2.1 Volume changes:

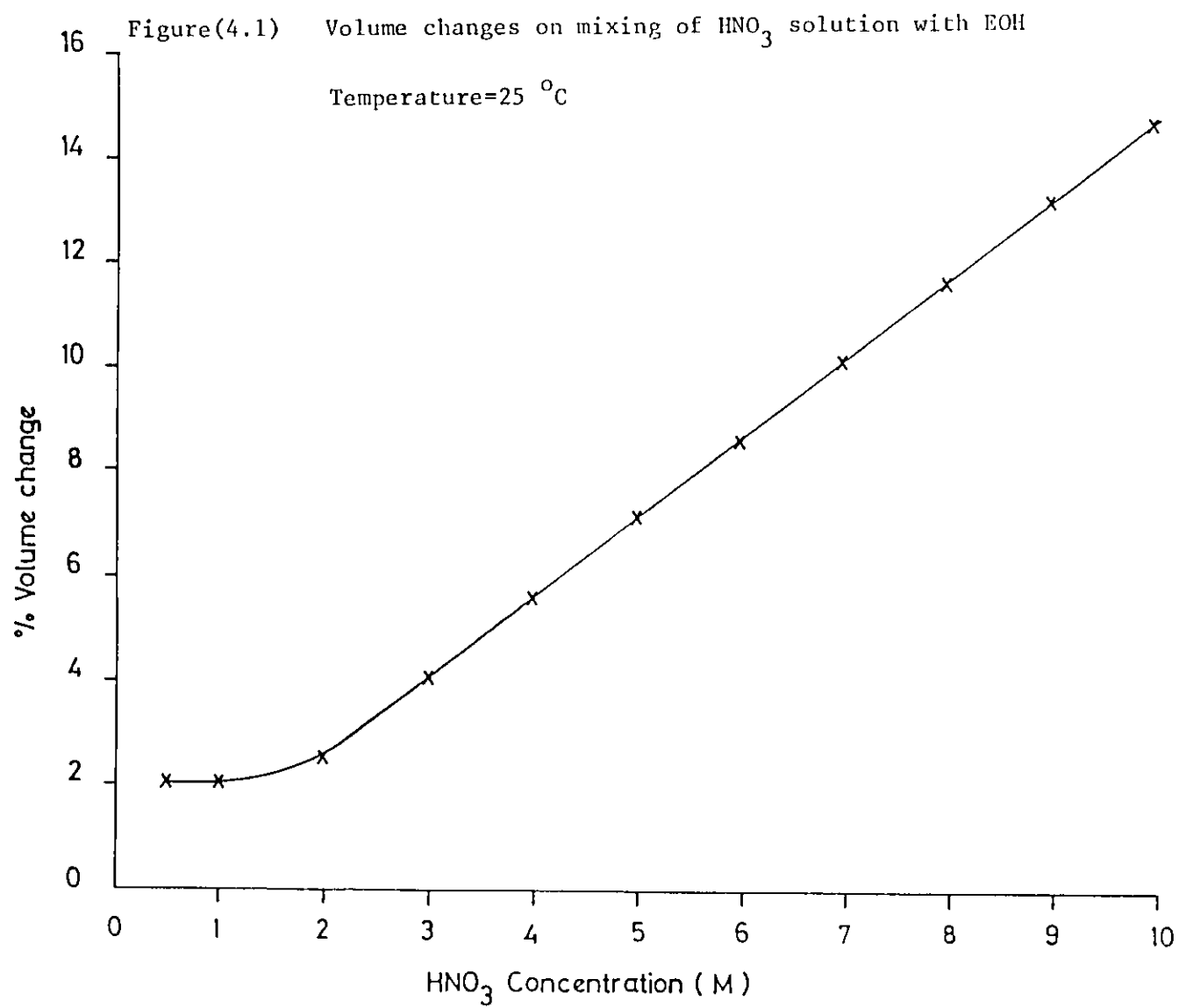
Results for the volume changes are expressed in terms of V_{org}/V_{aq} and also percentage volume change, i.e. percentage increase in the organic phased volume or percentage decrease in the volume of the aqueous phase, Table (4.1) and Figure (4.1).

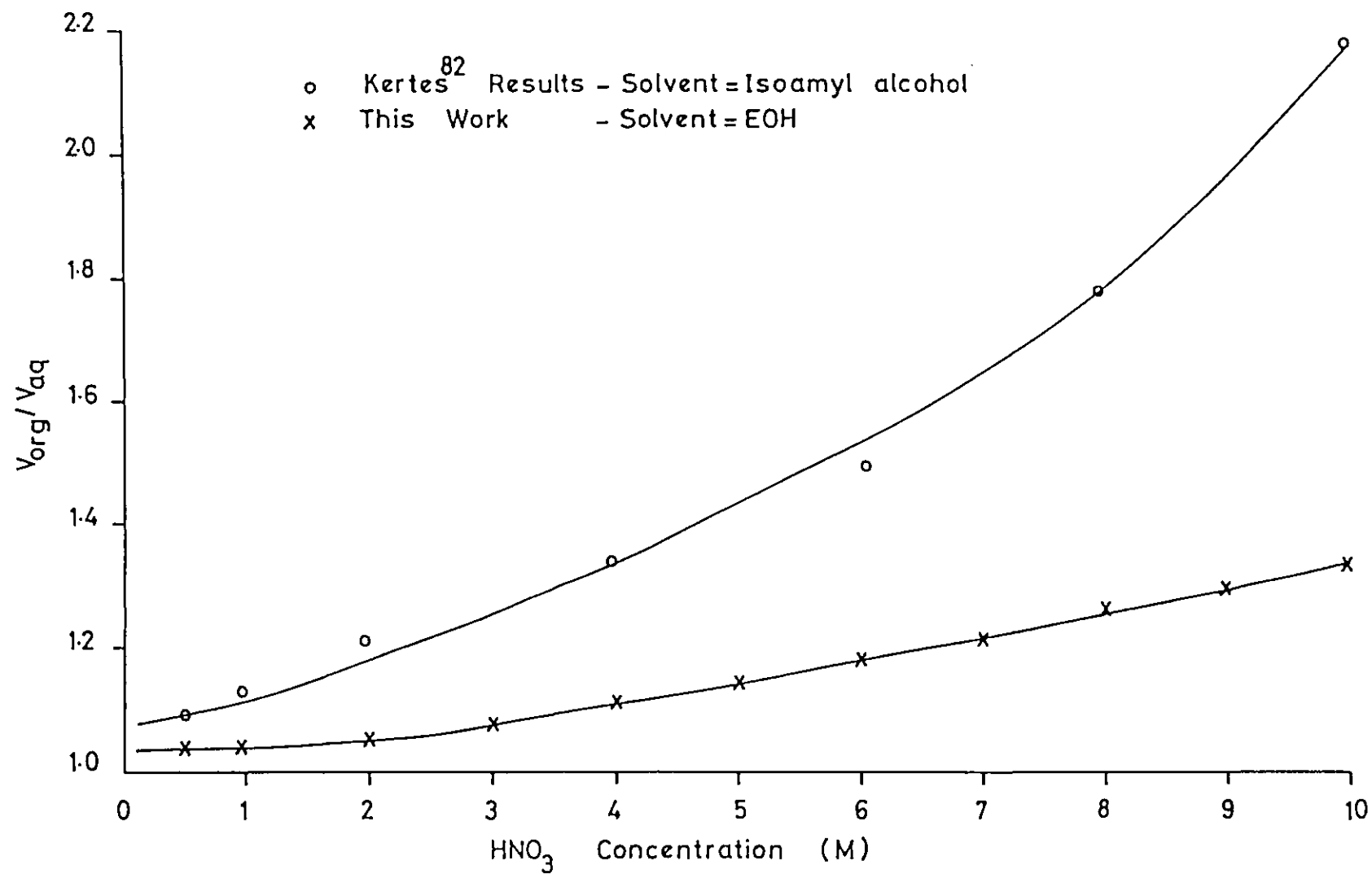
Figure (4.1) shows that the percentage volume change stays constant at about 2% in the lower region of the nitric acid concentrations up to 2M HNO_3 after which it rises linearly, up to 14.5% at 10M HNO_3 the highest concentration studied. These results may be explained in terms of the solubility of the aqueous phase in the organic phase. Solubility of water in EOH is about 3% by volume which could explain the initial 2% volume change considering that some of the alcohol also dissolves in the aqueous phase. The increase in the volume of the organic phase at higher acid concentrations is due to the increase in the solubility and the extraction of HNO_3 into EOH. These results agree with those obtained by Kertes^[82] who studied the extraction of HNO_3 by isoamyl alcohol and reported an increase in V_{org}/V_{aq} with increasing initial HNO_3 concentration in the aqueous phase. These results are compared with those obtained in this work in Figure (4.2) which shows that the increase in V_{org}/V_{aq} as a function of HNO_3 concentration is much higher for isoamyl alcohol than EOH. The reasons are: (a) much higher mutual solubilities of isoamyl alcohol and aqueous solutions: solubility of isoamyl alcohol in H_2O is 2.8 volume % and H_2O in isoamyl alcohol is 7.4 volume % (see Table (2.2) for the solubilities of EOH) and (b) the extraction of HNO_3 by isoamyl alcohol is higher than the extraction of HNO_3 by EOH (see Kertes^[82] for the distribution coefficient values).

Table (4.1) Volume changes on mixing HNO₃ solutions with EOH at 25°C

Initial volume of aqueous phase = 10 cm³
Initial volume of organic phase = 10 cm³

Initial HNO ₃ concentration (M)	Final volume of aqueous phase (V _{aq}) (cm ³)	Final volume of organic phase (V _{org}) (cm ³)	$\frac{V_{org}}{V_{aq}}$	Percentage volume change
0.001	9.80	10.20	1.041	2.0
0.010	9.80	10.20	1.041	2.0
0.100	9.80	10.20	1.04	2.0
0.250	9.80	10.20	1.041	2.0
0.500	9.80	10.20	1.041	2.0
1	9.80	10.20	1.041	2.0
2	9.75	10.25	1.051	2.5
3	9.60	10.40	1.084	4.0
4	9.45	10.55	1.116	5.5
5	9.30	10.70	1.150	7.0
6	9.15	10.85	1.186	8.5
7	9.00	11.00	1.222	10.0
8	8.85	11.15	1.260	11.5
9	8.70	11.30	1.299	13.0
10	8.55	11.45	1.339	14.5



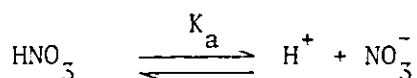


Figure(4.2) Plot of the ratio of organic phase volume to aqueous phase volume against nitric acid concentration for the systems EOH-HNO₃ and isoamyl alcohol-HNO₃.

4.2.2 Extraction of HNO_3

The distribution coefficients for the extraction of HNO_3 by EOH are shown in Table (4.2) which also gives the HNO_3 concentration in the organic and the aqueous phases. The extraction of nitric acid by EOH below 1M HNO_3 was found to be poor ($D < 0.04$) and therefore it may be assumed that only undissociated HNO_3 is extracted and that extraction of the ionised HNO_3 is negligible. Assuming that there is no polymerisation of HNO_3 in the organic phase, the extraction of HNO_3 can be explained by the following equations:

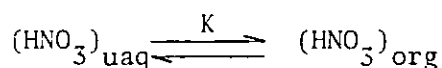
(a) the dissociation of HNO_3 ;



$$\text{where } K_a = \frac{[\text{H}^+][\text{NO}_3^-] \gamma_{+}^2}{[\text{HNO}_3]_{\text{uaq}} (\gamma_{\text{uaq}})} \quad (4.1)$$

(subscript u refers to undissociated HNO_3)

(b) the distribution of the undissociated HNO_3 between the organic and the aqueous phases:



$$\text{where } K = \frac{[\text{HNO}_3]_{\text{org}} (\gamma_{\text{org}})}{[\text{HNO}_3]_{\text{uaq}} (\gamma_{\text{uaq}})} \quad (4.2)$$

Hence the concentration of HNO_3 in the organic phase is

$$C_{\text{org}} = [\text{HNO}_3]_{\text{org}}$$

Table (4.2) Extraction of HNO_3 by EOH at 25°C

Initial HNO_3 concentration in aqueous phase (M)	Final HNO_3 concentration in aqueous phase (M)	Final HNO_3 concentration in organic phase (M)	Distribution coefficient D
0.990	0.952	0.038	0.040
1.980	1.812	0.168	0.093
2.965	2.563	0.402	0.157
3.940	3.230	0.710	0.220
4.950	3.935	1.015	0.258
6.010	4.677	1.333	0.285
7.020	5.408	1.612	0.298
8.010	6.100	1.910	0.313
9.010	6.831	2.179	0.319
10.00	7.524	2.476	0.329

or from Equation (4.2)

$$C_{\text{org}} = K[\text{HNO}_3]_{\text{uaq}} (\gamma_{\text{uaq}}) (\gamma_{\text{org}})^{-1}$$

Similarly the concentration in the aqueous phase is:

$$C_{\text{aq}} = [\text{HNO}_3]_{\text{uaq}} + [\text{NO}_3^-]_{\text{aq}}$$

or from Equation (4.1)

$$C_{\text{aq}} = [\text{HNO}_3]_{\text{uaq}} \{1 + (K_a [\text{H}^+]^{-1} (\gamma_{\text{uaq}}) (\gamma_{\pm})^{-2})\}$$

From the definition of the distribution coefficient, D, we have:

$$D = C_{\text{org}}/C_{\text{aq}}$$

$$\text{or } D = K (\gamma_{\text{uaq}}) (\gamma_{\text{org}})^{-1} / \{1 + (K_a [\text{H}^+]^{-1} (\gamma_{\text{uaq}}) (\gamma_{\pm})^{-2})\}$$

$$\text{Hence } K = \{D(\gamma_{\text{org}})(\gamma_{\text{uaq}})^{-1}\} + \{D K_a [\text{H}^+]^{-1} (\gamma_{\text{org}}) (\gamma_{\pm})^{-2}\} \quad (4.3)$$

If all the assumptions which were made to derive Equation (4.3) are valid, then the equilibrium constant, k, must be a constant independent of the nitric acid concentration. In order to calculate K from Equation (4.3), the activity coefficients of various species in the aqueous and the organic phase are needed. The activity coefficients of the species in the aqueous phase are obtainable from the literature (reference [83]) and the activity coefficients of HNO_3 in the organic phase can be calculated as follows;

In the study of the extraction of HNO_3 by TBP^[71] (dielectric constant = 7.95), the dissociation of the nitric acid in the organic phase has been assumed to be negligible. The same assumption is made in this system, HNO_3 -EOH (dielectric constant = 4.41) and hence the partition law may be written as:

$$a_{\text{org}} = C_{\text{org}} \gamma_{\text{org}} = S a_{\text{aq}} \quad (\text{ref. 71})$$

where a is the activity and S is a constant.

Also

$$a_{\text{aq}} = (C_{\text{aq}} \gamma_{\text{saq}})^2 \quad (\text{ref. 84})$$

Hence

$$C_{\text{org}} \gamma_{\text{org}} = S (C_{\text{aq}} \gamma_{\text{saq}})^2 \quad (4.4)$$

At concentrations of $C_{\text{org}} < 0.1\text{M}$, γ_{org} can be assumed to be unity and hence S to be calculated from

$$C_{\text{org}} = S (C_{\text{aq}} \gamma_{\text{saq}})^2$$

S is calculated to be 7.57×10^{-2} and this value is used in Equation (4.4) to calculate the activity coefficient of HNO_3 , γ_{org} , at higher concentrations of nitric acid, Table (4.3). Using these values of γ_{org} , the equilibrium constant, K , at various concentrations of HNO_3 is calculated, Table (4.3), giving a value of 1.17 ± 0.03 . As K is constant within the experimental error, we can conclude that the assumptions which were made to derive Equation (4.3) and also the assumption that HNO_3 is undissociated in the organic phase are valid.

The existence of HNO_3 in the organic phase as monomer may imply the formation of hydrogen-bonded complex between HNO_3 and EOH similar to that of HDBP-EOH (see Chapter 6).

Table 4.3 Values of the activity coefficients and the equilibrium constant for the extraction of HNO_3 by EOH at 25°C

HNO_3 concentration in aqueous phase, C_{aq} (M)	Stoich. activity coefficient γ_{saq}	Degree of dissociation α	$[\text{H}^+]$ (αC_{aq}) (M)	Mean ionic activity coefficient $\gamma_{\pm}$	Activity coefficient of associated HNO_3 γ_{uaq}	Activity coefficient of HNO_3 in organic phase γ_{org}	Equilibrium constant K
0.952	0.744	0.975	0.928	0.763	1.341	1.000	1.17
1.812	0.839	0.955	1.730	0.874	1.742	1.041	1.18
2.563	0.945	0.931	2.386	1.028	2.184	1.105	1.14
3.230	1.100	0.904	2.920	1.223	2.674	1.346	1.16
3.935	1.298	0.867	3.412	1.491	3.290	1.946	1.17
4.677	1.575	0.828	3.873	1.842	4.096	3.081	1.24
5.408	1.760	0.785	4.245	2.247	5.061	4.254	1.16
6.100	2.008	0.742	4.526	2.708	6.174	5.946	1.17
6.831	2.292	0.694	4.741	3.311	7.609	8.516	1.16
7.524	2.566	0.650	4.891	3.966	9.226	11.40	1.16

4.2.3 Effect of HDBP and H₂MBP on the Extraction of HNO₃:

Greenfield and Hardy^[86] studied the extraction of HNO₃ by HDBP in CCl₄ and reported that some HNO₃ is extracted by HDBP depending on the concentration of HDBP in the organic phase. The extraction of HNO₃ by HDBP and H₂MBP in EOH were studied and it was found that the extraction of HNO₃ by EOH was unaffected in the presence of 10⁻² M HDBP or H₂MBP. It is possible that a small amount of HNO₃ is extracted by both HDBP and H₂MBP which is not detected because of the insensitivity of the method of analysis used to measure the extracted HNO₃.

C H A P T E R 5

THEORY OF EXTRACTION OF PHOSPHATE COMPOUNDS

5.1 HDBP

The extraction of HDBP has been studied by a number of authors^[8-14,87] and the transfer mechanism is now generally discussed in terms of the following factors:

- (i) The dissociation of HDBP in the aqueous phase: HDBP is a weak organic acid only slightly ionized in aqueous solutions. It is about ten times stronger than phosphoric acid and values for its dissociation constant (in the range $pK = 1$ to 1.7) have been reported. However, for the purpose of this work, the dissociation constant of HDBP has been determined independently (see next chapter).
- (ii) The distribution of the undissociated part of HDBP between the phases: there has been enough evidence to suggest that essentially undissociated HDBP is extracted by the organic solvent. Such evidence is provided by the increase in the extraction of HDBP by the solvent with increasing H^+ ion concentration in aqueous phase^[10].
- (iii) The state of HDBP in the aqueous phase: Dyrssen^[9] and Hardy and Scargill^[10] have explained the solubility data for HDBP in aqueous solutions by assuming the formation of dimers but in explaining the transfer mechanism of HDBP from one phase to another they have neglected the dimerisation of HDBP in aqueous phase arguing that the concentration of HDBP

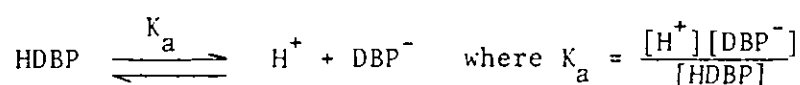
in the aqueous phase is too small for any significant dimerisation. Dyrssen and Hay^[11] from distribution studies of HDBP between various organic solvents and nitrate solutions found no indication of dimeric species of HDBP in the aqueous phase. Kuca^[12] reported the formation of dimers in concentrated nitrate media (ionic strength 6) but because of low C_{aq} , neglected the formation of such species in explaining the distribution results for the extraction of HDBP from a nitrate solution (ionic strength 1) by CCl_4 . From the distribution studies of HDBP between CCl_4 or benzene and 0.1M H_2SO_4 , Liem^[87] has reported the formation of dimers in aqueous phase at $C_{aq} > 10^{-3}M$. For the purpose of this work as C_{aq} is always very small the formation of dimers in the aqueous phase has been neglected.

- (iv) The state of HDBP in the organic phase: the existence of HDBP monomers and dimers in a number of different organic solvents has been reported by Dyrssen^[9] and Hardy and Scargill^[10]. Dyrssen and Hay^[11] and Liem^[87] have reported higher polymeric species of HDBP in hexane at $C_{org} > 0.05M$ from the sharp increase of the distribution coefficient values with the HDBP concentration which was taken as an indication of the breaking up of an eight-membered ring of dimers to some polymeric species in the form of an extended chain. Similarly, from isopiestic studies of species of dioctyl phosphoric acid in octane, Baes^[88] reported the formation of trimeric species of the acid. Myers et al.^[89] reported from static differential vapour-pressure measurements with di-2-ethylhexyl phosphoric acid and with a mixture of the acid and the sodium salt of the acid in wet benzene, the formation of dimeric species for the pure acid and indications of acid dimer and tetramers in the acid-salt mixture. Ferraro and Peppard^[90] interpreted the results of proton magnetic resonance studies of

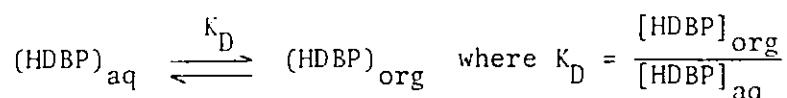
acidic organophosphorus compounds in terms of polymer-dimer-monomer equilibria. In this work it is assumed that HDBP only exists as monomers and dimers in the organic phase as for the range of concentration of HDBP (10^{-5} - 10^{-2} M) used it is unlikely that extended polymerisation will take place.

By assuming that the concentration of HDBP in these experiments is low enough to use concentrations instead of activities in the equilibrium reactions, the following reactions are valid for the transfer of HDBP between the two phases:

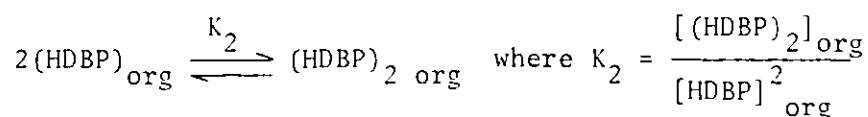
The dissociation of HDBP in aqueous phase:



The distribution of the monomer species between the phases:



The dimerisation of HDBP in the organic phase:



The following equations are also valid;

$$C_A = C_{\text{org}} + C_{\text{aq}} \quad (5.1)$$

$$D = C_{\text{org}}/C_{\text{aq}} \quad (5.2)$$

$$C_{\text{org}} = 2[(\text{HDBP})_2]_{\text{org}} + [\text{HDBP}]_{\text{org}} \quad (5.3)$$

$$C_{\text{aq}} = [\text{HDBP}]_{\text{aq}} + [\text{DBP}^-]_{\text{aq}} \quad (5.4)$$

Using Equation (5.3) and the definitions of K_D and K_2 ;

$$C_{\text{org}} = 2K_2 K_D^2 [\text{HDBP}]_{\text{aq}}^2 + K_D [\text{HDBP}]_{\text{aq}}$$

Similarly, using Equation (5.4) and the definition of K_a ;

$$C_{\text{aq}} = [\text{HDBP}]_{\text{aq}} \phi \quad \text{where} \quad \phi = (1 + K_a [\text{H}^+]^{-1})$$

Hence

$$D_{\text{HDBP}} = \frac{2K_2 K_D^2 [\text{HDBP}]_{\text{aq}}}{\phi} + \frac{K_D}{\phi}$$

or

$$D_{\text{HDBP}} = \frac{2K_2 K_D^2 C_{\text{aq}}}{\phi^2} + \frac{K_D}{\phi} \quad (5.5)$$

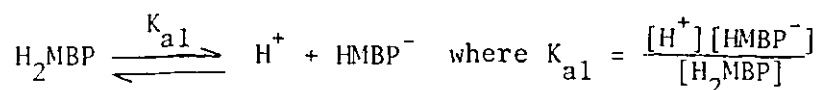
5.2 H₂MBP

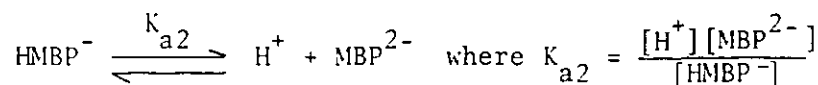
The transfer mechanism of H₂MBP which is a dibasic organic acid can be treated similarly to that of HDBP to derive an equation similar to Equation (5.5).

No information is available on the state of H₂MBP in the aqueous phase. But since the concentration of H₂MBP in the aqueous phase is always low in these experiments it can be assumed to be monomeric. However, Peppard et al.^[91] has reported that H₂MBP is extensively polymeric (10-15 molecules) in solvents of low polarity such as heptane.

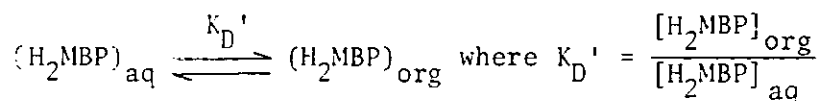
Using concentrations instead of activities, i.e. the activity coefficients of H₂MBP species are assumed to be unity, the following equations are valid for the transfer of H₂MBP between the two phases;

The dissociation of H₂MBP in aqueous phase:

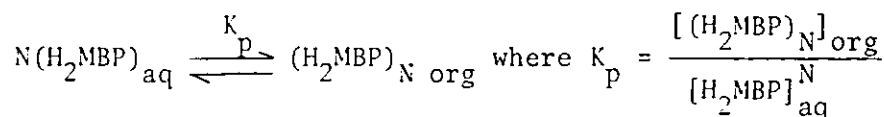




The distribution of the monomer species between the phases:



The polymerisation of H_2MBP in the organic phase:



Equations (5.1), (5.2) and the following are also valid for the experiments:

$$C_{\text{org}} = N[\text{H}_2\text{MBP}]_N^{\text{org}} + [\text{H}_2\text{MBP}]_{\text{org}} \quad (5.6)$$

$$C_{\text{aq}} = [\text{H}_2\text{MBP}]_{\text{aq}} + [\text{HMBP}^-]_{\text{aq}} + [\text{MBP}^{2-}]_{\text{aq}} \quad (5.7)$$

Using Equation (5.6) and the definitions of K_D' and K_P ;

$$C_{\text{org}} = N K_P K_D'^N [\text{H}_2\text{MBP}]_{\text{aq}}^N + K_D' [\text{H}_2\text{MBP}]_{\text{aq}}$$

Similarly, using Equation (5.7) and the definitions of K_{a1} and K_{a2} ;

$$C_{\text{aq}} = [\text{H}_2\text{MBP}]_{\text{aq}} \phi' \quad \text{where } \phi' = 1 + K_{a1}[\text{H}^+]^{-1} + K_{a1}K_{a2}[\text{H}^+]^{-2}$$

Hence

$$D_{\text{H}_2\text{MBP}} = \frac{N K_P K_D'^N [\text{H}_2\text{MBP}]_{\text{aq}}^{N-1}}{\phi'} + \frac{K_D'}{\phi'}$$

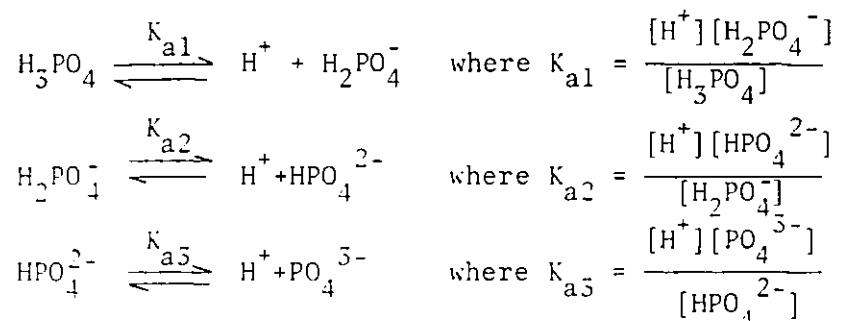
or

$$D_{\text{H}_2\text{MBP}} = \frac{N K_P K_D'^N C_{\text{aq}}^{N-1}}{\phi'^N} + \frac{K_D'}{\phi'} \quad (5.8)$$

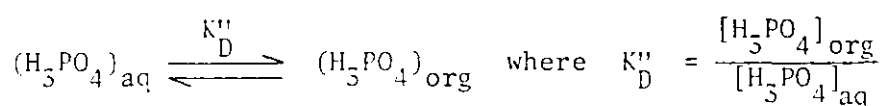
5.5 $\underline{\text{H}_3\text{PO}_4}$

There is no published information available on the polymerisation of phosphoric acid in the aqueous phase but Higgins and Baldwin^[29] reported the polymerisation of highly concentrated H_3PO_4 in TBP ($> 10\text{M}$). However, at the concentrations used in these experiments ($10^{-5} - 10^{-2}\text{M}$) it is rather unlikely for H_3PO_4 to polymerise in either the aqueous or the organic phase. Therefore the following equilibrium reactions are valid for the transfer of H_3PO_4 between the two phases;

The dissociation of H_3PO_4 in aqueous phase;



The distribution of the undissociated species;



Equations (5.1), (5.2) and the following are valid for the experiments;

$$C_{\text{org}} = [\text{H}_3\text{PO}_4]_{\text{org}} = K''_{\text{D}} [\text{H}_3\text{PO}_4]_{\text{aq}} \quad (5.9)$$

$$C_{\text{aq}} = [\text{H}_3\text{PO}_4]_{\text{aq}} + [\text{H}_2\text{PO}_4^-]_{\text{aq}} + [\text{HPO}_4^{2-}]_{\text{aq}} + [\text{PO}_4^{3-}]_{\text{aq}} \quad (5.10)$$

Using Equation (5.10) and the definitions of K_{a1} , K_{a2} and K_{a3} ;

$$C_{\text{aq}} = [\text{H}_3\text{PO}_4]_{\text{aq}} \phi''$$

$$\text{where } \phi'' = 1 + K_{a1}[\text{H}^+]^{-1} + K_{a1}K_{a2}[\text{H}^+]^{-2} + K_{a1}K_{a2}K_{a3}[\text{H}^+]^{-3}$$

$$\text{Hence } D_{H_3PO_4} = K_D'' / \phi'' \quad (5.11)$$

C H A P T E R 6

EXTRACTION OF PHOSPHATE COMPOUND BY EOH

RESULTS AND DISCUSSION

6.1 Effect of Phosphate Concentration on D

6.1.1 HDBP:

The variation of D_{HDBP} with the total initial concentration of HDBP in the aqueous phase is shown in figure (6.1). These results clearly show that D_{HDBP} is independent of the concentration of HDBP at both acidities and temperatures.

The relationship for D_{HDBP} from Chapter (5) is:

$$D_{\text{HDBP}} = \frac{2K_2 K_D^2}{\phi^2} C_{\text{aq}} + \frac{K_D}{\phi}$$

This relationship applies to the results in figure (6.1) only if the first term of the equation, which makes D_{HDBP} dependent on HDBP concentration, is negligible, i.e. K_2 must be very small. This would imply that very little dimerisation occurs in the organic phase and hence the relationship for D_{HDBP} becomes:

$$D_{\text{HDBP}} = K_D / \phi \tag{6.1}$$

However, the extraction results, figure (6.1), indicate that HDBP exists mainly as monomer in the organic phase which is in agreement with several investigations performed a number of years ago [9-11, 34, 35, 92]. These works showed that the more polar solvents

such as ketone, alcohols and carboxylic acids tend to depolymerise and complex dialkyl phosphoric acid.

EOH breaks up, or prevents the formation of, HDBP dimer by forming hydrogen bonds between the phosphoryl and acid group of HDBP and the polar group of the solvent. The probable structure of the EOH - HDBP complex is shown in figure (6.2).

The results in figure (6.1) compare the values of D_{HDBP} at two different HNO_3 concentration, i.e. 0.5M and 3M, and two different temperatures, 25°C and 50°C . These results illustrate that equation (6.1) is valid for any HNO_3 concentration or temperature as D_{HDBP} is independent of HDBP concentration. But both variations in HNO_3 concentration or temperature show some effect on the values of D_{HDBP} . The effect of HNO_3 concentration on D_{HDBP} will be discussed in more detail in the following sections. D_{HDBP} at 50°C is slightly lower than at 25°C for 3M HNO_3 which from a practical standpoint may be insignificant. The difference in values may be explained in terms of the extraction of HNO_3 by EOH which was found to be about 5 to 6% higher at 50°C than at 25°C for 3M HNO_3 . This would have the effect of reducing the amount of EOH available for the extraction of HDBP and hence reducing the HDBP distribution coefficients. To illustrate this : at 3M HNO_3 , the concentration of HNO_3 in the organic phase at 25°C is about 0.43M, table (4.2), and the concentration of pure EOH used in these experiments is about 6M. Therefore there is only 5.57M EOH available for the extraction of HDBP. When the concentration of HNO_3 in the organic phase is increased to 0.45M as the consequence of increasing the temperature to 50°C , there will be only 5.55M EOH available for the extraction of HDBP. However the decrease in D_{HDBP}

as the result of increasing temperature is perhaps rather small because there will be an increase in the extraction of HDBP - HNO_3 complex due to the increase in HNO_3 extraction (see section 6.4).

6.1.2 H_2MBP :

Results for the extraction of H_2MBP , figure (6.1), show that $D_{\text{H}_2\text{MBP}}$ is also independent of H_2MBP concentration regardless of the acidity of the aqueous phase or the temperature. Therefore in the expression derived for $D_{\text{H}_2\text{MBP}}$ in the previous chapter that is

$$D_{\text{H}_2\text{MBP}} = \frac{NK_p K_D' N}{\phi' N} C_{\text{aq}}^{N-1} + \frac{K_D'}{\phi'}$$

the first term which makes $D_{\text{H}_2\text{MBP}}$ dependent on the H_2MBP concentration is negligible, i.e. K_p is very small. Hence the new relationship for H_2MBP to fit the data in figure (6.1) is:

$$D_{\text{H}_2\text{MBP}} = K_D' / \phi' \quad (6.2)$$

The extraction results for H_2MBP , figure (6.1), also indicate that H_2MBP does not polymerise in the organic phase and exists mainly as monomer. Similarly to HDBP, the depolymerisation of H_2MBP in the organic phase is brought about by hydrogen bond formation between EOH and H_2MBP and hence the possible structure of EOH - H_2MBP complex would be as shown in figure (6.2).

The results in figure (6.1) also show that increasing the temperature, reduces $D_{\text{H}_2\text{MBP}}$ which may be due to the increase in the extraction of HNO_3 by the solvent caused by increasing the temperature as was explained for HDBP.

6.1.3 H₃PO₄ :

The expression derived for the distribution coefficient of H₃PO₄, D_{H₃PO₄}, in Chapter (5), i.e. $D_{H_3PO_4} = K_D'' / \phi''$, imply that D_{H₃PO₄} is independent of H₃PO₄ concentration. This agrees with the results obtained for the extraction of H₃PO₄, figure (6.1). Hence we can say that the extraction of H₃PO₄ by EOH is similar to the extraction of HDBP and H₂MBP and that H₃PO₄ does not polymerise in either aqueous phase or the organic phase. Similar to HDBP and H₂MBP, the possible structure of EOH - H₃PO₄ complex is shown in figure (6.2).

As the results in figure (6.1) show, the temperature change does not have any significant effect on the values of D_{H₃PO₄}. This is perhaps because since the amount of H₃PO₄ extracted by EOH is rather low, the small decrease in D_{H₃PO₄} caused by increasing the temperature was not detected.

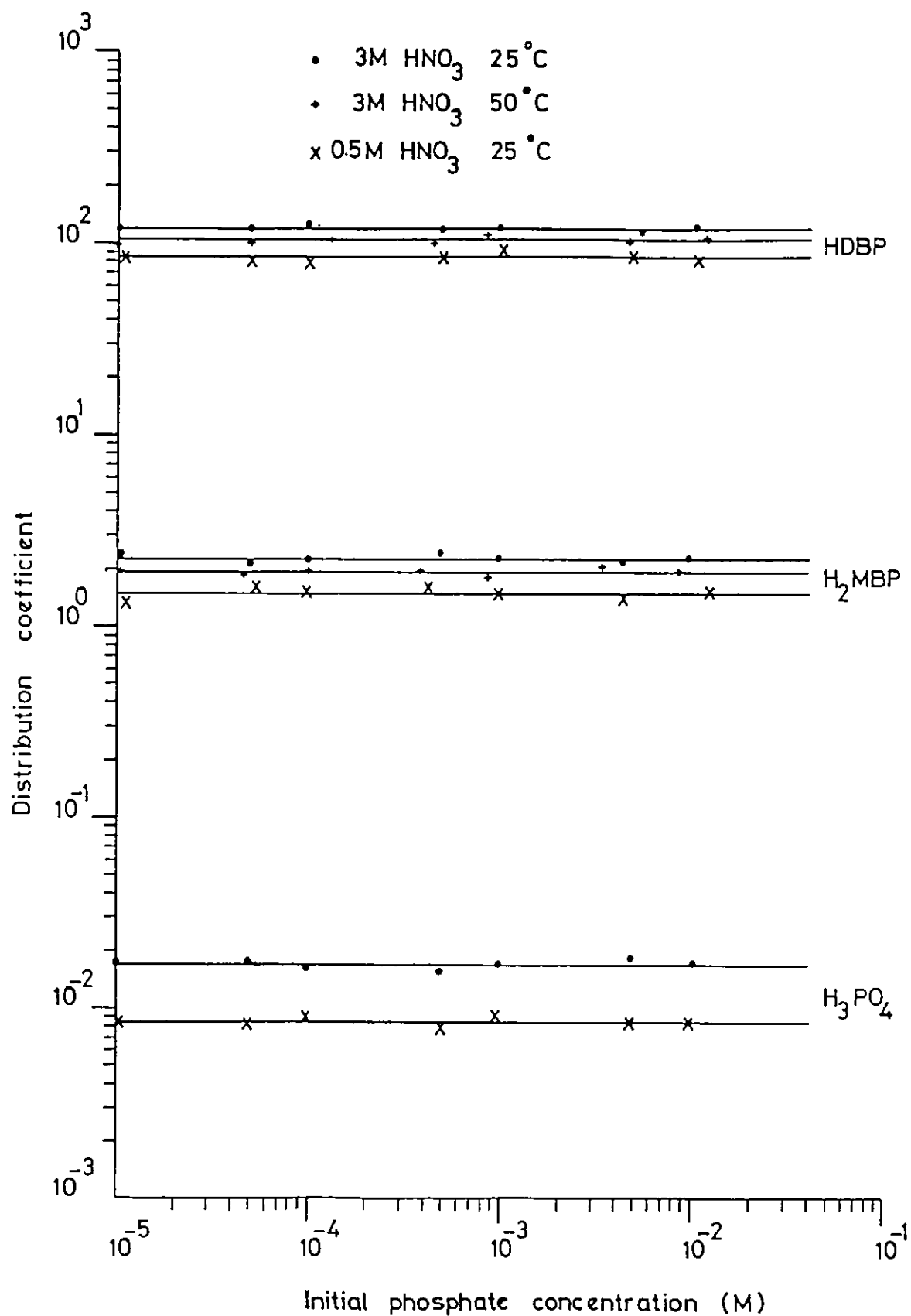
6.2 Comparison of the Extraction of Phosphates

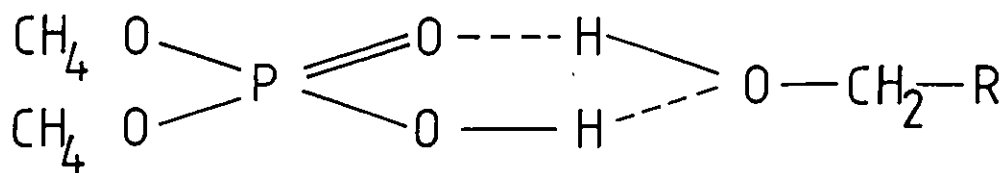
Results in figure (6.1) show the following orders for the extraction of phosphate compounds by EOH;

$$D_{HDBP} > D_{H_2MBP} > D_{H_3PO_4}$$

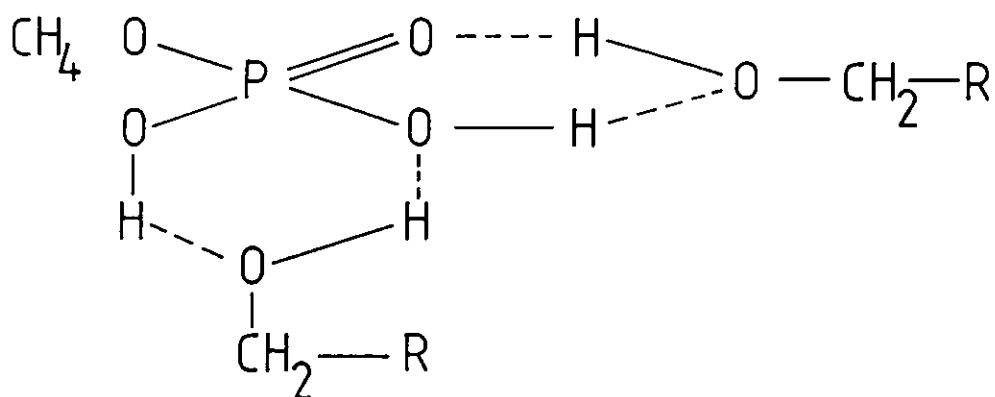
This order of extraction is expected for any solvent, because increasing the number of butyl groups and decreasing the number of hydrophilic groups decreases compatibility with the water structure and increases compatibility with the organic phase. Therefore HDBP is more

Figure(6.1) Extraction of phosphate compounds from nitric acid solution by EOH.

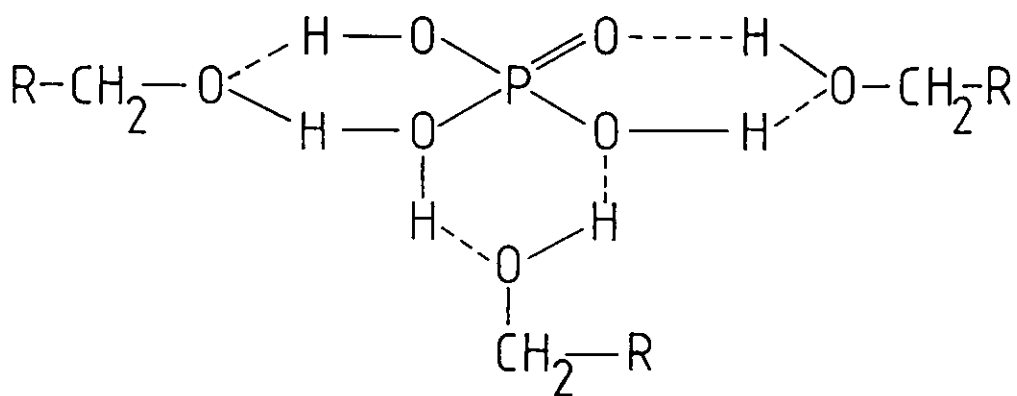




HDBP-EOH Complex



H₂MBP-EOH Complex



H₃PO₄-EOH Complex

Figure(6.2) Structure of hydrogen-bonded complex between EOH and phosphate compounds.

compatible with the organic phase than H_2MBP which is more compatible with the organic phase than H_3PO_4 .

6.3 Effect of Hydrogen Ion Concentration on the Distribution Coefficients

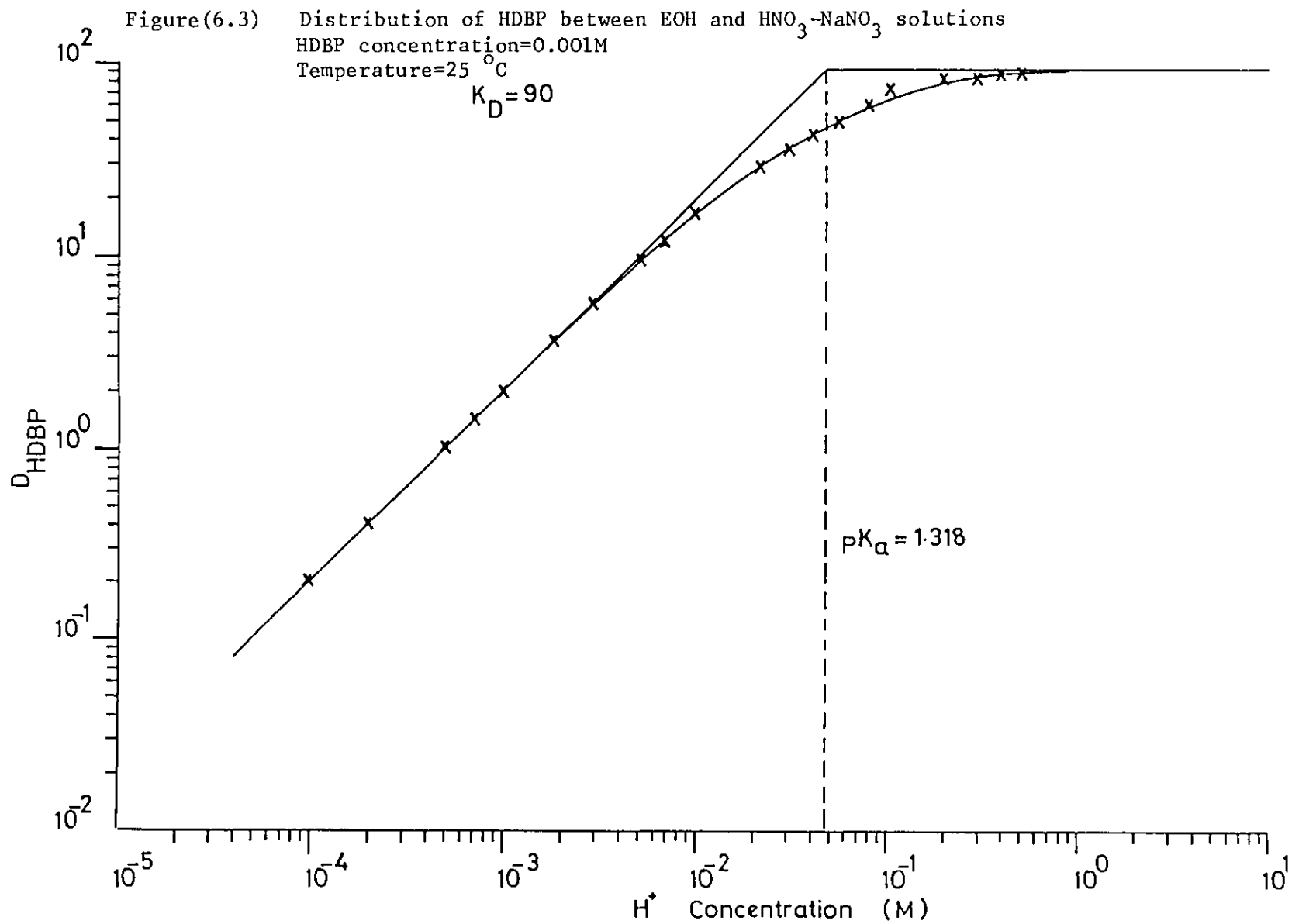
Distribution coefficient values have been obtained as a function of hydrogen ion concentrations of the aqueous phase at constant ionic strength of 0.5M. Results are plotted in figures (6.3), (6.4) and (6.5) for HDBP, H_2MBP and H_3PO_4 respectively. These results show an increase in the values of the distribution coefficient with increasing hydrogen ion concentration. This is best explained in terms of the suppression of the dissociation of the acidic phosphates with increasing hydrogen ion concentration and the consequent increase in extractable undissociated molecules of the phosphate compounds. The results shown in figures (6.3), (6.4) and (6.5) have been used to determine the values of the dissociation constants and the distribution constants for HDBP, H_2MBP and H_3PO_4 ;

(a) HDBP: from equation (6.1) we have

$$D_{HDBP} = K_D / (1 + K_a [H^+]^{-1})$$

Figure (6.3) is the plot of $\log D_{HDBP}$ against $\log[H^+]$ and the normalized curve $\log y = \log(x+1)$ fits the data very well. The horizontal asymptote ($\log y = 0$) gives $\log K_D$ and the point of intersection of the two asymptotes gives $pK_a = -\log[H^+]$.

From figure (6.3) the following values are obtained by fitting the normalized curve ;



$$pK_a = 1.318 \pm 0.020 \quad K_D = 90 \pm 9$$

The pK_a value has also been calculated using the pH titration data, figure (3.2), and a value of 1.424 ± 0.043 is obtained (Appendix B). This value is the thermodynamic value of the dissociation constant and cannot be compared directly with the value obtained from figure (6.3). But since the ionic strength of the solutions for the results in figure (6.3) was kept constant at 0.5M it is possible to correct the pK_a value to obtain the thermodynamic value. The equation used is ;

$$pK_a^T = pK_a + \frac{0.512\sqrt{I}}{1+1.6\sqrt{I}} \text{ at } 25^\circ\text{C}^{[93]} \quad (6.3)$$

where pK_a^T = thermodynamic value of pK_a

I = ionic strength of the solution

Hence $pK_a^T = 1.318 + 0.17 = 1.488 \pm 0.020$

This value compares well with the value obtained from the pH titration results.

The values of pK_a reported in the literature vary from 0.80 to 1.72 and the majority are not estimates of the thermodynamic values, table (6.1). The reason for the discrepancy in the values of pK_a could be the following ;

Table (6.1) The dissociation constant of HDBP in aqueous solutions,
at 25°C .

pK_a	Medium	HDBP Concentration (M)	References
1.00	1M(HClO ₄ +NaClO ₄)	1.33×10^{-5}	9
1.00	0.1M(HClO ₄ +NaClO ₄)	1.33×10^{-5}	9
1.13	1M(HNO ₃ +NaNO ₃)	10^{-3}	12
1.20	1M(HNO ₃ +NaNO ₃)	3×10^{-5}	"
1.04	1M(HClO ₄ +NaClO ₄)	10^{-3}	"
1.18	1M(HClO ₄ +NaClO ₄)	3×10^{-5}	"
0.80	1M(HNO ₃ +NaNO ₃)	7.36×10^{-4}	13
1.00	0.1M(HClO ₄ +NaClO ₄)	-	94
1.29	H ₂ O	-	95
1.720	H ₂ O	-	96
1.424	H ₂ O	10^{-2}	This work
1.488	0.5M(HNO ₃ +NaNO ₃)	10^{-3}	This work

- (i) the initial concentration of HDBP seem to affect the value of pK_a as shown from the reported values of Kuca^[9], table (6.1).
- (ii) the impurities in HDBP would also affect the value of pK_a . Kumler and Eiler^[96] have reported a value of 1.72 for pK_a . They have used the method of Pilmmmer and Burch^[42] for the purification of HDBP and it has been reported that this method would not produce a highly pure solution of HDBP^[10].

The value of pK_a in this work have been obtained by two independent methods and for two different concentrations of HDBP in water and nitric acid and they are in good agreement. Hence the average of the two values is taken as the true thermodynamic value of pK_a for HDBP ($pK_{a(\text{average})} = 1.456 \pm 0.024$).

Using the value of $pK_a = 1.488 \pm 0.020$ determined from the extraction results to be consistent with the distribution coefficient values, K_D is calculated from the results shown in figure (6.1) and the equation (6.1);

$$\text{at } 0.5M \text{ HNO}_3 \quad K_D = 90.5 \pm 9.6$$

$$\text{at } 3.0M \text{ HNO}_3 \quad K_D = 118.5 \pm 12$$

At $0.5M \text{ HNO}_3$ the value of K_D compares well with the value obtained from figure (6.3). At $3M \text{ HNO}_3$ the value of 118.5 is higher, this will be explained in the following section. A value of $K_D = 178$ for the system $0.1M \text{ HNO}_3, \text{EOH}$ is reported by Horwitz et al [14] which is much higher than the value of 90 obtained in this work. The reason for this discrepancy is the choice of the pK_a value which Horwitz has taken the value of 1.00 reported by Dyrssen [9].

(b) $\underline{H_2MBP}$: using equation (6.2);

$$D = K'_D / \phi'$$

$$\text{or} \quad D = K'_D / (1 + K_{a1} [H^+]^{-1} + K_{a1} K_{a2} [H^+]^{-2})$$

$$(\phi' = 1 + K_{a1} [H^+]^{-1} + K_{a1} K_{a2} [H^+]^{-2} \quad \text{from Chapter 5})$$

the term $K_{a1} K_{a2} [H^+]^{-2}$ is rather small compared to the term $1 + K_{a1} [H^+]^{-1}$ ($pK_{a2} = 6.865$ from the pH titration, Appendix B) and hence it can be neglected. Therefore;

$$D = K'_D / (1 + K_{a1} [H^+]^{-1}) \quad (6.4)$$

Figure (6.4) is the plot of $\log D_{H_2MBP}$ against $\log[H^+]$ and the normalized curve $\log y = \log(x+1)$ fits the data. The following values are obtained by fitting the normalized curve;

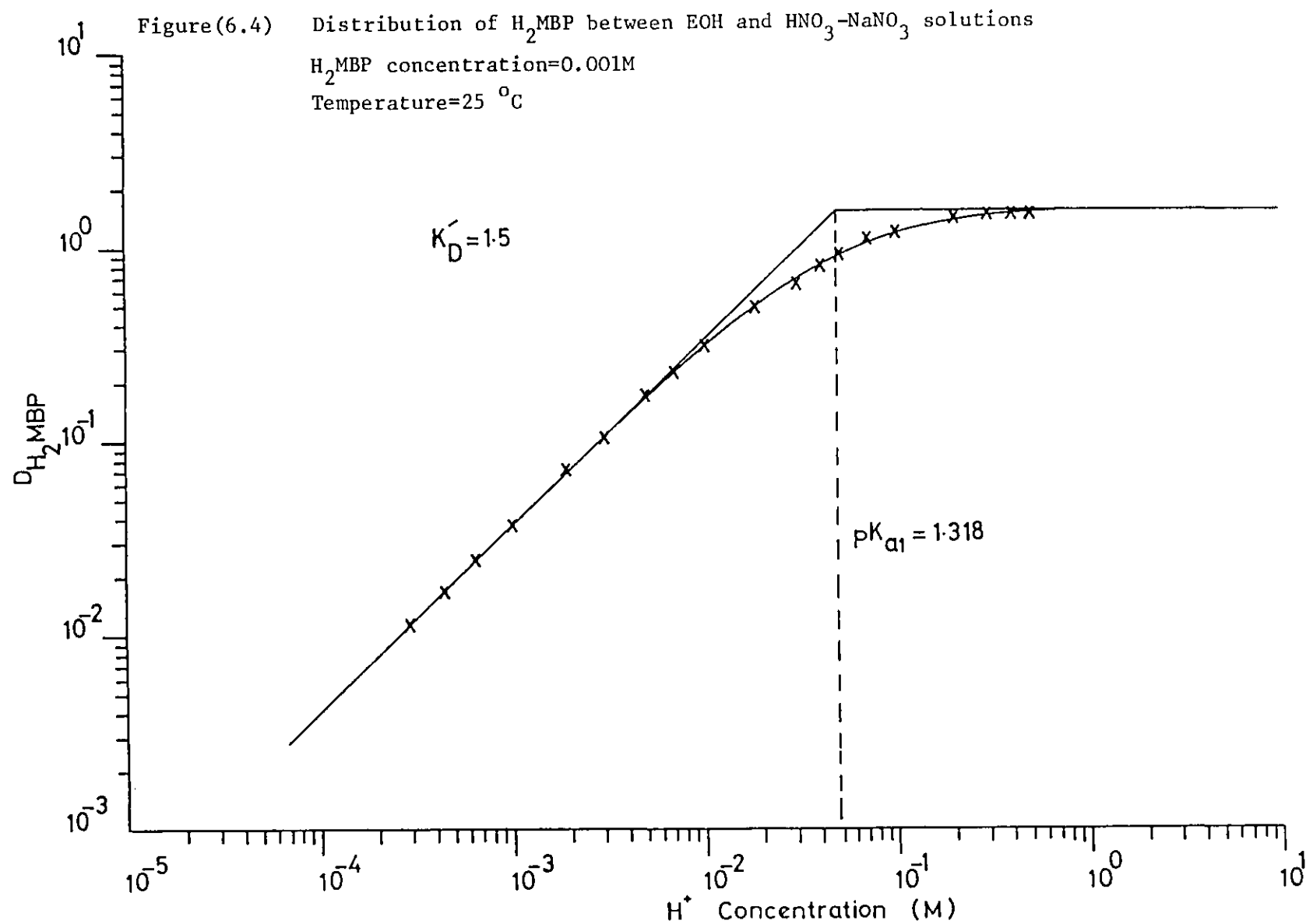
$$pK_{a1} = 1.318 \pm 0.02 \quad K_D = 1.5 \pm 0.15$$

The ionic strength of solutions was kept constant at 0.5M, hence using equation (6.3), the thermodynamic value of pK_{a1} is 1.488 ± 0.02 .

The value of pK_{a1} obtained from the titration results is 1.378 ± 0.041 (Appendix B). This value is lower than the value obtained from figure (6.4). Kumler and Eiler [96] have studied the acidic strength of various phosphate compounds and reported the factors affecting the acidity of these compounds to be the solvation, inductive, statistical and steric effects. Of these the solvation effect is chiefly responsible for the monoalkyl acids being stronger than phosphoric acid and dialkyl acids stronger than the monoalkyl acids. Therefore, it is rather unlikely for the pK_{a1} of H_2MBP to be lower than the pK_a value of HDBP as this would imply that H_2MBP is a stronger acid than HDBP. Although in general there is no doubt about the accuracy of the pH titration method as it is shown from the determination of the pK_{a1} for phosphoric acid (Appendix B), the pK_{a1} of 1.378 determined by this method cannot be accepted as the true value of the pK_{a1} for H_2MBP . The value of 1.488 determined from the extraction results is a more reasonable value for the thermodynamic pK_{a1} of H_2MBP .

Kumler and Eiler [96] have reported the following values for the dissociation constants of H_2MBP ;

$$pK_{a1} = 1.890 \quad pK_{a2} = 6.840$$



The pK_{a1} which perhaps is more affected by the purity of the H_2MBP solution is much higher than the value obtained in this work.

However there is good agreement for the pK_{a2} .

Using equation (6.2) with $pK_{a1} = 1.488 \pm 0.02$ and the results in figure (6.1), K_D' is calculated to be 1.59 ± 0.16 at $0.5M HNO_3$ which is in good agreement with the value of K_D' obtained from figure (6.4).

(c) H_3PO_4 : the expression derived for the distribution coefficient of H_3PO_4 is;

$$D = K_D''/\phi''$$

$$\text{or } D = K_D''/(1 + K_{a1}[H^+]^{-1} + K_{a1}K_{a2}[H^+]^{-2} + K_{a1}K_{a2}K_{a3}[H^+]^{-3})$$

$$(\phi'' = 1 + K_{a1}[H^+]^{-1} + K_{a1}K_{a2}[H^+]^{-2} + K_{a1}K_{a2}K_{a3}[H^+]^{-3} \text{ from Chapter 5}).$$

$$\text{From the literature; } pK_{a1} = 2.124$$

$$pK_{a2} = 7.206$$

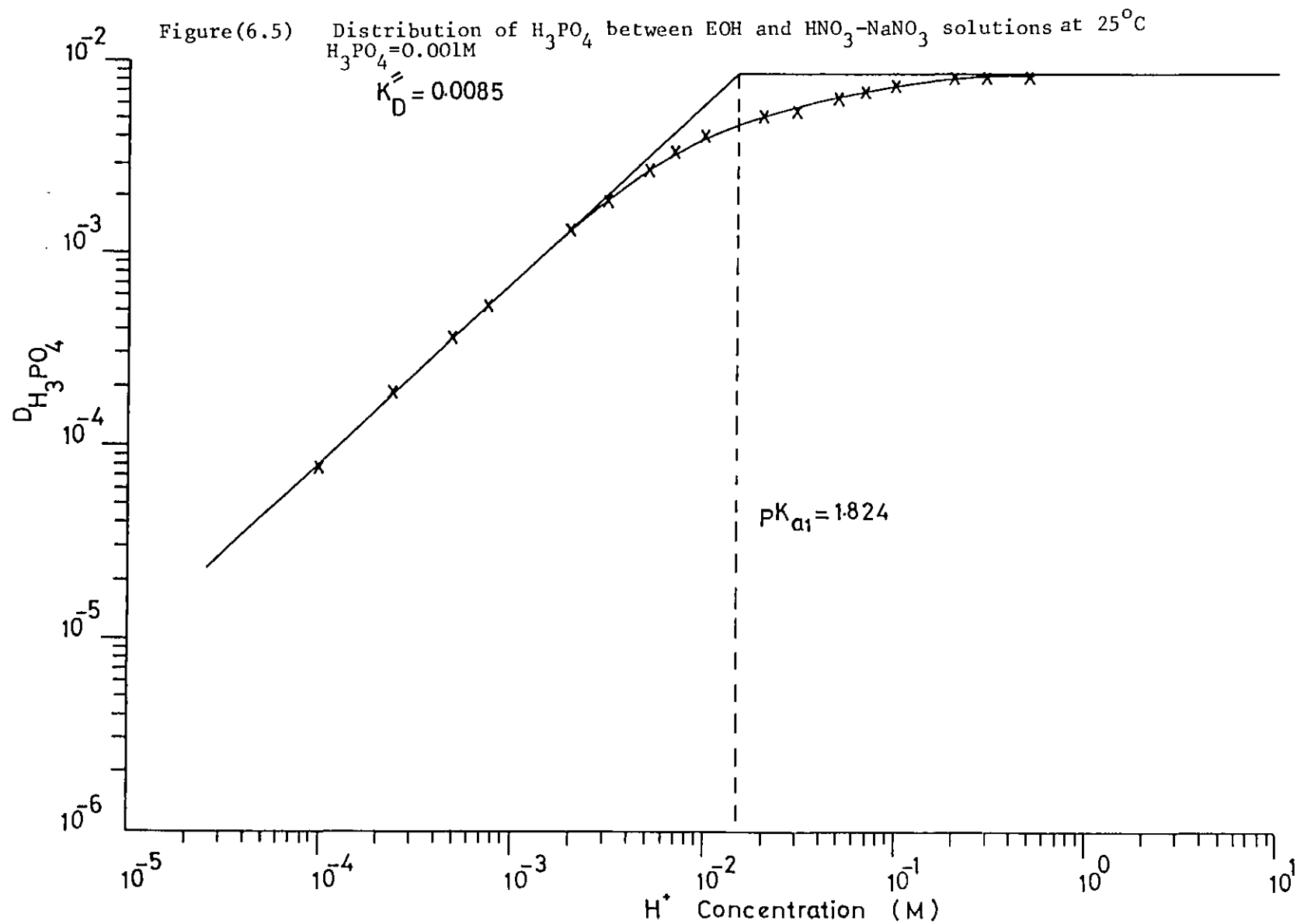
$$pK_{a3} = 12.30$$

These values make the terms $K_{a1}K_{a2}[H^+]^{-2}$ and $K_{a1}K_{a2}K_{a3}[H^+]^{-3}$ very small compared with the term $1 + K_{a1}[H^+]^{-1}$ and therefore they can be neglected. Hence;

$$D = K_D''/(1 + K_{a1}[H^+]^{-1}) \quad (6.5)$$

Figure (6.5), $\log D_{H_3PO_4}$ against $\log[H^+]$, shows that the normalized curve, $\log y = \log(x+1)$, fits the data and the following values are obtained;

$$pK_{a1} = 1.824 \pm 0.01 \quad K_D'' = 0.0085 \pm 0.0005$$



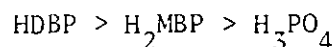
Using equation (6.3) and the ionic strength of 0.5M, the thermodynamic value of pK_{a1} is 1.994 ± 0.01 . This value is in reasonable agreement with the reported value which illustrate both the validity and the accuracy of the graphical method using the extraction results to determine the dissociation constants of the acids.

Using the expression for the distribution coefficient of H_3PO_4 and the data in figure (6.1), at 0.5M HNO_3 , $K'_D = 0.00858 \pm 0.0005$. This value agrees well with the value of K''_D obtained from figure (6.5).

Comparing the values of K_D obtained for the phosphate compounds;

$$\begin{aligned} \text{HDBP} : K_D &= 90 \pm 9 \\ \text{H}_2\text{MBP} : K'_D &= 1.5 \pm 0.15 \\ \text{H}_3\text{PO}_4 : K''_D &= 0.0085 \pm 0.0005 \end{aligned}$$

These values again show that the order of extractability is;



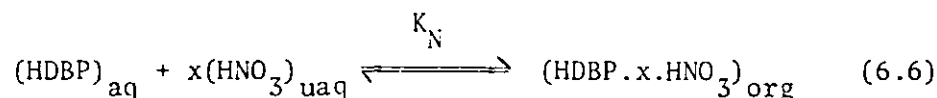
6.4 Effect of HNO_3 Concentration on the Distribution Coefficients

Table (6.2) shows the results for the extraction of phosphate compounds as a function of HNO_3 concentration, from 1 to 10M. An increase in values of the distribution coefficients with increasing HNO_3 concentration is seen, although there is a slight decrease in the values of the distribution coefficients for HDBP and $H_2\text{MBP}$ at very high HNO_3 concentration. This may be due to the competition between the extractable HNO_3 and the phosphate compounds. This was shown quantitatively for the increase in temperature which also applies here (see section 6.1.1).

Table (6.2) Distribution coefficient values for the extraction of phosphate compounds as a function of HNO_3 concentration at 25°C.

Initial HNO_3 concentration (M)	HDBP			H_2MBP			H_3PO_4		
	D	ϕ	$D\phi$	D	ϕ'	$D\phi'$	D	ϕ''	$D\phi''$
0.990	97	1.0459	101.6	1.69	1.0459	1.77	8.86×10^{-3}	1.0143	8.98×10^{-3}
1.980	107	1.0215	109.3	1.98	1.0215	2.02	1.10×10^{-2}	1.0067	1.11×10^{-2}
2.965	115	1.0132	116.5	2.24	1.0132	2.27	1.59×10^{-2}	1.0041	1.60×10^{-2}
3.940	120	1.0091	121.1	2.50	1.0091	2.52	2.37×10^{-2}	1.0028	2.38×10^{-2}
4.950	127	1.0064	127.8	2.70	1.0064	2.72	2.90×10^{-2}	1.0020	2.91×10^{-2}
6.010	134	1.0046	134.6	2.84	1.0046	2.85	3.13×10^{-2}	1.0014	3.13×10^{-2}
7.020	135	1.0034	135.5	3.11	1.0034	3.12	3.02×10^{-2}	1.0011	3.02×10^{-2}
8.010	137	1.0027	137.4	3.06	1.0027	3.07	3.13×10^{-2}	1.0008	3.13×10^{-2}
9.010	136	1.0021	136.3	3.03	1.0021	3.04	3.00×10^{-2}	1.0006	3.00×10^{-2}
10.00	136	1.0017	136.2	3.00	1.0017	3.01	3.13×10^{-2}	1.0005	3.13×10^{-2}

Table (6.2) also shows the values of $D\emptyset$, $D\emptyset'$ and $D\emptyset''$ which according to equations (6.1), (6.4) and (6.5) are the equilibrium constants (K_D , K_D' and K_D'') for HDBP, H_2MBP and H_3PO_4 respectively. These values vary with HNO_3 concentration. Therefore equations (6.1), (6.4) and (6.5) do not hold for concentrated HNO_3 solutions and additional reactions may be involved. One such reaction could be the extraction of phosphates - HNO_3 complexes which has been reported previously for HDBP [10,12,86]. A reaction for the extraction of HDBP - HNO_3 complex can be written as ;



where x = number of $(HNO_3)_{uaq}$ molecules

$$\text{and } K_N = \frac{[HDBP.x.HNO_3]_{org} \gamma'_{org}}{[HDBP]_{aq} (a_{(HNO_3)_{uaq}})^x}$$

where γ'_{org} = activity coefficient of $(HDBP.x.HNO_3)_{org}$

and $a_{(HNO_3)_{uaq}}$ = activity of the undissociated nitric acid in the aqueous phase.

The concentration of $(HDBP)_{aq}$ is rather low and therefore its activity coefficient is assumed to be unity.

From equation(6.6), the dissociation of HDBP in the aqueous phase, the distribution of the HDBP monomer between the phases (see Chapter (5)) and assuming K_D to be 90 as determined in the previous section, a new relationship for D_{HDBP} can be derived;

$$C_{org} = [HDBP]_{org} + [HDBP.x.HNO_3]_{org}$$

or
$$C_{org} = K_D [HDBP]_{aq} + \frac{K_N}{\gamma'_{org}} [HDBP]_{aq} (a_{(HNO_3)_{uaq}})^x$$

and
$$C_{aq} = [HDBP]_{aq}$$
 as before

Hence
$$D = \frac{K_D}{\phi} + \frac{K_N}{\phi \gamma'_{org}} (a_{(HNO_3)_{uaq}})^x \quad (6.7)$$

rearranging
$$(D\phi - K_D) \gamma'_{org} = K_N (a_{(HNO_3)_{uaq}})^x$$

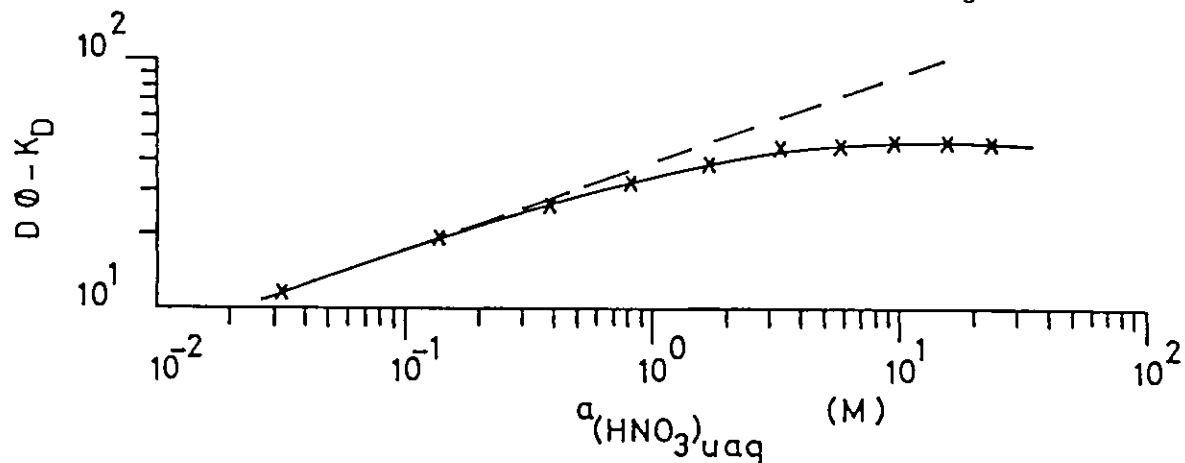
If the assumptions are valid the plot of $\log\{(D\phi - K_D) \gamma'_{org}\}$ against $\log(a_{(HNO_3)_{uaq}})$ should be a straight line with the slope of x and $\log K_N = \log\{(D\phi - K_D) \gamma'_{org}\}$ when $\log(a_{(HNO_3)_{uaq}}) = 0$.

The activity coefficient of $(HDBP.x.HNO_3)_{org}$, γ'_{org} , is not known but since the concentration of HDBP in the organic phase is rather low (highest initial HDBP concentration = $10^{-2}M$), γ'_{org} is assumed to be unity and $\log(D\phi - K_D)$ is plotted against $\log a_{(HNO_3)_{uaq}}$, figure (6.6). This figure shows that only the first two points, which correspond to rather low HNO_3 concentrations in the organic phase, lie on a straight line and as the HNO_3 concentration in the organic phase increases, the corresponding points lie further away from this line. Hence we have suggested that the organic phase is dominated by the nitric acid and γ'_{org} to be substituted by the activity coefficient of nitric acid in the organic phase, γ_{org} (table 4.3). Figure (6.7) shows a plot of $\log\{(D\phi - K_D) \gamma_{org}\}$ versus $\log a_{(HNO_3)_{uaq}}$ which consists of two straight lines with the following values;

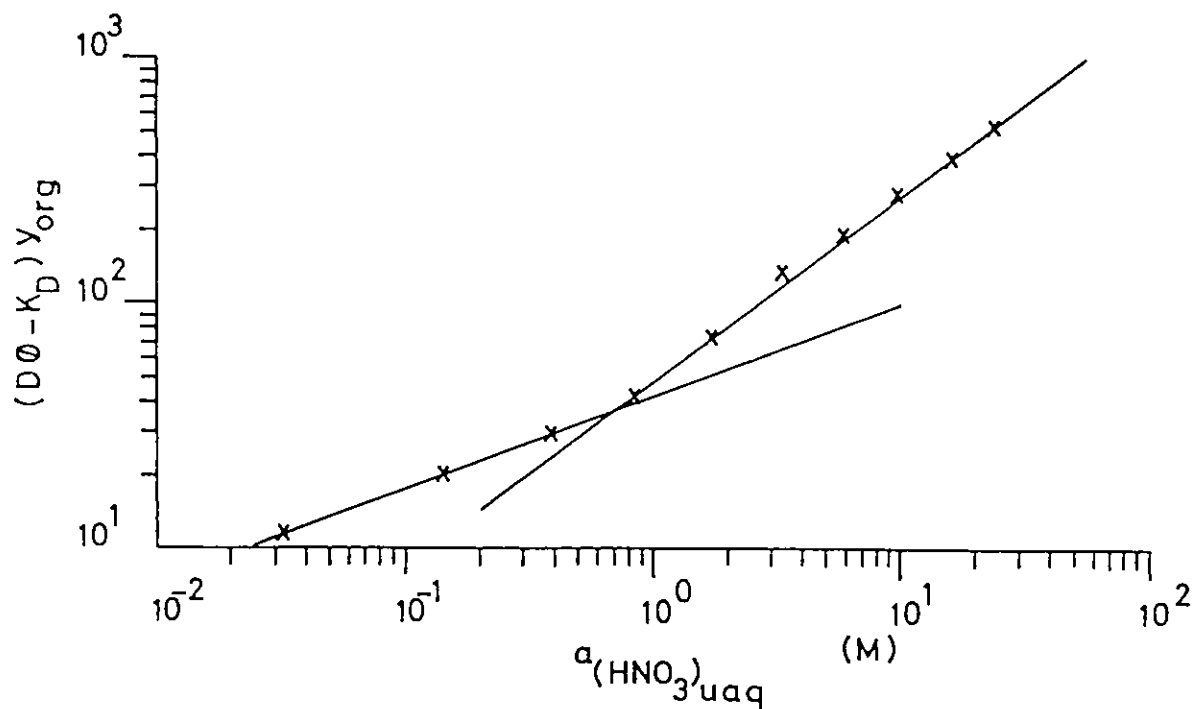
From 1 to 3M HNO_3 ; $x_1 = 0.5$ $K_{N1} = 41 \pm 5$

From 4 to 10M HNO_3 ; $x_2 = 0.75$ $K_{N2} = 48 \pm 5$.

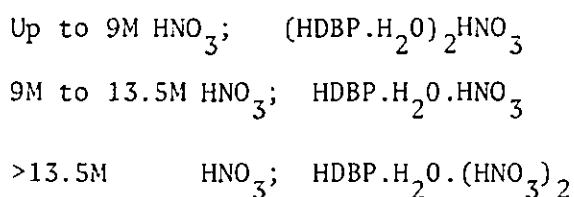
Figure(6.6) Plot of $\log(D\phi - K_D)$ versus $\log a_{(\text{HNO}_3)_{\text{uag}}}$ for the distribution of HDBP between EOH and HNO_3 solutions.



Figure(6.7) Plot of $\log((D\phi - K_D)\gamma_{\text{org}})$ versus $\log a_{(\text{HNO}_3)_{\text{uag}}}$ for the distribution of HDBP between EOH and HNO_3 solutions.

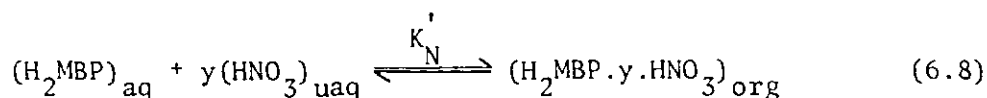


From the values of x it is possible to determine the composition of the HDBP - HNO_3 complex. Up to 3M HNO_3 , the complex has the form of $2\text{HDBP} \cdot \text{HNO}_3$ and above 3M to 10M HNO_3 the complex changes to $3\text{HDBP} \cdot 2\text{HNO}_3$. The very close values of K_{N1} and K_{N2} is an indication that these two complexes have similar solubilities in the organic phase. Kertes et al [97] reported the following complexes between HDBP and HNO_3 in carbon tetrachloride;



However, the type of complexes formed between HDBP and HNO_3 is dependent on the organic phase and for different systems different complexes could be formed. Also from our results it is not possible to determine if there is any water molecules in the complexes.

For H_2MBP the reaction between H_2MBP and HNO_3 can be written as;



where y = number of $(\text{HNO}_3)_{\text{uaq}}$ molecules

$$\text{and } K_N' = \frac{[\text{H}_2\text{MBP} \cdot y \cdot \text{HNO}_3]_{\text{org}} \gamma_{\text{org}}''}{[\text{H}_2\text{MBP}]_{\text{aq}} (a_{(\text{HNO}_3)_{\text{uaq}}})^y}$$

where γ_{org}'' = activity coefficient of $(\text{H}_2\text{MBP} \cdot y \cdot \text{HNO}_3)_{\text{org}}$

The new relationship for the distribution coefficient of H_2MBP is;

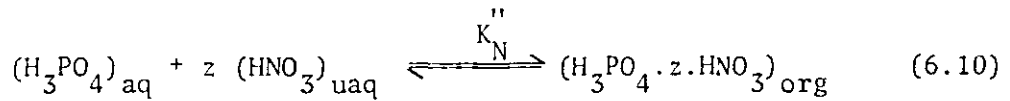
$$D_{\text{H}_2\text{MBP}} = \frac{K_D'}{\phi'} + \frac{K_N'}{\phi' \gamma_{\text{org}}''} (a_{(\text{HNO}_3)_{\text{uaq}}})^y \quad (6.9)$$

Similar to HDBP, the plot of $\log(D\phi' - K_D')$ against $\log a_{(\text{HNO}_3)_{\text{uaq}}}$ figure (6.8), is not a straight line, but the plot of $\log\{(D\phi' - K_D')\gamma_{\text{org}}\}$ versus $\log a_{(\text{HNO}_3)_{\text{uaq}}}$, figure (6.9), consists of two straight lines with the following values;

$$\begin{aligned} \text{From 1 to 3M HNO}_3; \quad y_1 &= 0.5 & K'_{N1} &= 1.3 \pm 0.2 \\ \text{From 4 to 10M HNO}_3; \quad y_2 &= 0.77 & K'_{N2} &= 1.6 \pm 0.2 \end{aligned}$$

The y values imply that similar complexes are formed between $\text{H}_2\text{MBP-HNO}_3$ and HDBP-HNO_3 , i.e. up to 3M HNO_3 the complex is; $2\text{H}_2\text{MBP.HNO}_3$ and above 3M to 10M HNO_3 ; $3\text{H}_2\text{MBP.2HNO}_3$. This is perhaps expected as HDBP and H_2MBP have similar properties.

In the case of H_3PO_4 , the reaction between H_3PO_4 and HNO_3 and the new relationship for the distribution coefficient of H_3PO_4 are;



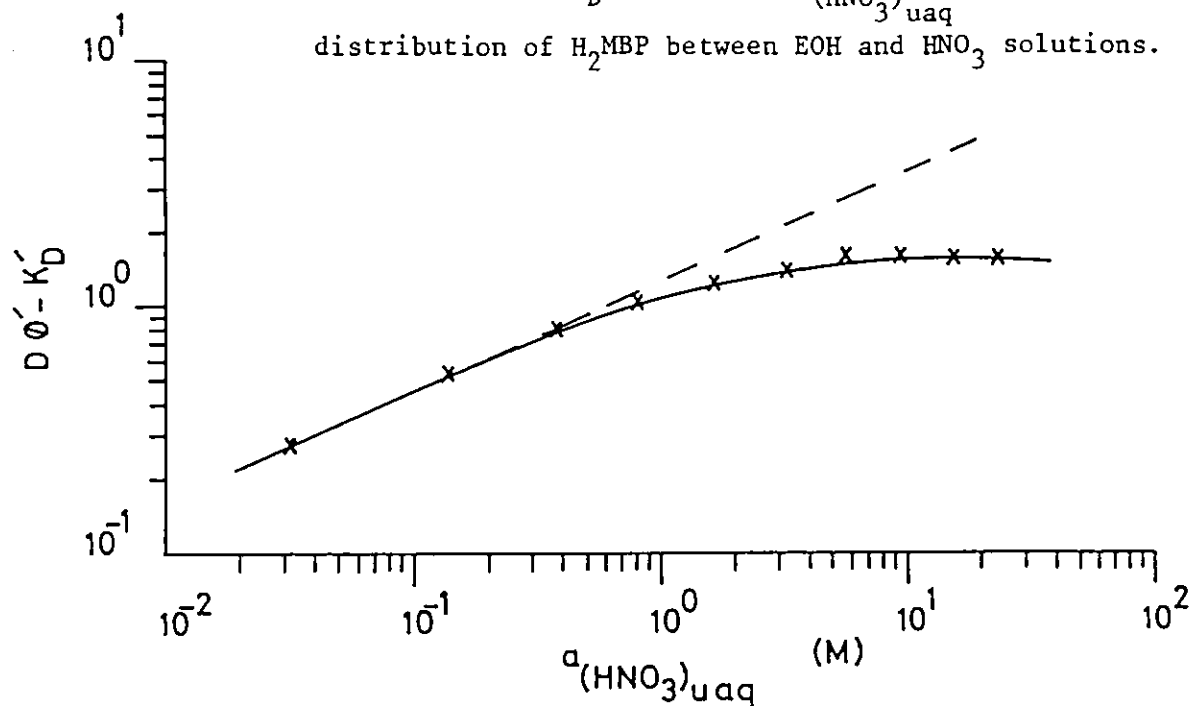
where z = number of $(\text{HNO}_3)_{\text{uaq}}$ molecules

$$\text{and} \quad K''_{\text{N}} = \frac{[\text{H}_3\text{PO}_4 \cdot z \cdot \text{HNO}_3]_{\text{org}} \gamma'''_{\text{org}}}{[\text{H}_3\text{PO}_4]_{\text{aq}} (a_{(\text{HNO}_3)_{\text{uaq}}})^z}$$

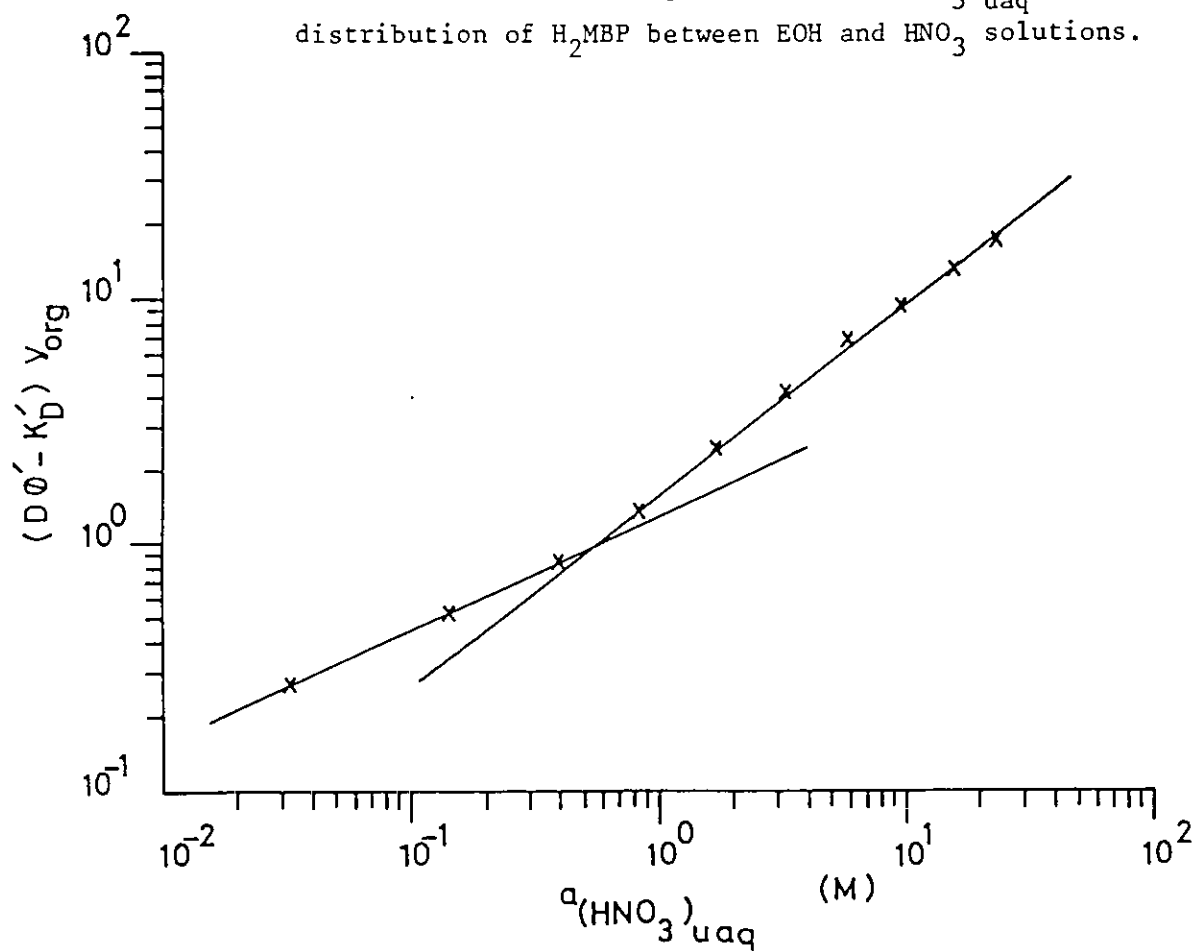
where γ'''_{org} = activity coefficient of $(\text{H}_3\text{PO}_4 \cdot z \cdot \text{HNO}_3)_{\text{org}}$

$$\text{hence} \quad D_{\text{H}_3\text{PO}_4} = \frac{K''_{\text{D}}}{\phi'' \gamma'''_{\text{org}}} (a_{(\text{HNO}_3)_{\text{uaq}}})^z \quad (6.11)$$

Figure(6.8) Plot of $\log(D\phi' - K_D')$ versus $\log a_{(\text{HNO}_3)_{\text{uaq}}}$ for the distribution of H_2MBP between EOH and HNO_3 solutions.



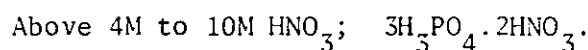
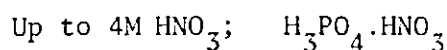
Figure(6.9) Plot of $\log((D\phi' - K_D')\gamma_{\text{org}})$ versus $\log a_{(\text{HNO}_3)_{\text{uaq}}}$ for the distribution of H_2MBP between EOH and HNO_3 solutions.



Again the plot of $\log(D\emptyset'' - K_D'')$ against $\log a_{(\text{HNO}_3)_{\text{uaq}}}$, figure (6.10), is not a straight line, but figure (6.11), the plot of $\log\{(D\emptyset'' - K_D'')\gamma_{\text{org}}\}$ versus $\log a_{(\text{HNO}_3)_{\text{uaq}}}$, consists of two straight lines with the following values;

$$\begin{aligned} \text{From 1M to 4M HNO}_3; \quad z_1 &= 1.14 & K_{N1}'' &= 2.5 \times 10^{-2} \pm 0.001 \\ \text{From 4M to 10M HNO}_3; \quad z_2 &= 0.71 & K_{N2}'' &= 2.7 \times 10^{-2} \pm 0.001 \end{aligned}$$

Therefore the complexes between H_3PO_4 and HNO_3 are;



It is reasonable to assume the formation of a 1:1 complex between H_3PO_4 and HNO_3 as it is suggested by the z values up to 4M HNO_3 . But it is rather unlikely that the ratio of HNO_3 to H_3PO_4 in the complex, would fall with increasing HNO_3 concentration as it is suggested by the complex $3\text{H}_3\text{PO}_4 \cdot 2\text{HNO}_3$.

The new relationships for the distribution coefficients of the phosphate compounds and their constants are summarized below;

$$D_{\text{HDBP}} = \frac{K_D}{\emptyset} + \frac{K_N}{\emptyset \gamma_{\text{org}}} (a_{(\text{HNO}_3)_{\text{uaq}}})^x \quad (6.12)$$

where $K_D = 90 \pm 9$

$$K_N(\text{average}) = 45 \pm 5$$

$$x_1 = 0.5$$

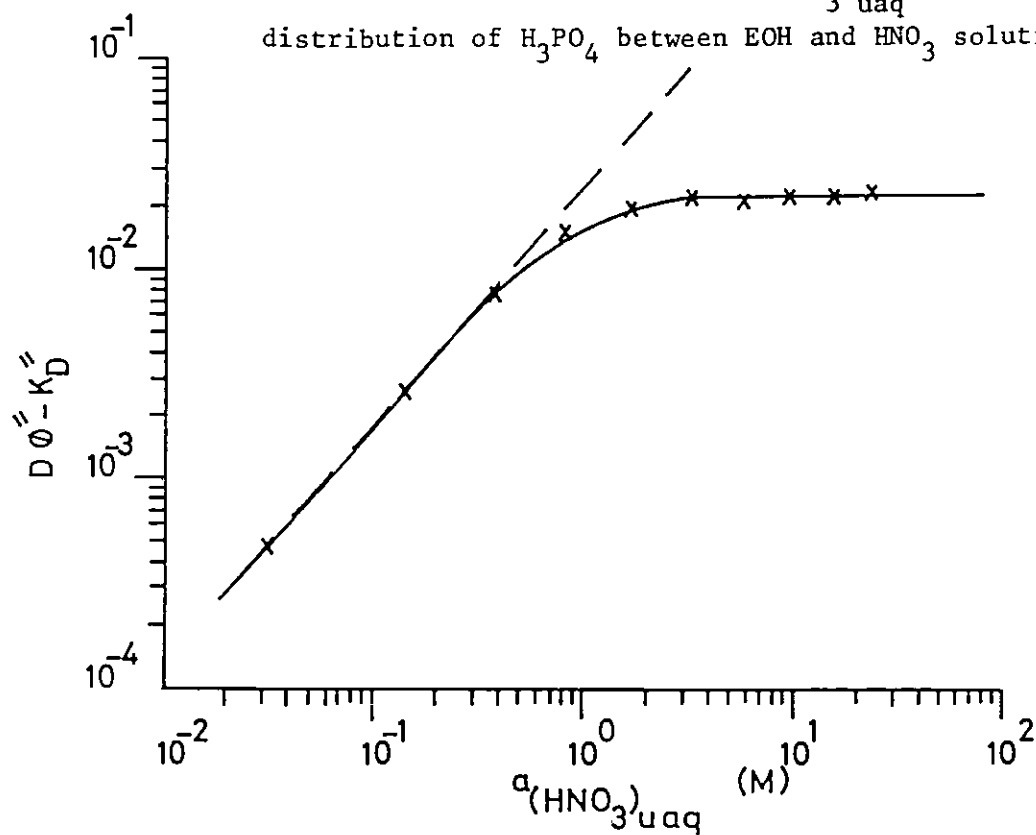
Up to 3M HNO_3

$$x_2 = 0.75$$

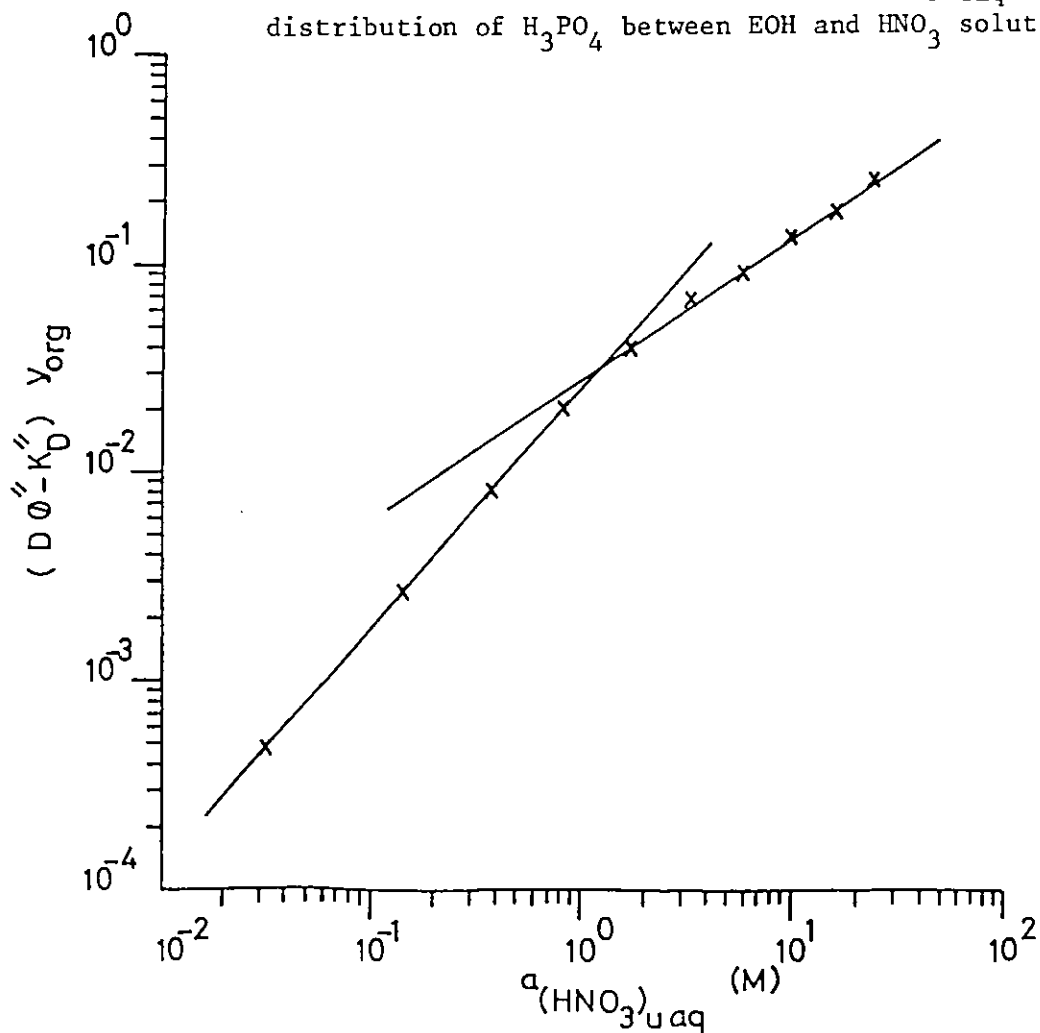
from 4M to 10M HNO_3

$$D_{\text{H}_2\text{MBP}} = \frac{K_D'}{\emptyset'} + \frac{K_D'}{\emptyset' \gamma_{\text{org}}} (a_{(\text{HNO}_3)_{\text{uaq}}})^y \quad (6.13)$$

Figure(6.10) Plot of $\log(D\phi'' - K_D'')$ versus $\log a_{(\text{HNO}_3)_{\text{uaq}}}$ for the distribution of H_3PO_4 between EOH and HNO_3 solutions.



Figure(6.11) Plot of $\log((D\phi'' - K_D'')\gamma_{\text{org}})$ versus $\log a_{(\text{HNO}_3)_{\text{uaq}}}$ for the distribution of H_3PO_4 between EOH and HNO_3 solutions.



where $K_D' = 1.50 \pm 0.15$
 $K_N' \text{ (average)} = 1.5 \pm 0.2$
 $y_1 = 0.5$ Up to 3M HNO_3
 $y_2 = 0.77$ from 4M to 10M HNO_3

$$D_{\text{H}_3\text{PO}_4} = \frac{K_D''}{\phi} + \frac{K_N''}{\phi \gamma_{\text{org}}} (a_{(\text{HNO}_3)_{\text{uaq}}})^z \quad (6.14)$$

where $K_D'' = 0.0085 \pm 0.0005$
 $K_N'' \text{ (average)} = 0.026 \pm 0.001$
 $z_1 = 1.14$ Up to 4M HNO_3
 $z_2 = 0.71$ from 5M to 10M HNO_3

The experiments discussed here suggest that the phosphate compounds form complexes with nitric acid and that the extraction of these complexes by EOH increases the apparent distribution coefficients. The fit between the distribution data and the model equations 6.12, 6.13 and 6.14 suggests simple compositions for these complexes. At the lower concentrations of HNO_3 some reliance can be placed upon these stoichiometries but at the higher HNO_3 concentrations, above 6M, where the distribution coefficient is essentially independent of HNO_3 concentration the proposed compositions can only be regarded as very tentative.

6.5 Stripping of Phosphate Compounds

Results in the previous sections clearly show that the extraction of the phosphate compounds by the solvent is dependent on the hydrogen ion concentration of the aqueous phase. Therefore by

reducing the acidity of the aqueous phase it was possible to transfer the phosphate compounds from the organic phase back into the aqueous phase. This was done by first washing the organic phase with an equal volume of distilled water: this was to remove the extracted nitric acid and also some of the phosphates, followed by the sodium carbonate wash. The optimum concentration of the sodium carbonate solution was found to be 0.1M. If the first water wash is not used then a much higher concentration of sodium carbonate solution would be needed for the stripping. Results for the stripping of HDBP, H_2MBP and H_3PO_4 are shown in tables (6.3), (6.4) and (6.5). These results were obtained by first contacting the phosphate compounds in 3M HNO_3 with EOH and then stripping the phosphate from EOH by the water and Na_2CO_3 washes. About 99% recovery of HDBP was attained by these procedures, table (6.3) shows that distribution coefficient values for both the first water wash and the Na_2CO_3 wash which are independent of HDBP concentrations as expected. In the cases of H_2MBP and H_3PO_4 more than 99.9% of the compounds were recovered, tables (6.4) and (6.5).

Table (6.3) Stripping of HDBP from EOH at 25°C

Initial HDBP concentration in 3M HNO_3 (M)	D (H_2O wash)	D (Na_2CO_3 wash)
10^{-5}	93.5	0.0159
5×10^{-5}	94.0	0.0167
10^{-4}	92.1	0.0145
5×10^{-4}	91.8	0.0173
10^{-3}	92.9	0.0163
5×10^{-3}	94.4	0.0161
10^{-2}	95.2	0.0155

Table (6.4) Stripping of H_2MBP from EOH at $25^{\circ}C$

Initial H_2MBP concentration in $3M HNO_3$ (M)	D H_2O wash	H_2MBP concentration in the first H_2O wash (M)	H_2MBP concentration in the Na_2CO_3 wash (M)
6.94×10^{-6}	1.391	2.90×10^{-6}	4.05×10^{-6}
4.85×10^{-5}	1.420	2.00×10^{-5}	2.84×10^{-5}
0.95×10^{-4}	1.410	0.39×10^{-4}	0.60×10^{-4}
4.67×10^{-4}	1.410	1.94×10^{-4}	2.76×10^{-4}
0.93×10^{-3}	1.340	0.40×10^{-3}	0.53×10^{-3}
4.49×10^{-3}	1.330	1.93×10^{-3}	2.55×10^{-3}
0.95×10^{-2}	1.450	0.39×10^{-2}	0.56×10^{-2}

Table (6.5) Stripping of H_3PO_4 from EOH at $25^{\circ}C$

Initial H_3PO_4 concentration (M)	D H_2O wash
10^{-5}	7.3×10^{-3}
5×10^{-5}	8.0×10^{-3}
10^{-4}	7.9×10^{-3}
5×10^{-4}	7.85×10^{-3}
10^{-3}	8.0×10^{-3}
5×10^{-3}	7.8×10^{-3}
10^{-2}	7.9×10^{-3}

6.6 Transfer Kinetics

The rate of transfer of the phosphate compounds into the organic solvent (EOH) have been studied and equilibration times of 30 and 50 seconds were obtained for HDBP, H_2MBP and H_3PO_4 respectively (figures 6.12, 6.14 and 6.16). Such fast equilibration times are usually an indication that the transfer of the solute is simply mass transfer controlled. This was further shown by looking at the effect of temperature, phosphate concentration and HNO_3 concentration on the rate of transfer of the phosphate compounds into EOH and also calculating the mass transfer coefficients.

Calculation of mass transfer coefficients^[98] : In a batch stirred cell for the transfer of solute from phase (2) to phase (1), the following material balance equation applies:

$$d(V_1 C_1) = K_{01}(DC_2 - C_1)Fdt \quad (6.15)$$

where V = volume

F = interfacial area

D = distribution coefficient

K_{01} = overall mass transfer coefficient based on phase (1).

t = contact time

C_1 and C_2 = the well-mixed concentrations of solute in phase (1) and (2) respectively.

Also from an overall material balance :

$$d(V_1 C_1) + d(V_2 C_2) = 0 \quad (6.16)$$

Assuming constant mass transfer coefficient, steady state, equilibrium and constant volume the combination and integration of equations (6.15) and (6.16) will give,

$$\ln\left(1 - \frac{C_1}{C_1^*}\right) = - \left(1 + D \frac{V_1}{V_2}\right) K_{01} F t / V_1 \quad (6.17)$$

where C_1^* = equilibrium concentration of solute in phase (1)
at $t = \infty$

Hence a plot of $\ln\left(1 - \frac{C_1}{C_1^*}\right)$ versus t will give a straight line

of slope $- \left(1 + D \frac{V_1}{V_2}\right) K_{01} \frac{F}{V_1}$.

Figures (6.13), (6.15) and (6.17) show the plot of

$\log\left(1 - \frac{C_1}{C_1^*}\right)$ versus t for HDBP, H_2MBP and H_3PO_4 respectively and

from the slopes $\left(- \left(1 + D \frac{V_1}{V_2}\right) \frac{K_{01} F}{V_1 \times 2.303}\right)$ the values of $K_{01} F$ are

calculated and shown in table (6.6). The stirrer was kept at a constant speed throughout the kinetics experiments and therefore the interfacial area, F , has the same value for HDBP, H_2MBP and H_3PO_4 systems.

Table (6.6) Overall mass transfer coefficient values for HDBP, H₂MBP and H₃PO₄

Initial phosphate concentration (M)			HNO ₃ concentration (M)	Temperature °C	K ₀₁ ^F cm ³ s ⁻¹		
HDBP	H ₂ MBP	H ₃ PO ₄			HDBP	H ₂ MBP	H ₃ PO ₄
8.74×10 ⁻⁴	1.036×10 ⁻³	10 ⁻³	3	25	0.0827±0.02	1.363±0.1	1.918±0.3
1.014×10 ⁻²	0.98×10 ⁻²	-	3	25	0.0827±0.02	1.366±0.1	-
8.74×10 ⁻⁴	1.036×10 ⁻³	-	0.5	25	0.0924±0.02	1.413±0.1	-
8.74×10 ⁻⁴	1.036×10 ⁻³	-	3	50	0.0920±0.02	1.360±0.1	-

Results in table (6.6) show that for HDBP and H_2MBP K_{01}^F is independent of temperature and concentration. This implies that the rate of HDBP and H_2MBP extraction is not affected by changes in temperature and concentration and therefore the system is diffusion controlled [99]. The transfer kinetics of H_3PO_4 is also expected to be the same as HDBP and H_2MBP , i.e. K_{01}^F unaffected by changes in temperature and concentrations.

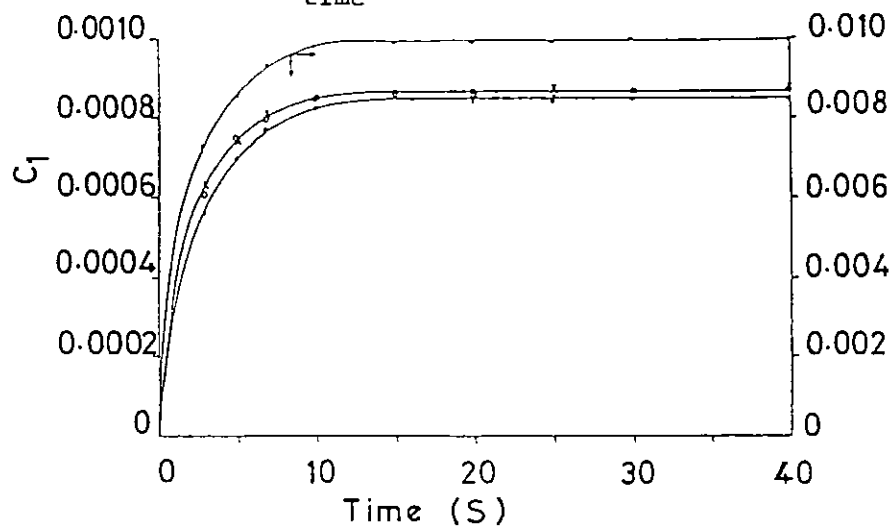
Note: in figures (6.12) to (6.17) the following applies;

C_1 = concentration of phosphate compounds in EOH

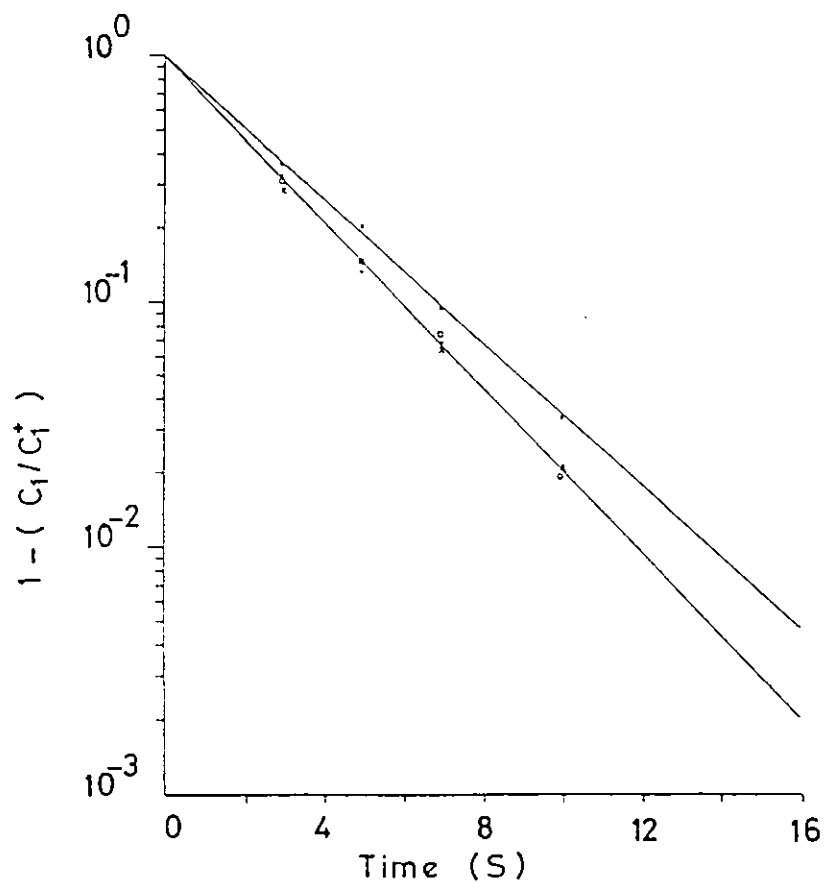
C_1^+ = equilibrium concentration of phosphate compounds
in EOH

x :	3M HNO_3 , 25 $^{\circ}$ c	} initial HDBP concentration = $8.75 \times 10^{-4} M$	
• :	0.5M HNO_3 , 25 $^{\circ}$ c		initial H_2MBP concentration = $1.04 \times 10^{-3} M$
0 :	3M HNO_3 , 50 $^{\circ}$ c		initial H_3PO_4 concentration = $10^{-3} M$
+	3M HNO_3 , 25 $^{\circ}$ c	initial HDBP concentration = $1.02 \times 10^{-2} M$	
		initial H_2MBP concentration = $0.98 \times 10^{-2} M$	

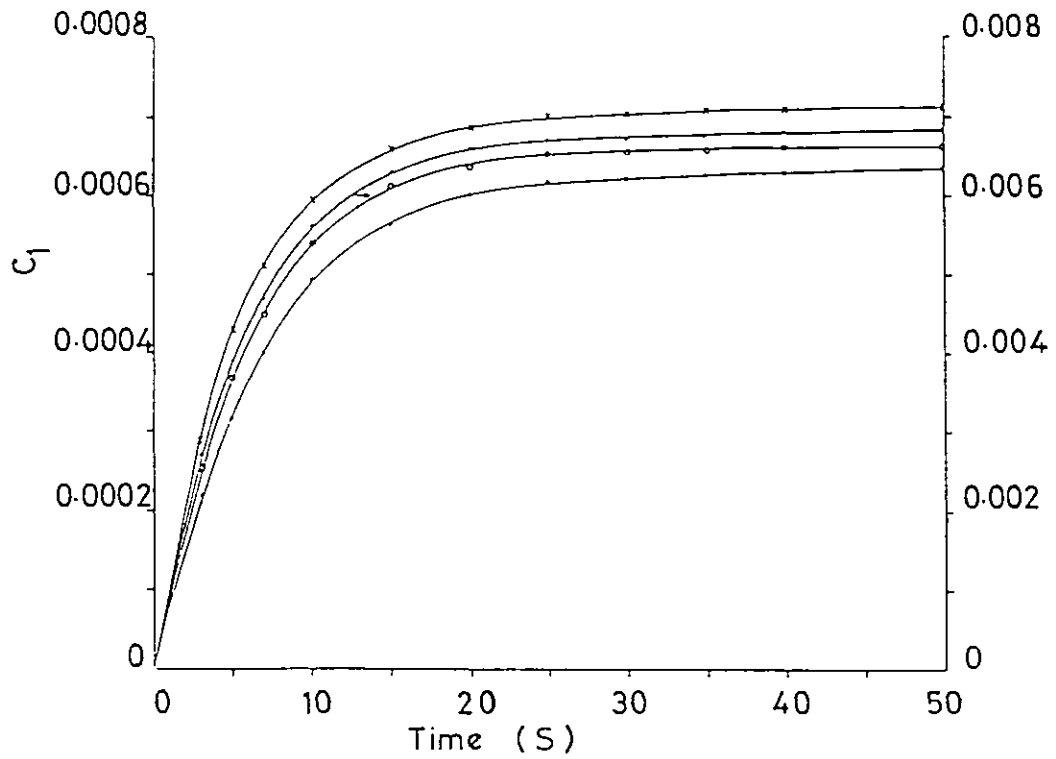
Figure(6.12) Variation of HDBP concentration in EOH with time



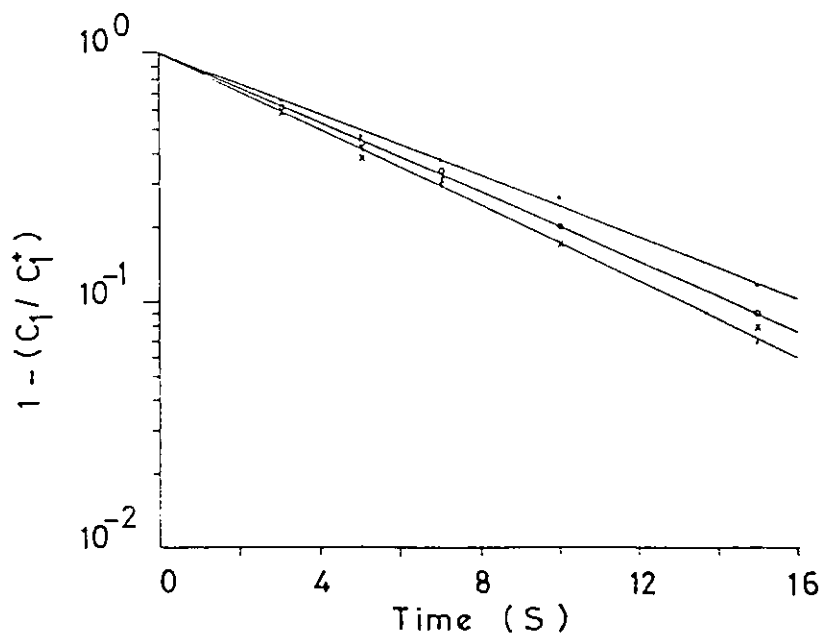
Figure(6.13) Plot of $\log(1-(C_1/C_1^+))$ versus time for HDBP.

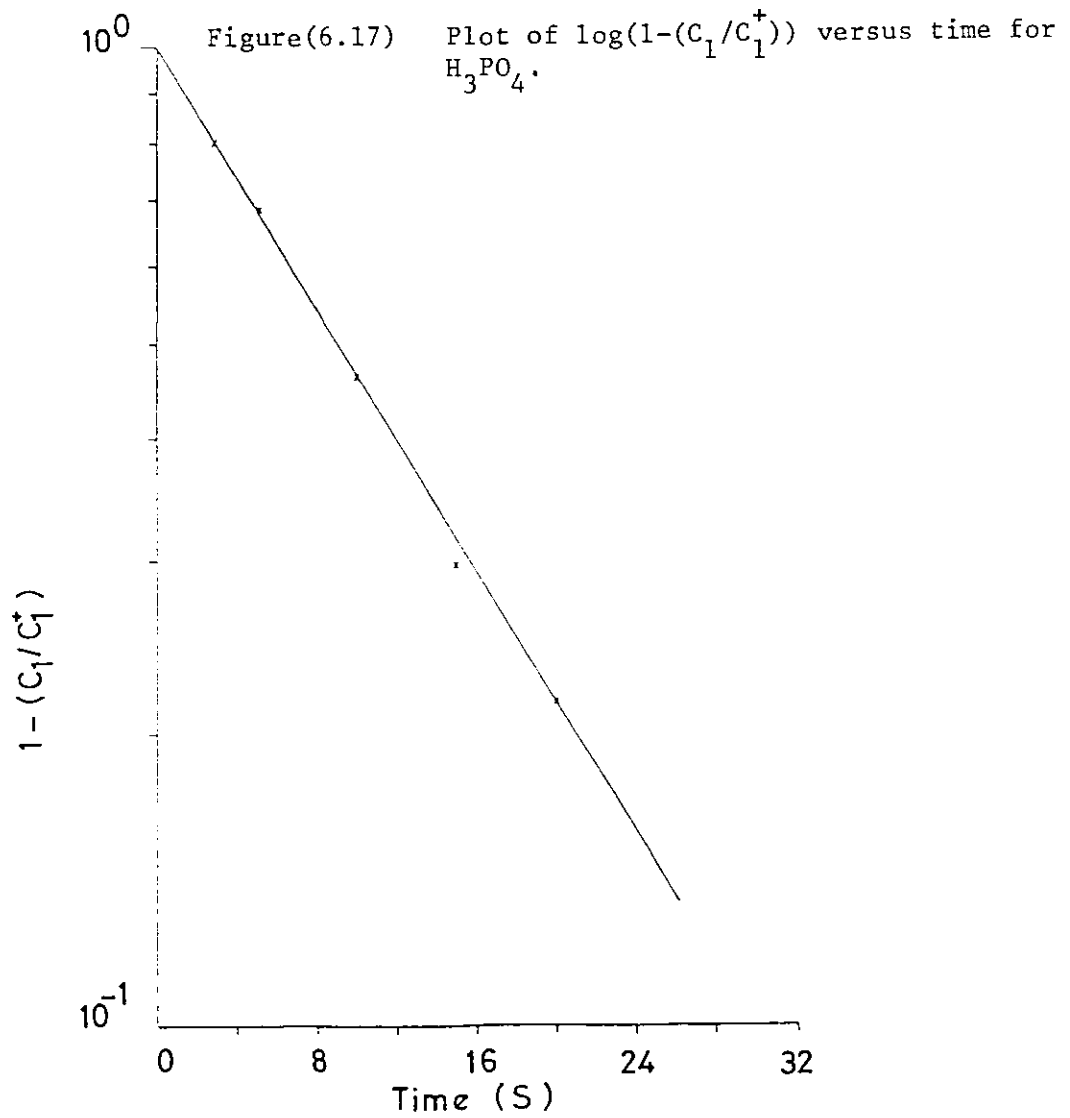
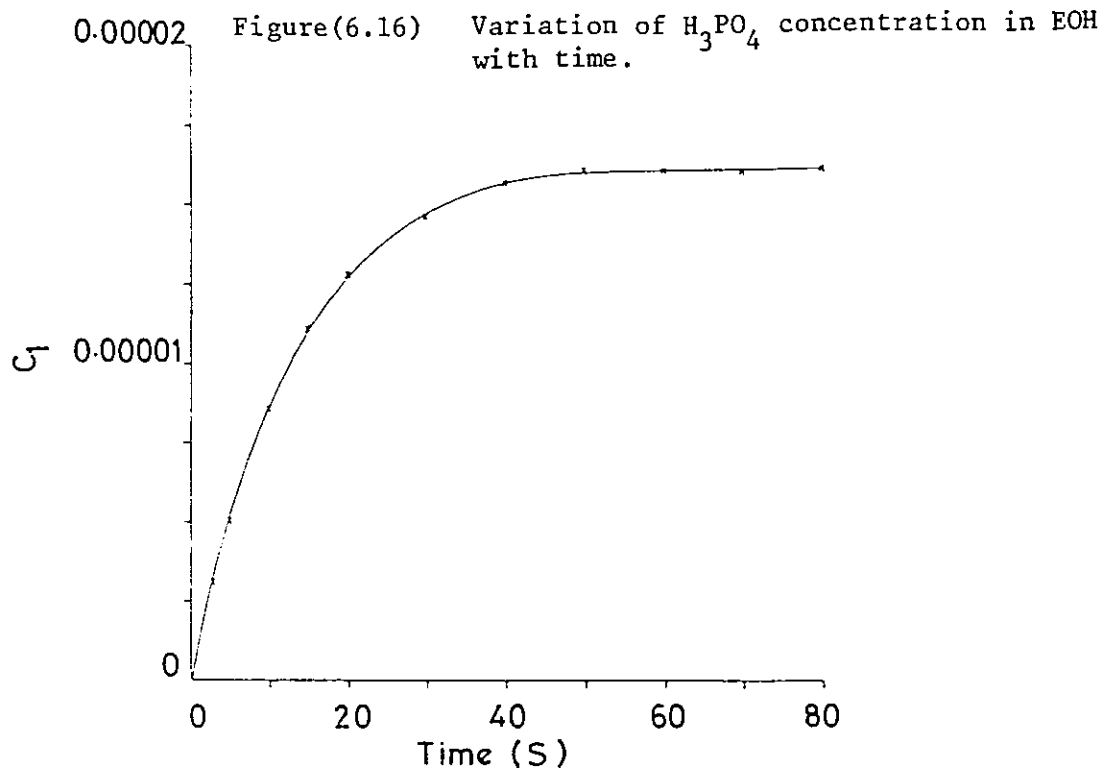


Figure(6.14) Variation of H_2MBP concentration in EOH with time.



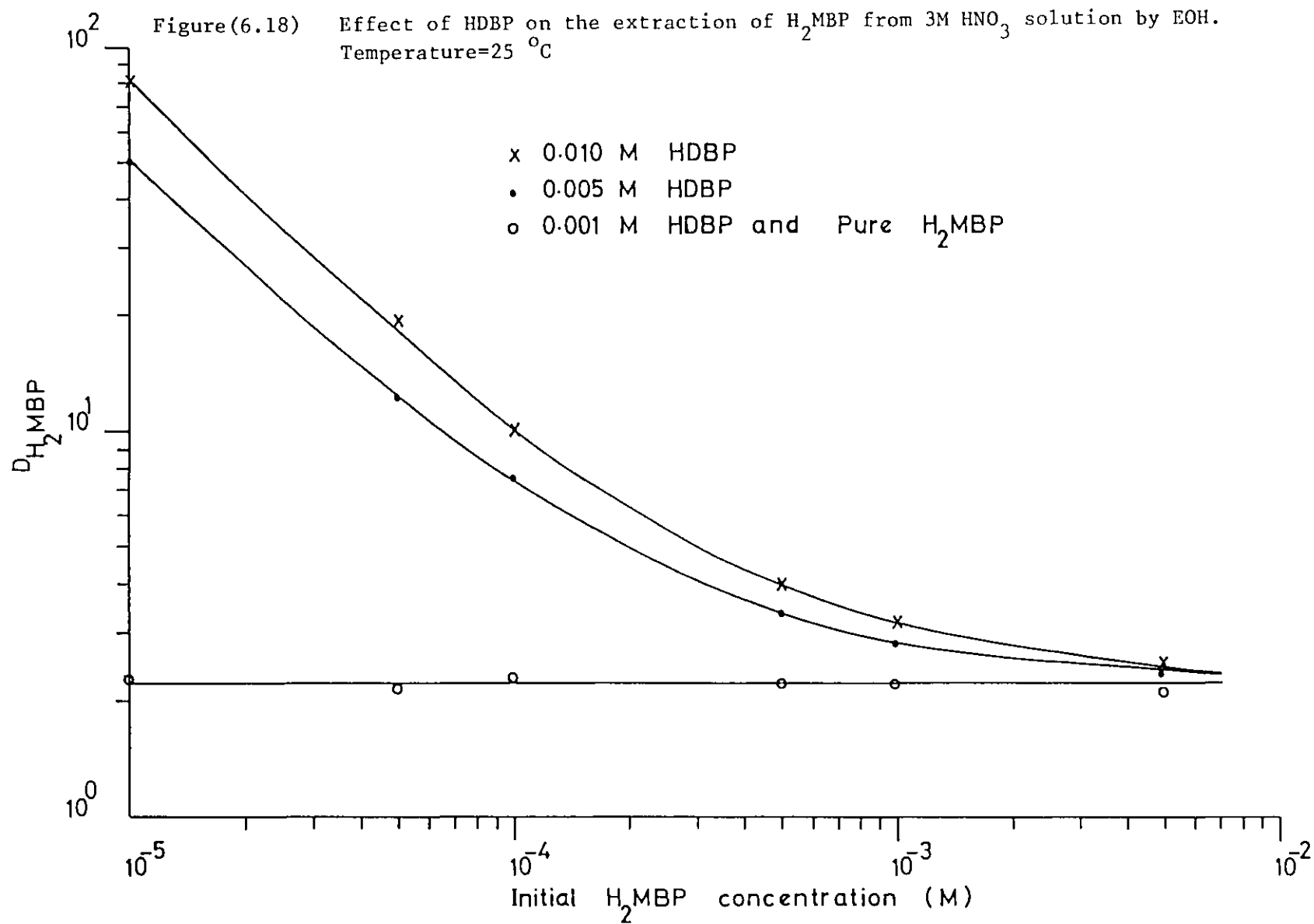
Figure(6.15) Plot of $\log(1-(C_1/C_1^+))$ versus time for H_2MBP .





6.7 Extraction of Mixtures of Phosphates

Mixtures of HDBP and H_2MBP solutions in $3M\ HNO_3$ were extracted with EOH. Assuming the distribution coefficient values of HDBP in the presence of H_2MBP do not change, the changes in the values of the distribution coefficients of H_2MBP in the presence of HDBP are calculated and plotted in figure (6.18). These results show that D_{H_2MBP} increases in the presence of 0.005M and 0.01M HDBP and the increase seems to be dependent upon the ratio of the concentrations of HDBP to H_2MBP . However, the increase in the extraction of H_2MBP in the presence of HDBP is due to the association between the two phosphate compounds. The association is through the hydrogen bonding in a manner analogous to structures shown in figure (6.2). Results in figure (6.18) imply that such bonding between HDBP and H_2MBP only seems to occur when the amount of HDBP in the organic phase is much higher than H_2MBP . This is perhaps because of the presence of the highly polar solvent, EOH, which prevents the hydrogen bonding between the two phosphate compounds, unless the concentration of one of the compounds is in large excess of the other. The association complex between HDBP and H_2MBP has been reported by Hardy and Scargill [10] for the kerosene - $1M\ HNO_3$ system. Their results show that D_{H_2MBP} increases approximately as the 1.8^{th} power of the initial HDBP concentration at $> 0.05M$ HDBP. This does not seem to happen in the system $EOH - 3M\ HNO_3$ where the increase in D_{H_2MBP} only occurs when the amount of HDBP present is much higher than H_2MBP . The assumption that D_{HDBP} does not change in the presence of H_2MBP could not be verified due to the experimental technique used in this work where a solution containing both HDBP and H_2MBP could only be analyzed



for the total amount of phosphate and not for the individual compounds.

A range of concentration of HDBP and H_2MBP (10^{-3} to $10^{-2}M$) separately and also together were added to a range of concentrations of H_3PO_4 ($10^{-5}M$ to $10^{-2}M$) in $3M HNO_3$. No significant difference was found in the extraction of H_3PO_4 in the presence of HDBP or H_2MBP from that of pure H_3PO_4 . Thamer [32] has reported a complex of the type $2HDBP.2H_3PO_4$ in the $HClO_4$ -kerosene system for H_3PO_4 concentration of $1M$ or higher. But the results obtained in this work implies that there is no complex formation between H_3PO_4 and HDBP or H_2MBP which may be due to the low phosphate compounds concentrations used in these experiments or the presence of the highly polar solvent, EOH.

6.8 The Use of a Diluent

6.8.1 A Suitable Diluent:

So far experiment results have shown that EOH is a suitable solvent for the extraction of phosphate compounds from aqueous media. Its physical properties also make it generally a good solvent for the proposed solvent extraction process. It does have, however, a rather high viscosity which may cause certain problem in the extraction process, e.g. high cost of pumping. The use of a diluent would reduce the viscosity and would also have the advantage of reducing the loss of EOH to the aqueous phase.

Selecting the best diluent could prove to be difficult due to the number available. But perhaps the most obvious choice is odourless kerosene which is already widely used in conjunction with TBP in the nuclear industry. Kerosene has most of the properties

of a suitable diluent and perhaps most important of all its behaviour under radioactive conditions is well known. Table (6.7) summarizes some of its most important physical properties.

The viscosity of mixtures of EOH, kerosene has been measured at 25°C and plotted in figure (6.19).

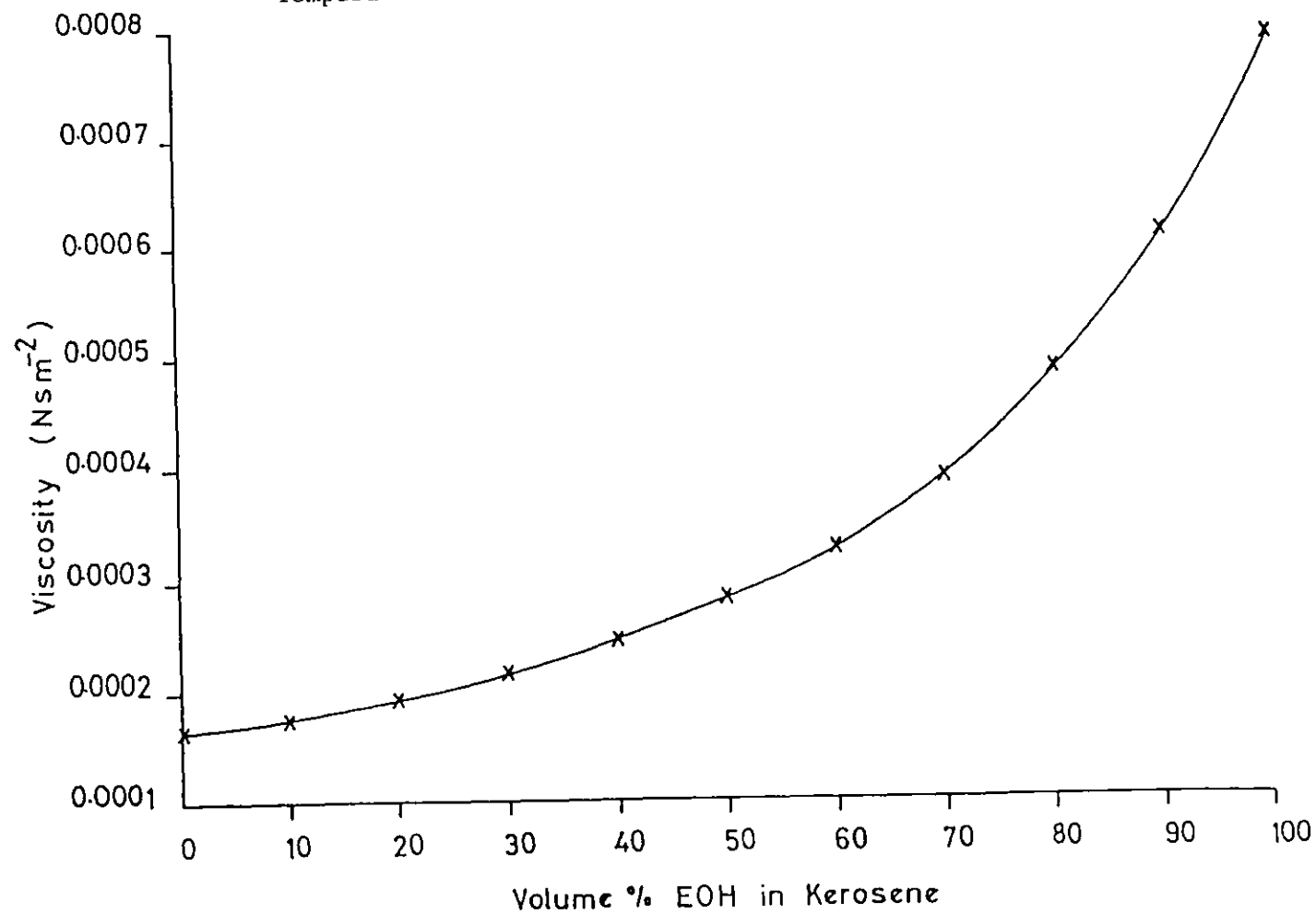
Table (6.7) Physical properties of odourless kerosene (Shell Chemicals U.K. Ltd)

Density at 20°C (kg m ⁻³)	781
Flash Point °C	70
Autoignition Temperature (°C)	250
Evaporation Rate, (n-butyl acetate = 1)	0.01
Vapour Pressure at 20°C (N m ⁻²)	66.65
Viscosity at 25°C (Ns m ⁻²)	1.6×10 ⁻⁴
Refractive Index at 20°C	1.437
Composition : Aromatic (% Vol.)	2.5
Benzene (p.p.m.Vol.)	<100
Total Sulphur (p.p.m)	100

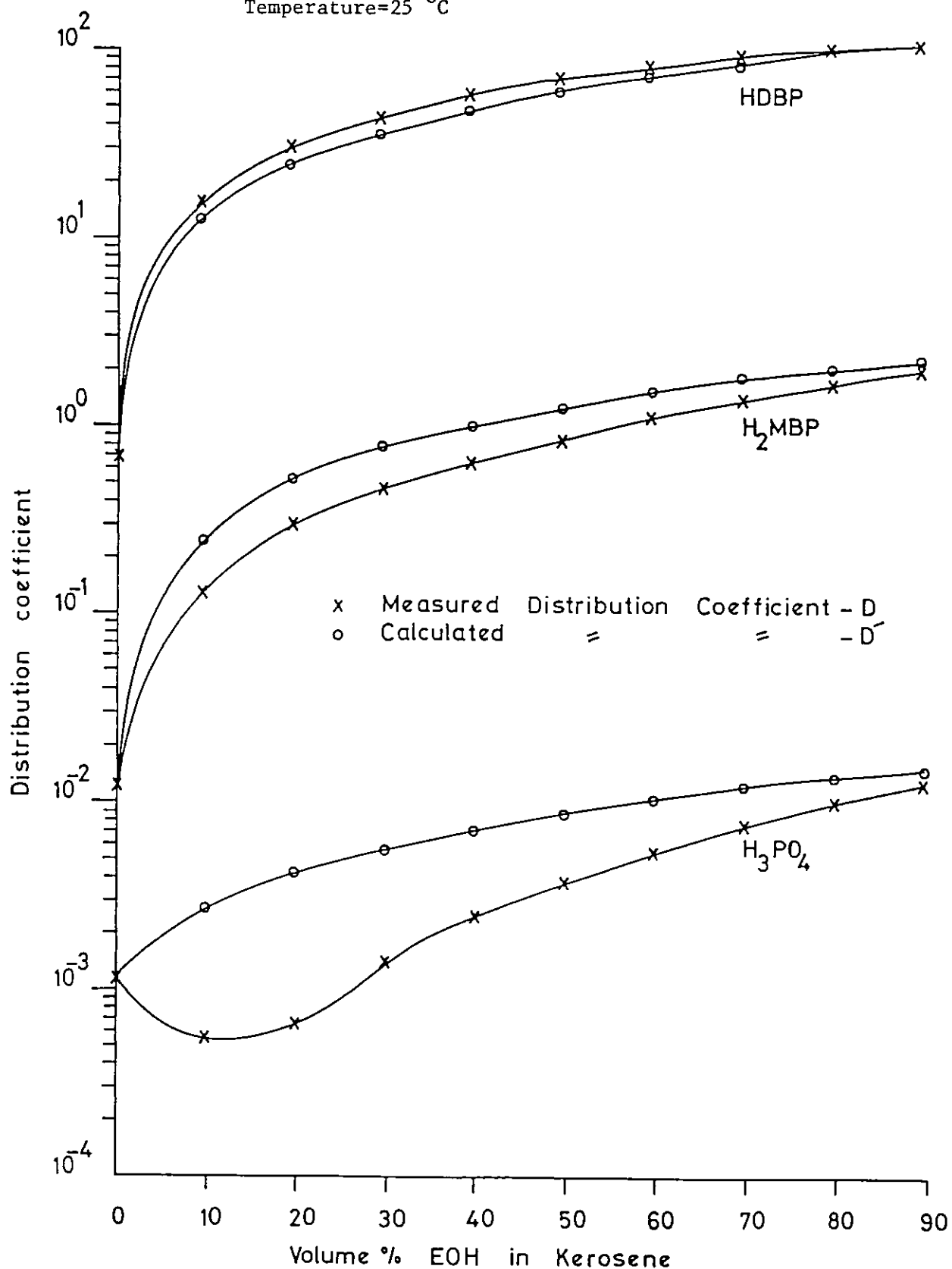
6.8.2 Extraction of Phosphate Compounds with Mixtures of EOH, Kerosene

Solutions of HDBP, H₂MBP and H₃PO₄ in 3M HNO₃ were extracted with mixtures of EOH, kerosene at various volume ratios. The distribution coefficients, D, obtained are shown in figure (6.20) and are compared with the calculated distribution coefficient, D', which is determined from the following equation;

Figure(6.19) Viscosity of mixtures of EOH,kerosene.
Temperature=25 °C



Figure(6.20) Extraction of phosphate compounds from 3M HNO_3 solution
by mixtures of EOH, kerosene
Temperature=25 °C



$$D' = V_{\text{EOH}} D_{\text{EOH}} + V_{\text{K}} D_{\text{K}} \quad (6.18)$$

where D_{EOH} and D_{K} are the distribution coefficients obtained from the extraction of phosphate compounds by pure EOH and kerosene respectively, V_{EOH} and V_{K} are their volume fractions.

The values of D' are an indication of the effect of diluent on the solvent. In the case of HDBP, the values of D are higher than D' for all ratios of EOH, kerosene which implies that the diluent increases the extracting power of the solvent for HDBP. Kerosene has previously been used for the extraction study of HDBP and high values of distribution coefficient have been reported at high HDBP concentrations (see Chapter (2)). This could explain the increase in the extraction power of the solvent for HDBP when kerosene is used as the diluent. For H_2MBP and H_3PO_4 the opposite effect occurs where the values of D' are infact higher than D . This means a reduction in the extracting power of the solvent for H_2MBP and H_3PO_4 when kerosene is the diluent.

From the results in figures (6.19) and (6.20) the best mixture of EOH, kerosene for the extraction of the phosphate compounds is chosen to be 30% EOH in kerosene. At this ratio, the mixed solvent has a reasonable viscosity of 0.00022 Nsm^{-2} whereas increasing the ratio beyond 30% EOH, the viscosity of the mixtures starts to rise rather rapidly. However $D_{\text{H}_3\text{PO}_4}$ obtained at 10% and 20% EOH, kerosene mixtures are very low, infact they are even lower than the $D_{\text{H}_3\text{PO}_4}$ which is obtained by pure kerosene.

6.8.3 Extraction of Phosphate Compounds by 30% EOH in Kerosene

HDBP, H_2MBP and H_3PO_4 were extracted from 3M HNO_3 solutions by 30% EOH in kerosene. Results, figure (6.21), show that the distribution coefficients of HDBP vary with HDBP concentrations. This implies that both forms of HDBP, i.e. dimers and monomers, are present in the organic phase and the expression for the distribution coefficient values would be;

$$D_{HDBP} = \frac{2K_2 K_D^2}{\phi^2} C_{aq} + \frac{K_D}{\phi} \quad (6.19)$$

(see equation 5.5)

This equation is valid for the extraction of HDBP by 30% EOH in kerosene at low HNO_3 concentrations. At higher HNO_3 concentrations e.g. 3M, the effect of HNO_3 on the extraction of HDBP must be added to equation (6.19), see section 6.4. The presence of HDBP dimers in the system 30% EOH, kerosene is due to the effect of kerosene on HDBP. Hardy and Scargill ^[10] have reported the dimerisation of HDBP when extracted with pure kerosene.

In the cases of H_2MBP and H_3PO_4 , the distribution coefficients are independent of the phosphate concentrations. This indicate that the mechanism of extraction of H_2MBP and H_3PO_4 by 30% EOH in kerosene is similar to that of pure EOH, i.e. no polymerisation of either H_2MBP or H_3PO_4 and equations (6.2) and (5.11) are valid for the extraction of H_2MBP and H_3PO_4 respectively. However, these results also illustrate that the mechanism of extraction of H_2MBP and H_3PO_4 by pure kerosene would be similar to that of pure EOH or 30% EOH in kerosene.

Figure(6.21) Extraction of phosphate compounds from 3M HNO_3 solution by 30% EOH in kerosene and their comparison with the extraction of phosphates from 2M HNO_3 solution by hexone.
Temperature=25 °C

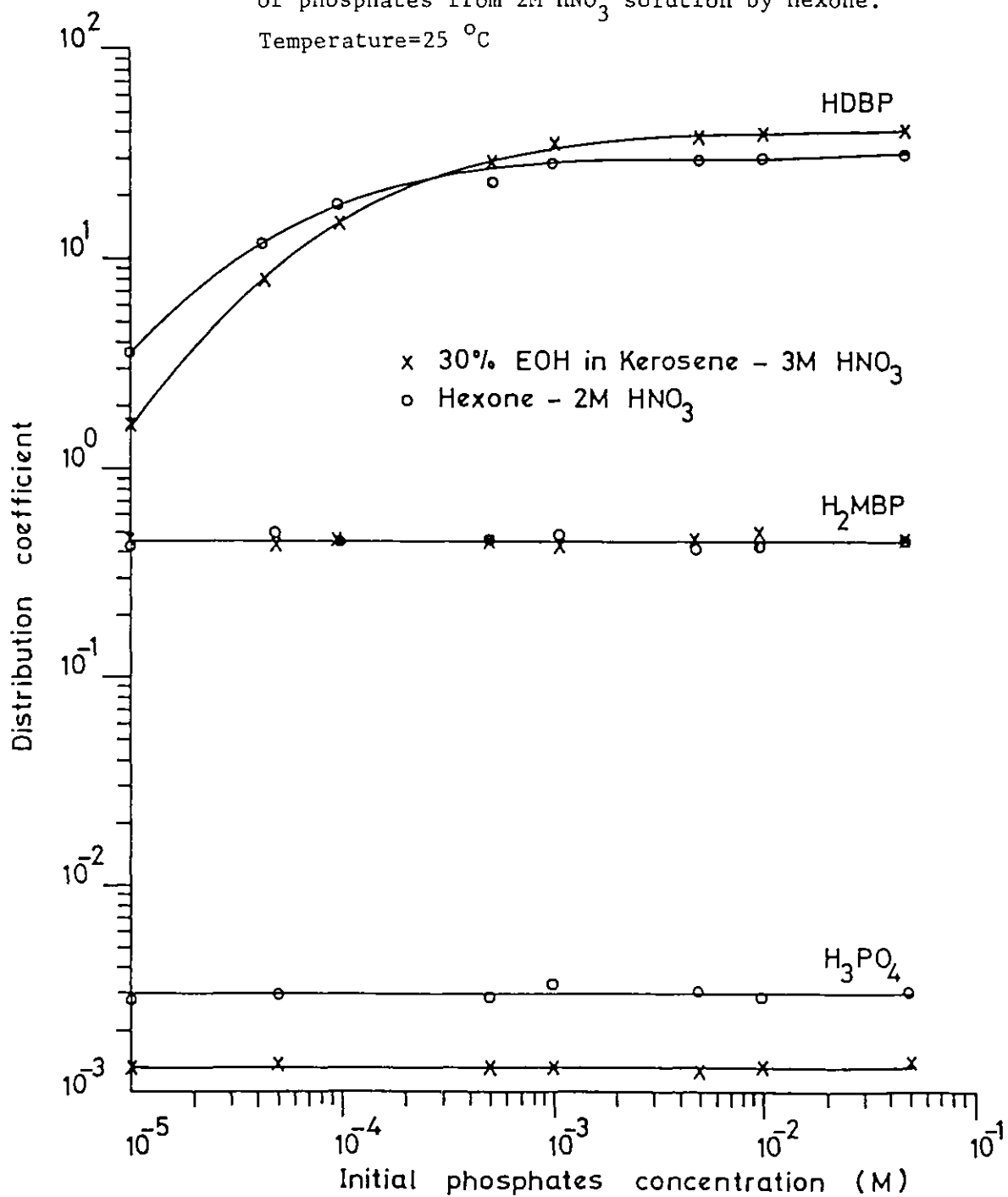


Figure (6.21) also shows the results for the extraction of phosphate compounds from 2M HNO_3 by hexone. These results show that hexone when compared with 30% EOH in kerosene extracts more of phosphoric acid, but similar amounts of H_2MBP and HDBP . The physical properties of hexone, table (6.8) [37], allow it to be used as an extractant

Table (6.8) Physical properties of 4-methylpentan - 2 - one
(hexone [37])

Molecular weight	100.16
Boiling point	115.9°C
Freezing point	- 80.3°C
Flash point, tag open cup	27.2°C
tag closed cup	15.6°C
Specific gravity at 20°C	800 Kg m^{-3}
Refractive index at 20°C	1.395
Solubility at 25°C, Hexone in water	2.00 Wt.%
Water in Hexone	2.20 Wt.%
Heat of evaporation	$3.622 \times 10^2 \text{ KJ Kg}^{-1}$
Specific heat	1.921 KJ Kg^{-1}
Surface tension	0.0254 N m^{-1}
Viscosity, at 0°C	$0.769 \times 10^{-4} \text{ N s m}^{-2}$
20°C	$0.585 \times 10^{-4} \text{ N s m}^{-2}$
30°C	$0.522 \times 10^{-4} \text{ N s m}^{-2}$
Vapour pressure at 30°C	$3.5 \times 10^3 \text{ N m}^{-2}$

without the use of a diluent. Also hexone has previously been used as a reprocessing solvent in the "Redox" process and its behaviour in nuclear contexts is well documented [100]. Therefore hexone may be an alternative for 30% EOH in kerosene. However, a main disadvantage of using hexone is its oxidation by strong oxidising agents such as nitric acid. Hexone, infact, reacts violently with HNO_3 at concentrations stronger than 3M and the safe limit should be set at about 2M [101]. This would require an acidity adjustment of HAR if hexone is to be used for the extraction of phosphate compounds.

C H A P T E R 7

EXTRACTION OF PHOSPHATE COMPOUNDS FROM 3M HNO₃ SOLUTION BY EOH IN THE PRESENCE OF METAL - IONS

7.1 Introduction

Phosphate compounds are reported to form strong complexes with a number of metal ions of various oxidation states in different aqueous and organic systems. Since the purpose of this project was to study the separation of HDBP, H₂MBP and H₃PO₄ from HAR, it was necessary to investigate the effect of metal ions present in HAR on the extraction of the phosphate compounds by EOH.

HDBP - metal ions complexes in various aqueous acidic solutions have been prepared and their structure reported. The type of complexes formed are reported to be dependent on the metal ions, acid and HDBP concentrations. A summary is shown in table (7.1). HDBP has also been widely used in the extraction, concentration and purification of metals: zirconium [102,108,109,115], uranium [109-114,116], thorium [117], americium [118], europium [2,118], yttrium [119], beryllium [120], strontium [122] and rare-earth elements [121,123]. The extraction mechanism of these metals by HDBP is controlled by the type of complexes formed in the organic phase which are in turn controlled by the nature of the diluent, the acidity of aqueous phase and the ratio of the concentrations of HDBP to the metal ion.

Hardy [108,109] found that in the extraction of tracer quantities of zirconium from aqueous nitric acid (ionic strength 2) by

Table (7.1) HDBP - metal ions complexes in aqueous solutions

Metal Ions	Structure and form of the Complex	Media	Reference
ZrO^{2+}	$Zr(NO_3)_2(DBP)_2$	6M HNO_3 , excess Zr	102, 103
	$Zr(NO_3)_2(DBP)_2(HDBP)_2$	6M HNO_3 , excess HDBP	102, 103
	$Zr(NO_3)_2(DBP)_2(HDBP)_4$	6M HNO_3 , large excess of HDBP	102, 103
	$Zr_4(OH)_{12}(DBP)_4$ or $Zr_4O_4(OH)_4(DBP)_4$	0.25M HNO_3 , excess HDBP	102
	$ZrO(DBP)_2$	1M HNO_3 , equivalent quantities	104
UO_2^{2+}	$UO_2(DBP)_2$	1M HNO_3 and 0.2M HNO_3 , excess HDBP	104, 105
	$UO_2(NO_3)H(DBP)_2$	6M HNO_3 , excess HDBP	105
	$UO_2(NO_3)H(DBP)_2(HDBP)_2$	6M HNO_3 , large excess of HDBP	105
Fe(III)	$Fe(DBP)_3$	1M HNO_3 and water	104, 106, 107
Al	$Al(DBP)_3$	water	107
Ce(III)	$Ce(DBP)_3$	water	107
La(III)	$La(DBP)_3$	1M HNO_3 and water	104, 107
Sc(III)	$Sc(DBP)_3$	1M HNO_3	104
Th(IV)	$Th(DBP)_4$	1M HNO_3 and H_2O	104, 107
Ag	$Ag(DBP)$	pH 5.6	104
Zn	$Zn(DBP)_2$	pH 5-6	104
Cd	$Cd(DBP)_2$	pH 5-6	104
Pb(II)	$Pb(DBP)_2$	Ph 5-6	104, 107
Co(II)	$Co(DBP)_2$	Ph 5-6	104, 107
Ni(II)	$Ni(DBP)_2$	pH 5.6	104, 107
Cu(II)	$Cu(DBP)_2$	pH 5-6	104, 107

solutions of HDBP in toluene, the compound $\text{Zr}(\text{NO}_3)_2(\text{DBP})_2(\text{HDBP})_2$ is formed in the organic phase. As the zirconium concentration is increased the composition tends towards $\text{Zr}(\text{NO}_3)_2(\text{DBP})_2$ and a white polymeric solid is separated. Solovkin et al ^[102] studied the extraction of macroquantities of zirconium from 6M HNO_3 solution by HDBP in n-decane. A third solid phase is reported to have formed on contacting the phases which is dissolved on adding large excess of HDBP. On the basis of the results obtained from the preparation and solubilities of HDBP-Zr complexes in 6M HNO_3 , Solovkin et al ^[102] suggested the formation of complexes $\text{Zr}(\text{NO}_3)_2(\text{DBP})_2$ and $\text{Zr}(\text{NO}_3)_2(\text{DBP})_2(\text{HDBP})_2$ initially in the aqueous phase. With sufficient excess of HDBP these complexes are converted completely into $\text{Zr}(\text{NO}_3)_2(\text{DBP})_2(\text{HDBP})_4$; this compound is subsequently distributed between the phases.

Similar polymeric complexes have also been reported to be formed between HDBP and other metal ions in the organic phase.

Studies have also been made on the complex formation between H_2MBP and certain metal ions. Solovkin et al ^[124] reported the complex $\text{Zr}(\text{MBP})_2$ prepared in 6M HNO_3 and $\text{Fe}_2(\text{MBP})_3 \cdot 2\text{H}_2\text{O}$ prepared in dilute HNO_3 solutions. The complex between H_2MBP and uranium has been reported ^[125] to be a mixture of $\text{UO}_2(\text{MBP}) \cdot 2\text{H}_2\text{O}$ and $\text{UO}_2(\text{HMBP})_2 \cdot 2\text{H}_2\text{O}$ in dilute HNO_3 solutions. The relative amount of complexes being dependent on the ratio $[\text{MBP}]/[\text{U}]$. Other H_2MBP - metal complexes published ^[126] are: $\text{Th}(\text{MBP})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Np}(\text{MBP})_2$.

The majority of the published work regarding complex formation between H_3PO_4 and metal ions is concentrated on the studies of the H_3PO_4 - Zr complexes and very little information is available for the complexes between H_3PO_4 and other metal ions. Clearfield and Stynes ^[127]

prepared the zirconium phosphate complex and reported its structure to be $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$. However, other workers [128-130] considered it unlikely that a zirconium rather than a zirconyl salt would precipitate from aqueous solution and hence, represented the compound as $\text{ZrO}(\text{H}_2\text{PO}_4)_2$ and $\text{ZrO}(\text{H}_2\text{PO}_4)_2 \cdot 1.6 \cdot \text{H}_2\text{O}$. Complex formation between molybdic acid and phosphoric acid has also been reported [131].

In this chapter the effect of six metal ions present in HAR in the concentration range of 10^{-5} to 10^{-2}M (ref. 132), on the extraction of the phosphate compounds by EOH from HNO_3 solution have been investigated.

7.2 Preliminary Experiments

Solutions of five metal nitrates; $\text{Cs}(\text{NO}_3)$, $\text{Ce}(\text{NO}_3)_3$, $\text{Fe}(\text{NO}_3)_3$, $\text{UO}_2(\text{NO}_3)_2$ and zirconyl nitrate and also molybdic acid were added to HDBP solution in 3M HNO_3 . With the exception of CsNO_3 and $\text{Ce}(\text{NO}_3)_3$, all others formed precipitate with HDBP. $\text{Ce}(\text{NO}_3)_3$ has been reported to form insoluble complex with HDBP in water, table (7.1), but in 3M HNO_3 no precipitate was formed which means that either a soluble complex is formed or there is no complex formation in 3M HNO_3 . There is no published information on the complex formation between caesium and HDBP or molybdic acid and HDBP. Other ions have been reported to form insoluble complexes with HDBP in nitric acid solution, table (7.1), which were also shown in these experiments.

Similar experiments were carried out for H_2MBP and H_3PO_4 , where only zirconium formed insoluble complexes with both H_2MBP and H_3PO_4 . It has been reported [124,125] that no precipitate is

formed on contacting uranium or iron with H_2MBP in $3M HNO_3$ solution. This work shows that other ions, except zirconium, also form soluble complexes with H_2MBP in $3M HNO_3$ solution. An insoluble complex has been reported to form between H_3PO_4 and molybdic acid although this did not happen in these experiments. This was presumably due to the range of concentration of the phosphate compounds used in these experiments being below that required for solid precipitate, i.e. 10^{-5} to $10^{-2}M$. It was however noted that at $5 \times 10^{-2}M H_3PO_4$ and $10^{-2}M$ molybdic acid such a complex, a yellowish precipitate, was formed in $3M HNO_3$ solution.

The effect of the metal ions on the extraction of HDBP from $3M HNO_3$ solution by EOH was checked by contacting the metal ion solution in $3M HNO_3$ with the HDBP solution in EOH. Zirconium was the only ion to affect the extraction of HDBP by EOH and also a third solid phase was formed in the organic solution at certain concentrations of HDBP and zirconium. This implies that the metal ion - HDBP complexes are rather weak and the bonds between the metal ion and HDBP readily broken by the alcohol. In a further series of experiments the insoluble complex between HDBP, zirconium and uranium were first formed in the aqueous phase and the suspensions contacted with EOH. The precipitates disappeared and the values of the distribution coefficient were unaffected. This confirms the fact that the HDBP - metal ion complex is broken by EOH and the HDBP extracted.

In the cases of H_2MBP and H_3PO_4 also zirconium was the only metal ion to affect their extraction by EOH : a third solid phase was formed in the organic solution in the case of H_2MBP and in the

aqueous solution in the case of H_3PO_4 .

Experiments were also carried out to check the effect of these metal ions on the kinetics of extraction of the phosphate compounds by EOH. The equilibration times were exactly the same as those reported in section 6.6. This implies that the presence of the metal ions does not affect the rate of transfer of the phosphate compounds into the alcohol phase.

The preliminary experiments are summarized in table (7.2). The effects of zirconium on the extraction of HDBP, H_2MBP and H_3PO_4 were studied in greater detail.

Table (7.2) Effect of metal ions on the extraction of phosphate compounds from 3M HNO₃ solution by EOH
 Phosphate concentration = 10⁻⁵ to 10⁻².

Metal compound concentration range (10 ⁻⁵ to 10 ⁻² M)	Form of complex in 3M HNO ₃			Effect on the distribution coefficient			Effect on the Equilibration time		
	HDBP	H ₂ MBP	H ₃ PO ₄	HDBP	H ₂ MBP	H ₃ PO ₄	HDBP	H ₂ MBP	H ₃ PO ₄
CsNO ₃	soluble	Soluble	Soluble	None	None	None	None	None	None
Ce(NO ₃) ₃	soluble	Soluble	Soluble	None	None	None	None	None	None
Fe(NO ₃) ₃	Insoluble	Soluble	Soluble	None	None	None	None	None	None
H ₂ MoO ₄	Insoluble	Soluble	Insoluble above 10 ⁻² M	None	None	None	None	None	None
UO ₂ (NO ₃) ₂	Insoluble	Soluble	Soluble	None	None	None	None	None	None
Zirconyl nitrate	Insoluble	Insoluble	Insoluble	Some	Some	Some	None	None	None

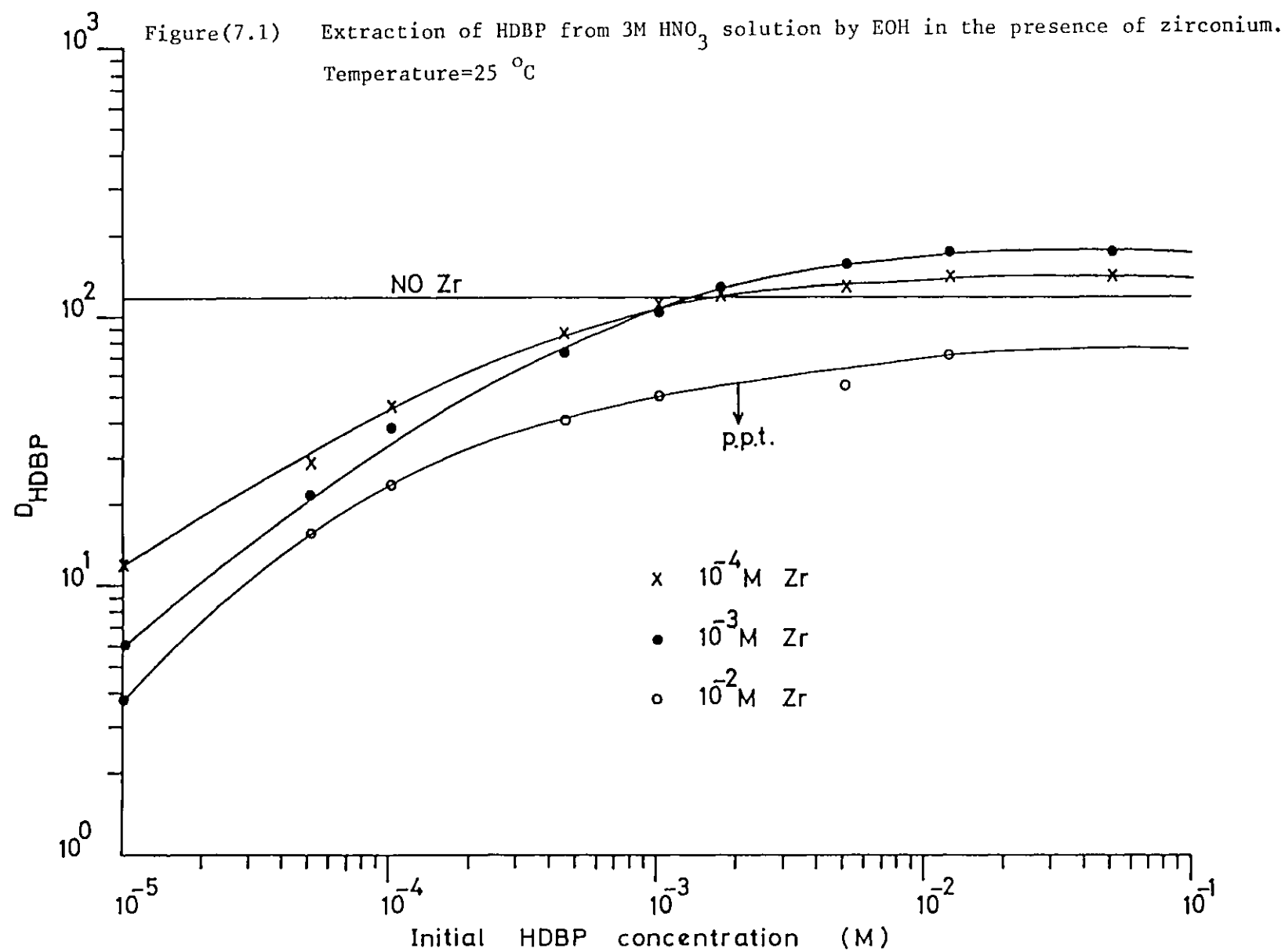
7.3 Effect of Zirconium on the Extraction of the Phosphate Compounds

7.3.1 HDBP

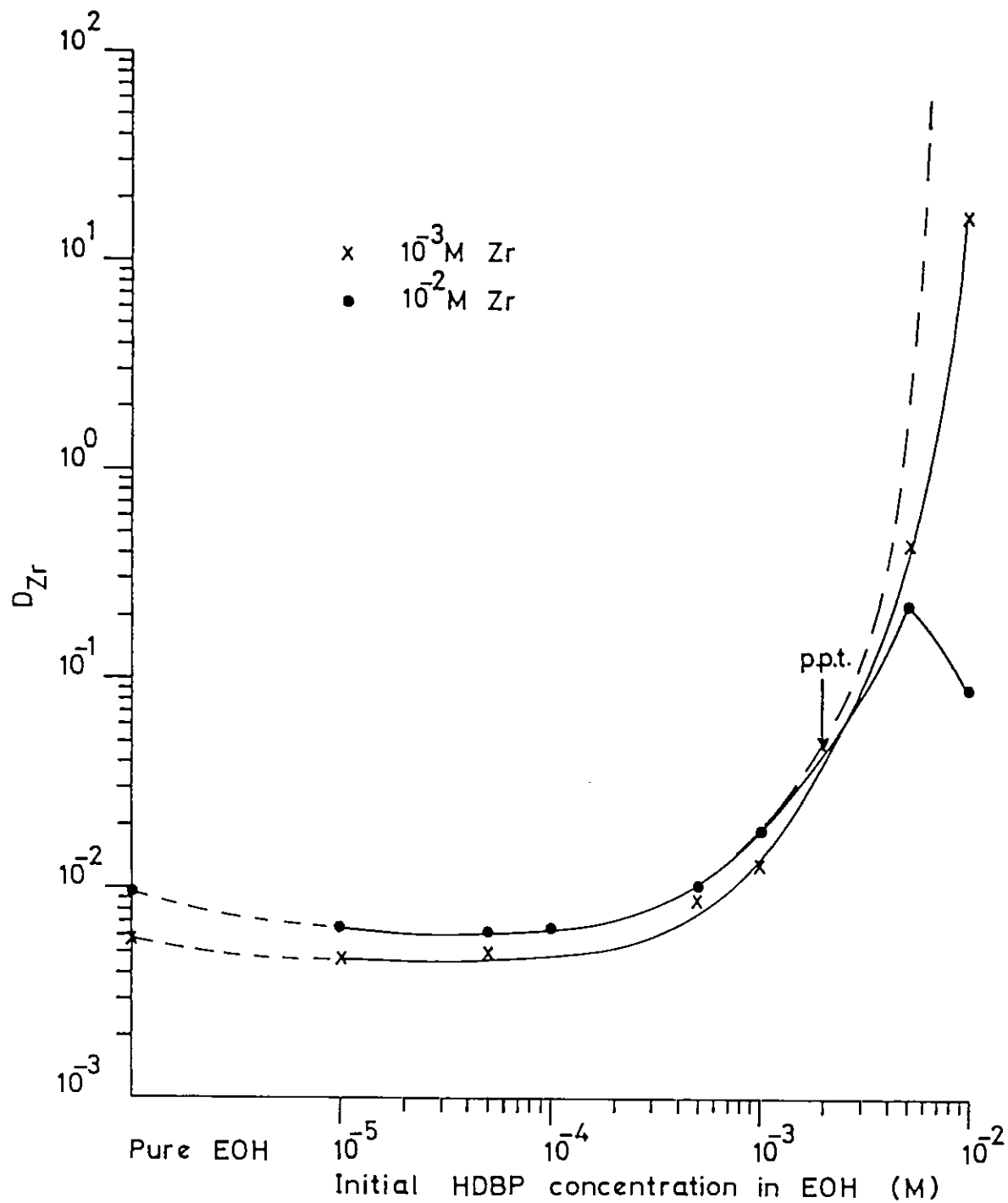
Results for the extraction of HDBP from 3M HNO_3 solution by EOH in the presence of zirconium at 10^{-4} , 10^{-3} and 10^{-2} M concentrations are shown in figure (7.1). At 10^{-5} M zirconium there was no significant effect on the extraction of HDBP. Results in figure (7.1) show that zirconium (10^{-4} ; 10^{-3} M) depresses the extraction of HDBP at low HDBP concentrations but at concentrations above about 10^{-3} M, more HDBP is extracted than in the absence of zirconium. At 10^{-2} M zirconium where the third solid phase is formed, D_{HDBP} is lower than for pure HDBP at all HDBP concentrations. Note that the distribution coefficient values are the ratio of the HDBP concentration in the organic phase to the HDBP concentration in the aqueous phase which excludes the amount of HDBP in the third solid phase.

Since some knowledge of the composition of the precipitate formed in the organic phase was essential for an understanding of the mechanism of the extraction of HDBP in the presence of zirconium, some studies were carried out on the distribution of zirconium between the phases and the solubility of the precipitate.

Results for the extraction of zirconium by HDBP-EOH mixtures are shown in figure (7.2). At low HDBP concentrations the extraction of zirconium by the solvent is constant and rather low. At concentrations of HDBP above about 5×10^{-4} M, D_{Zr} increases with increasing HDBP concentration but then falls when the third phase is formed. In this case also; i.e. determination of D_{Zr} , the amount of zirconium contained in the



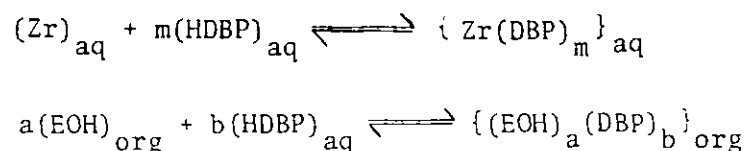
Figure(7.2) Distribution of zirconium between EOH-HDBP and 3M HNO_3 solutions at 25 °C.



third solid phase is excluded from the distribution coefficient values. The distribution of HDBP and zirconium between the three aqueous, organic and solid phases in terms of concentrations are shown in Appendix C.

The solubility experiments showed the third solid phase to be insoluble in EOH but readily dissolved in acetone and EOH-HDBP mixture (large amount of HDBP present).

At low concentrations of HDBP the effect of added zirconium is seen to be a reduction of D_{HDBP} qualitatively consistent with competition of zirconium and the extractant for the HDBP; e.g. :



Thus for a given HDBP concentration the greater the zirconium concentration the poorer the extraction of HDBP. Conversely for a given zirconium concentration increasing HDBP results in values of D_{HDBP} increasing to values characteristic of the system in the absence of zirconium.

This simple picture however does not explain the situation at higher HDBP and zirconium concentrations. It can be seen that at 10^{-3}M zirconium and concentrations of HDBP above about 10^{-3}M , D_{HDBP} actually rises above that in the absence of zirconium. The results on the distribution of zirconium show that this increase in D_{HDBP} is associated with the transfer of zirconium into the organic phase. Zirconium nitrate is extractable, albeit poorly, by the solvent, EOH, but this extraction is reduced in extent by low concentrations of HDBP presumably as a consequence of the formation

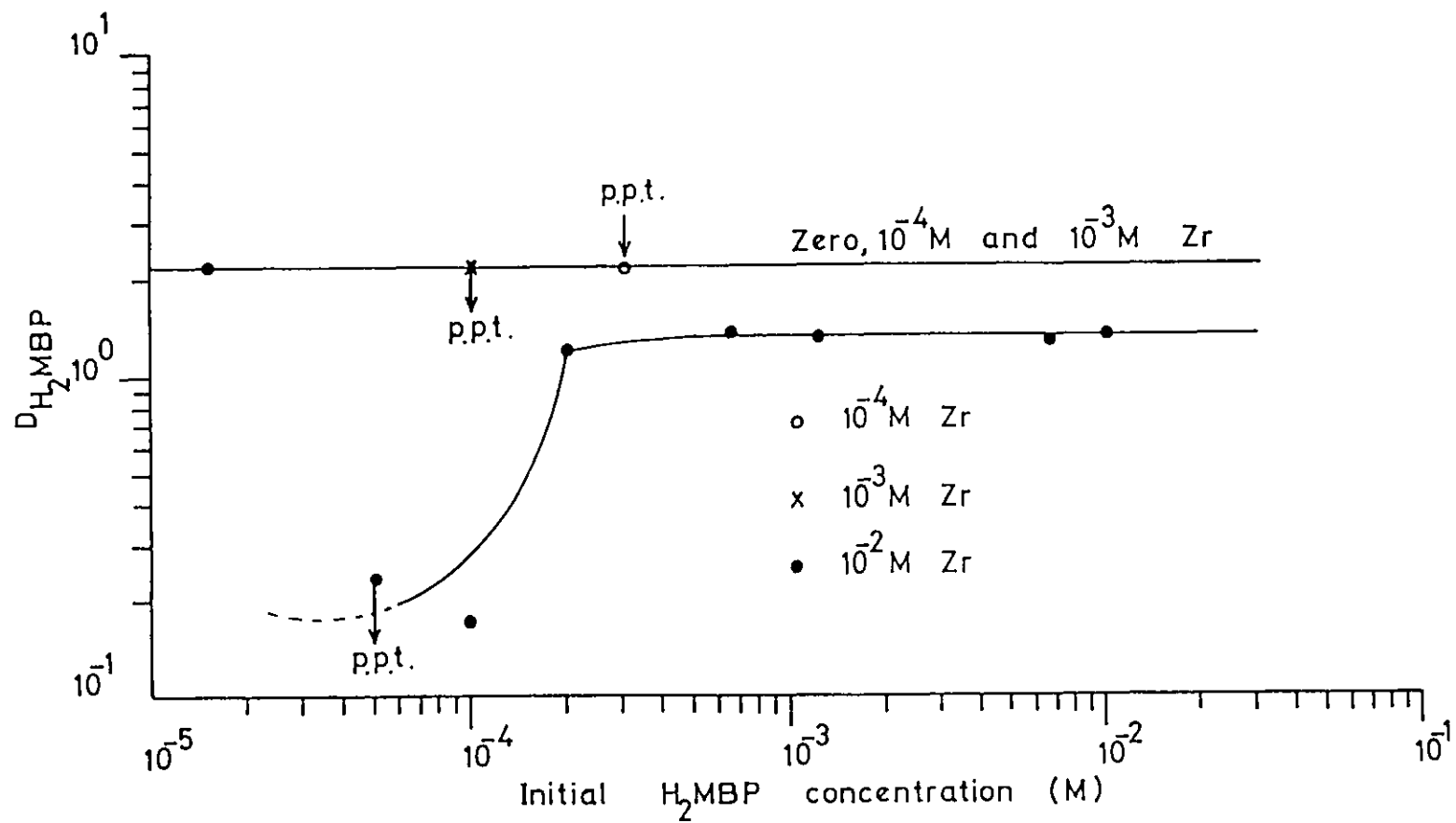
of the Zr - DBP complex. However at higher initial concentrations of HDBP the amount of DBP in the organic phase is such that complex formation between this and the extracted zirconium can occur significantly. This complex formation has the effect of increasing the nett amounts of both zirconium and HDBP extracted. In the analytical method used the zirconium complex in the organic (and the aqueous phase) will be estimated as DBP and consequently D_{HDBP} will increase and values above those in the absence of zirconium are possible and indeed are seen.

The extent of the increase in this apparent D_{HDBP} will be limited by the total amount of zirconium present and ultimately by the solubility of the Zr - DBP complex formed. Figure (7.1) shows that at 10^{-4} and 10^{-3} M zirconium the maximum increase obtained is quite small and indicates that rather little DBP is "fixed" in the organic phase this way. At 10^{-2} M zirconium precipitation of a complex in the organic phase occurs at quite low HDBP and since this solid is not measured as material in the organic phase the enhancement of the value of D_{HDBP} above the no zirconium case does not take place.

7.3.2 $\underline{H_2\text{MBP}}$

Figure (7.3) shows the results for the extraction of $H_2\text{MBP}$ from 3M HNO_3 solution by EOH in the presence of zirconium. At 10^{-5} M zirconium there was no significant effect on the extraction of $H_2\text{MBP}$ and the values of distribution coefficient obtained were the same as in the absence of zirconium. At 10^{-4} M zirconium a solid third phase was formed in the organic phase at 3×10^{-4} M $H_2\text{MBP}$, but $D_{H_2\text{MBP}}$ subsequently remains unchanged. At 10^{-3} M zirconium, $D_{H_2\text{MBP}}$ is still

Figure(7.3) Extraction of H_2MBP from 3M HNO_3 solution by EOH in the presence of zirconium.
Temperature=25 °C

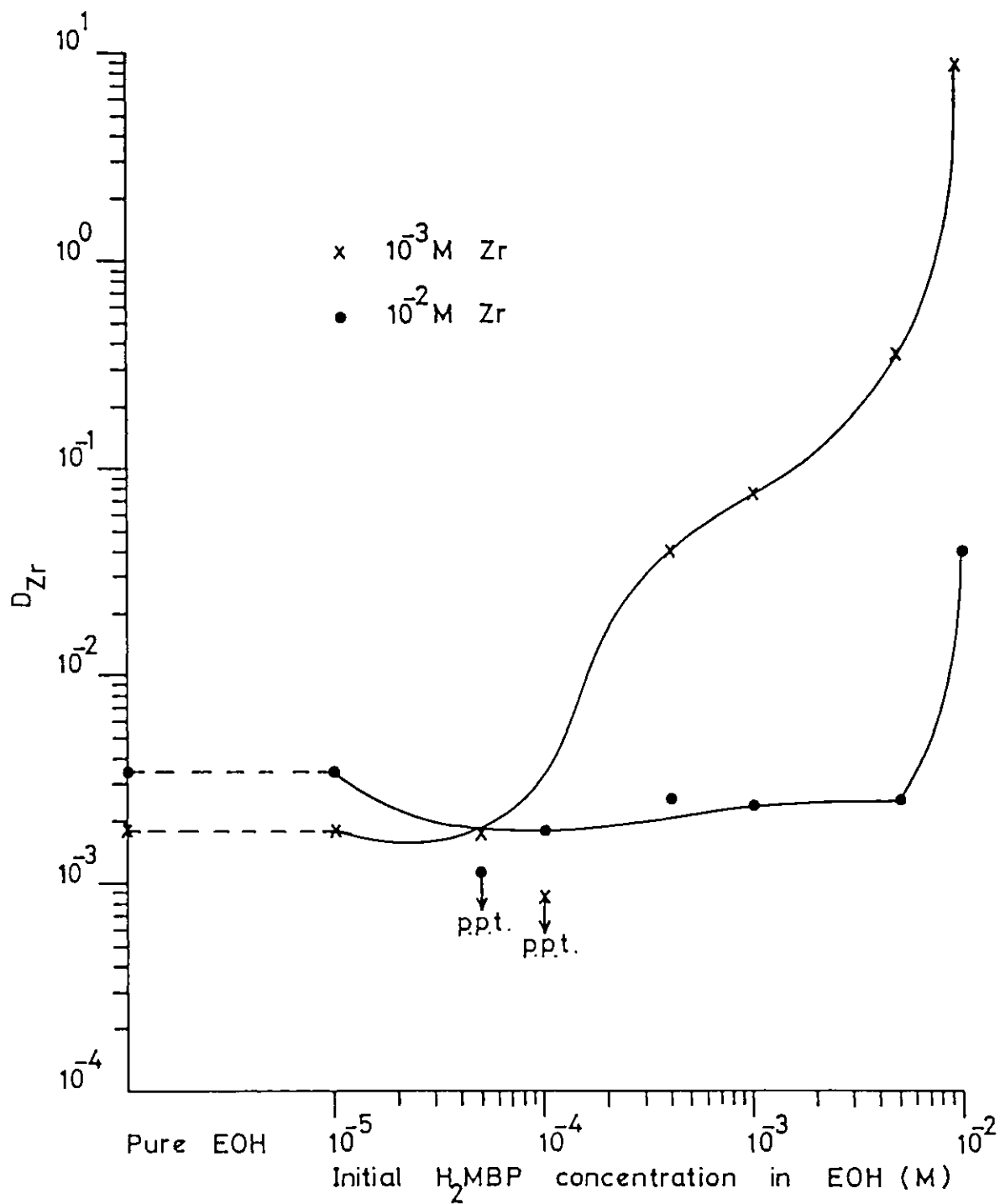


the same as in the absence of zirconium and the precipitate in the organic phase was formed at about 10^{-4} M H_2MBP . At 10^{-2} M zirconium D_{H_2MBP} is the same as in the absence of zirconium at very low H_2MBP concentrations but as soon as the precipitate forms (at about 5×10^{-5} M H_2MBP), D_{H_2MBP} falls to lower values. Subsequently D_{H_2MBP} rises to values somewhat less than the no zirconium case. The difference (1.4 compared with 2.2) may arise in part from the difficulty of measuring the H_2MBP at the low concentrations observed in this experiment.

Results for the extraction of zirconium by H_2MBP - EOH mixtures are shown in figure (7.4). These results illustrate that D_{-r} falls to low values as soon as the precipitate is formed and then starts to increase with increasing H_2MBP concentrations. The extraction results for zirconium also showed that most of the zirconium contained in the aqueous and the solid phases and very little in the organic phase. The distribution of H_2MBP and zirconium between the three phases in terms of concentrations are tabulated in Appendix C.

The behaviour of the H_2MBP - EOH - Zr system does not resemble that of HDBP to a great degree. At low concentrations of zirconium (10^{-4} M and 10^{-3} M) virtually no change in D_{H_2MBP} is recorded. This would seem to indicate that the complexing power of H_2MBP for zirconium is weaker than that of HDBP but the situation is complicated by the precipitation of zirconium complexes in the organic phase at quite low initial H_2MBP concentrations.

By comparison with HDBP it might have been expected that at the higher concentration of H_2MBP effects on D_{H_2MBP} would be noticed as a result of the formation of soluble complexes with



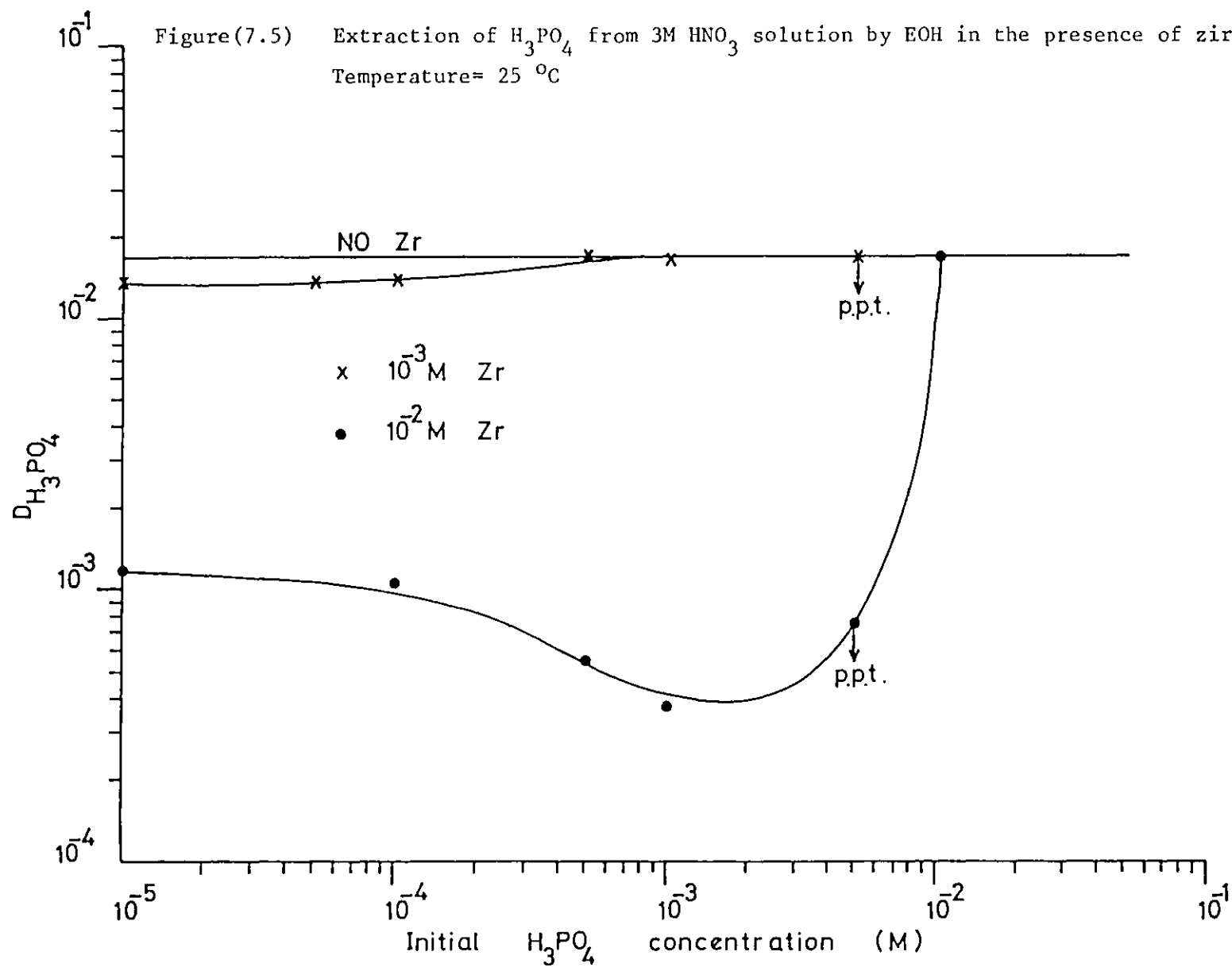
Figure(7.4) Distribution of zirconium between EOH- H_2MBP and 3M HNO_3 solutions at 25 °C.

zirconium. This effect is not seen since the majority of zirconium transferred to the organic phase is precipitated and the phosphate associated with the soluble fraction is small in comparison with the MBP not complexed with zirconium.

7.3.3 H₃PO₄

Results for the extraction of H₃PO₄ in the presence of zirconium from 3M HNO₃ solution by EOH are shown in figure (7.5). Of the four zirconium concentrations used in the extraction studies, 10⁻⁵M and 10⁻⁴M did not have any significant effect upon the extraction; i.e. the values of the distribution coefficient were the same as in the absence of zirconium. At 10⁻³M zirconium the extraction of H₃PO₄ is depressed at low concentrations but subsequently the distribution coefficient rises to values of no zirconium case. At 10⁻² zirconium, D_{H₃PO₄} decreases with increasing H₃PO₄ concentrations and then starts to increase to reach the values obtained in the absence of zirconium. Precipitate was present in the aqueous phase at high H₃PO₄ concentrations.

The effect of zirconium on the extraction of H₃PO₄ most nearly resembles that of H₂MBP. The complex with zirconium is weak and readily broken by EOH. The shape of the curve in figure (7.5) does not however indicate that the H₃PO₄ complexes are possibly stronger than those of H₂MBP.



C H A P T E R 8

RADIATION DAMAGE TO THE SOLVENT

8.1 Introduction

In separating the phosphate compounds from HAR by solvent extraction, the solvent (EOH) will be in contact with a highly active aqueous solution which could damage or degrade the solvent. The degradation of the solvent could have several consequences, e.g. reduction of the extracting power of the solvent for the phosphate compounds and formation of possible metal extracting products.

Radiolytic degradation studies of TBP have shown that most of the damage to the solvent is from the beta-gamma radiation from the fission products. The level of beta-gamma activity in the HAR per litre of solution is about 1 - 100 Curies ^[1] for present day wastes. This will increase with increasing fuel burn-up. The amount of activity which will be received by the solvent will be dependent upon the contact time between the phases and also the number of recycling of the solvent.

In this chapter the effect of gamma radiation damage on the solvent in terms of its extracting power for HDBP and H₂MBP is reported.

8.2 Experiments

EOH and 30% EOH in kerosene in contact with 3M HNO₃ solutions were irradiated in the cobalt source (dose rate ~ 0.5 Mrad h⁻¹). During the irradiation period the phases were kept more or less in equilibrium by shaking the container twice every 24 hours. After the

irradiation the phases were separated and the organic phase was contacted with HDBP and H_2MBP in 3M HNO_3 . Also some experiments were carried out by first washing the irradiated solvent with water and $0.1\text{M Na}_2\text{CO}_3$ solution and then contacting with HDBP and H_2MBP solutions.

8.3 Results and Discussion

There were some changes in the physical appearances of both the organic and the aqueous phases after the irradiation period depending on the time of irradiation. These changes are shown in table (8.1). Results for the extraction of HDBP and H_2MBP by the irradiated EOH and 30% EOH in kerosene are shown in tables (8.2) and (8.3).

The colour of the irradiated alcohol suggested that it is oxidised or nitrated by the nitric acid in the presence of gamma radiation. The alcohol did not show any colour change when irradiated in the absence of HNO_3 .

The colour change of the aqueous phase is due to the oxidation of the dissolved alcohol.

The oxidation of the alcohol could explain the reduction in its extracting power for HDBP and H_2MBP which is shown by the distribution coefficient values, table (8.2). Also since the water and Na_2CO_3 washes do not improve the extracting power of the alcohol we can say that the damage to the solvent has been permanent. Results in table (8.3) also show that the presence of kerosene in the organic phase has no appreciable effect upon the rate of oxidation of EOH.

The effect of irradiation upon these systems is rather complex

Table (8.1) Irradiation of EOH and 30% EOH in kerosene by gamma particles in presence of 3M HNO₃

Sample	Irradiation time (hrs)	Radiation dose (MR)	OBSERVATIONS			
			EOH		30% EOH	
			Organic phase	Aqueous phase	Organic phase	Aqueous phase
1	168.14	84	misty green	clear colourless	clear yellow	clear colourless
2	327.05	163	misty green	clear colourless	misty yellow	clear colourless
3	485.88	243	misty green	clear colourless	misty yellow	clear colourless
4	653.08	326	dark misty green	clear yellowish colour	dark misty yellow	clear yellowish colour

Table (8.2) Extraction of HDBP and H_2MBP from $3M HNO_3$ solution
by irradiated EOH

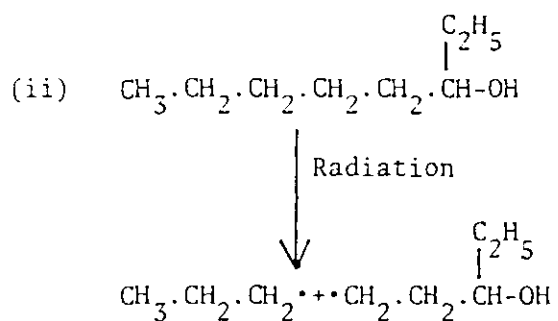
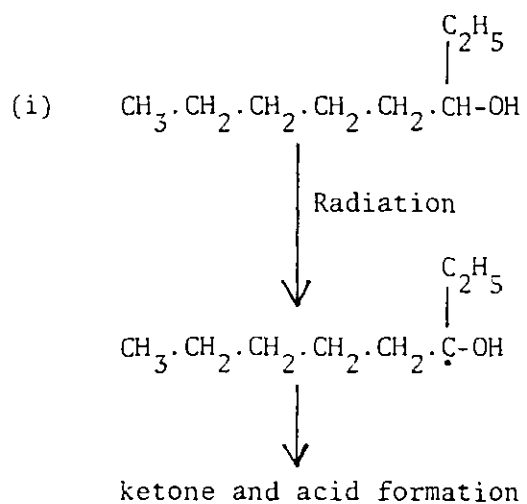
Sample	D_{HDBP}	D^*_{HDBP}	D_{H_2MBP}	$D^*_{H_2MBP}$
Unirradiated	117.2	115.0	2.19	2.21
1	110.0	108.6	1.38	1.22
2	98.6	96.3	1.07	1.08
3	93.1	93.1	0.89	0.90
4	84.8	84.9	0.82	0.82

Table (8.3) Extraction of HDBP and H_2MBP form $3M HNO_3$ solution by
irradiated 30% EOH in kerosene

Sample	D_{HDBP}	D^*_{HDBP}	D_{H_2MBP}	$D^*_{H_2MBP}$
Unirradiated	40.1	39.8	0.45	0.46
1	36.6	36.0	0.26	0.26
2	32.0	32.0	0.21	0.21
3	29.5	28.9	0.14	0.13
4	24.5	24.5	0.09	0.10

Note: D^* - organic phase was washed with water followed by Na_2CO_3
after the irradiation

but the scheme below indicates some of the routes leading to decomposition.



C H A P T E R 9

CONCLUSIONS, FLOWSHEET DECISION AND FUTURE WORK

9.1 Conclusions

The purification method developed and used for HDBP and H_2MBP produces highly pure solutions of these compounds (>99%). This method may not be suitable for large scale purification of these compounds because of large losses during the purification procedure.

The chemical method for the analysis of the phosphate compounds has proven to be sensitive and accurate. This method is as accurate as the radiochemical method for the solvent extraction studies of the phosphate compounds if the distribution coefficient values are moderate. For very high or very low distribution coefficient values this method is rather inaccurate to use.

The selected solvent is quite stable when in contact with nitric acid solutions up to 10M. Some nitric acid is extracted by EOH which exists as monomers in the organic phase.

The extraction studies have shown that EOH is an effective extractant for HDBP and H_2MBP and not so effective for H_3PO_4 . These studies have also shown that the phosphate compounds exist as monomers in the organic phase and they form complexes with undissociated nitric acid molecules. The model equations derived for the extraction of phosphate compounds are valid for any concentration at 25°C. The rise in temperature does not affect the distribution coefficient values

significantly. The phosphate compounds are effectively stripped from the organic phase by water and sodium carbonate (0.1M) washes. The kinetics of extraction is mass transfer controlled. The presence of HDBP in the solution increases the extraction of H_2MBP but neither have any significant effect on the extraction of H_3PO_4 . Kerosene could be used as a diluent at 30% mixtures of EOH in kerosene.

The metal ions, Cs, Ce, Fe, U and Mo do not interfere with the extraction of the phosphate compounds by EOH. The extraction of phosphate compounds is affected in a complicated way by the presence of zirconium. Both reduction and enhancement of the distribution coefficients occur and under conditions of high zirconium and higher HDBP and H_2MBP concentrations solid phases are produced which may cause certain problems in the solvent extraction process.

EOH is oxidised by 3M HNO_3 solution in the presence of gamma radiation. This causes a reduction in its extracting power for HDBP and H_2MBP . The presence of kerosene in the organic phase has no effect on the stability of EOH in the presence of gamma radiation.

9.2 Flowsheet Decision

Of the three possible flowsheets mentioned in Chapter 1, the most suitable for the proposed solvent extraction process would be: immediate treatment of HAR by solvent extraction after leaving Column I, to remove all the phosphate species including the TBP. The reason for the preference of this flowsheet to the other two are;

1. In the studies which were carried out to remove TBP from 3M HNO_3 solution by EOH, distribution coefficients of 888 were

obtained which indicate that TBP is effectively extracted by EOH. Therefore there will be no need for the TBP to be steam stripped from HAR before the solvent extraction treatment.

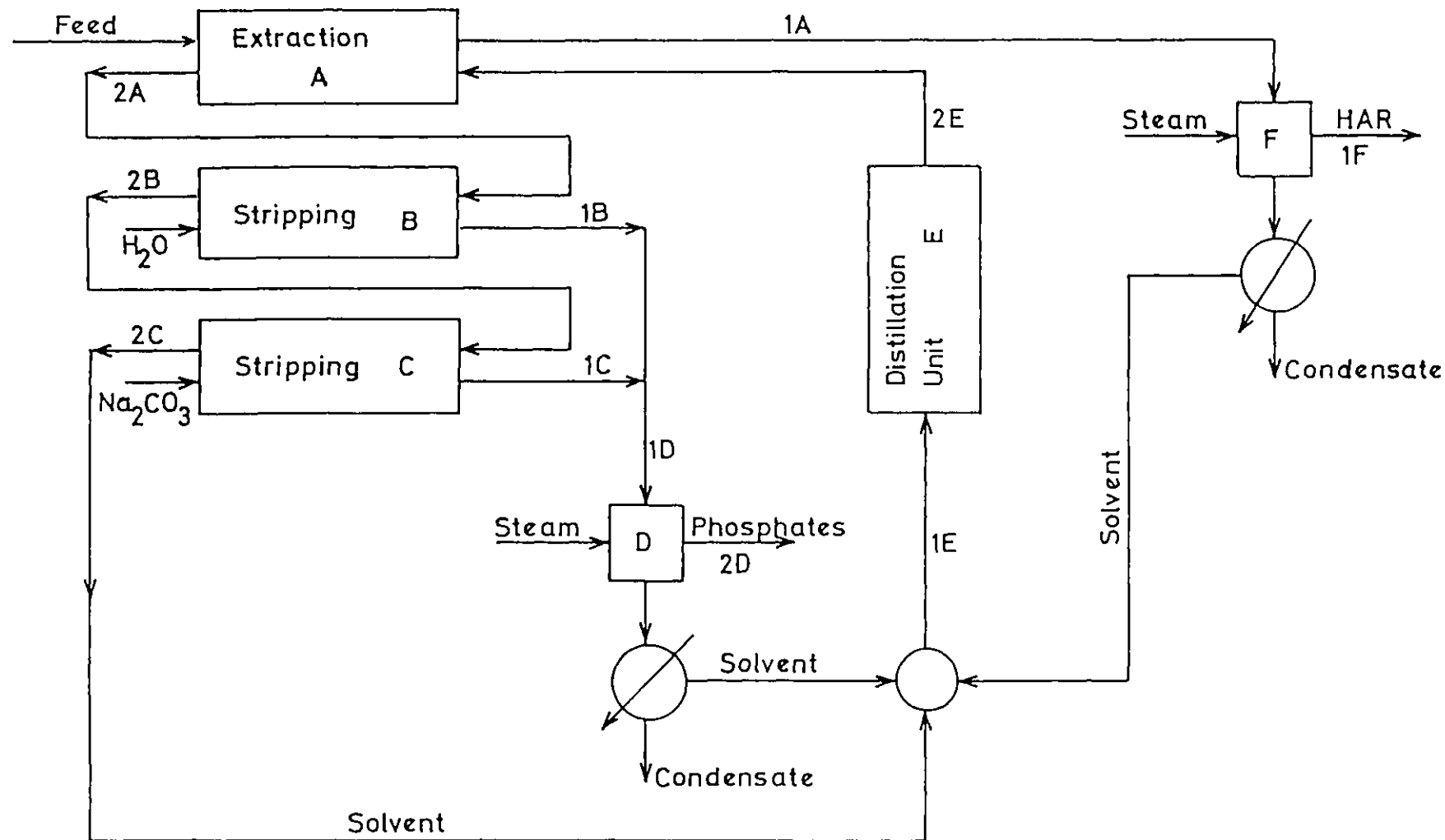
2. The solvent extraction studies have shown that the order of the extraction of the phosphate compounds by EOH is :

$\text{TBP} > \text{HDBP} > \text{H}_2\text{MBP} > \text{H}_3\text{PO}_4$. Thus HAR should be immediately treated after leaving Column I before the buildup of H_2MBP and H_3PO_4 which are difficult to remove.

An outline flowsheet based on using pure EOH as the extractant is shown in figure (9.1). A distillation unit as shown in the flow-sheet (distillation unit E) or other appropriate processes may be needed for the purification of the solvent because of the radiation damage and also to remove the TBP and odourless kerosene. The estimated composition of the streams in figure (9.1) are shown in Appendix D.

9.3 Future Work

More detailed studies of the complex formation between the phosphate compounds and nitric acid in EOH and the effect of zirconium on the extraction of HDBP and H_2MBP by EOH is recommended. Also further work is necessary to study the radiation damage to the solvent with the identification of the degradation products.



Figure(9.1) Outline flowsheet for the treatment of HAR by solvent extraction with EOH.

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Appendix A: Sample Calculation for the H_3PO_4 Distribution Coefficient

Aqueous phase: $10^{-3}M H_3PO_4$ in $3M HNO_3$

Organic phase: EOH

Initial activity of the aqueous phase (10ml) = 2.78×10^4 c.p.m.

The above value must be corrected for the dead time of the counter which is done as follows:

$$A = \frac{A_m}{1 - A_m t}$$

where A = actual activity

A_m = measured activity

t = dead time = 1.67×10^{-6} min.

Hence:

$$A = \frac{2.78 \times 10^4}{1 - (2.78 \times 10^4 \times 1.67 \times 10^{-6})}$$

$$A = 2.91 \times 10^4 \text{ c.p.m.}$$

Final activity of the organic phase (10ml) = 528.7 c.p.m. . The activity of the organic phase must be corrected for the difference in the densities of the organic and the aqueous phase which would affect the emission of the β -particles. The correction factors are taken from Dyrssen [9].

Final activity of the organic phase after correction for the density = 473.2 c.p.m.

The distribution coefficient, D , is calculated using the formula

$$D = \frac{V_{faq} A_{forg}}{(V_{iaq} A_{iaq}) - (V_{forg} A_{forg})}$$

where V and A are the volume and the activity respectively and the subscripts aq , org , f and i refer to the aqueous phase, organic phase, final and initial respectively.

$$\text{Hance} \quad D = \frac{9.6 \times 473.2}{(2.91 \times 10^5) - (10.4 \times 473.2)}$$

$$\underline{D = 1.588 \times 10^{-2}}$$

Appendix B: Calculation of the Dissociation Constants of HDBP,

H₂MBP and H₃PO₄ (ref 93)

1. Dissociation Constant of HDBP

1.1 Method of Calculation

The thermodynamic dissociation constant of a monobasic acid at 25°C is calculated using the formula:

$$pK_a = pH - \log \frac{[\text{non-protonated species}]}{[\text{protonated species}]} + \frac{0.512\sqrt{I}}{1+1.6\sqrt{I}}$$

$$\text{or } pK_a = pH - \log \frac{(C_A + [H^+] - [OH^-])}{(C_t - C_A + [OH^-] - [H^+])} + \frac{0.512\sqrt{I}}{1+1.6\sqrt{I}}$$

C_t is the concentration of the acid in the solution and it is calculated as:

$$C_t = \frac{V \cdot C_m}{(V+V_T)}$$

where V = initial volume of the acid.

V_T = volume of the titrant added.

C_m = initial molarity of the acid.

The concentration of [Na⁺] in the solution or C_A must be calculated similarly by

$$C_A = \frac{V_T \cdot C_n}{(V+V_T)}$$

where C_n = normality of the alkali added.

The ionic strength (I) is calculated by using the formula:

$$I = [Na^+] + [H^+]$$

In the above equation $[H^+]$ is the hydrogen ion concentration.

However initially only H^+ activity is available i.e. from pH values. The ionic strength (I) is, therefore, approximated initially to

$I = [Na^+] + 10^{-pH}$ in order to calculate (γ), the activity coefficient, from the equation

$$-\log \gamma = \frac{0.512\sqrt{I}}{1+1.6\sqrt{I}}$$

Then this approximate activity coefficient (γ) is used to calculate the hydrogen ion concentration (i.e. $[H^+] = \{H^+\}/(\gamma)$) and also the ratios of the activities of the non-protonated to protonated species which is :

$$\frac{(C_A + [H^+] - [OH^-])\gamma}{(C_t - C_A + [OH^-] - [H^+])}$$

Then the value of the activity coefficient (γ) is recalculated using the value of $[H^+]$ in the calculation of the ionic strength. This process should be repeated until successive values of the activities of the non-protonated to protonated species are constant.

1.2 Results

The pK_a value for HDBP is calculated by taking several points from the pH titration curve of pure HDBP, figure (3.2), and following the above method. Results are shown in table (B.1).

Table (B.1) Determination of the dissociation constant of HDBP

Titrant 0.1M NaOH (V _T) ml	pH	C _t (M)	C _A (M)	$\frac{[\text{non-protonated}]}{[\text{protonated}]}$	$\frac{0.512\sqrt{I}}{1+1.6\sqrt{I}}$	pK _a
5	2.37	1.048×10 ⁻²	4.762×10 ⁻³	9.44	0.0431	1.438
6	2.45	1.038×10 ⁻²	5.660×10 ⁻³	12.03	0.0433	1.414
7	2.55	1.028×10 ⁻²	6.542×10 ⁻³	15.50	0.0435	1.403
8	2.68	1.018×10 ⁻²	7.407×10 ⁻³	20.77	0.0436	1.406
9	2.86	1.009×10 ⁻²	8.257×10 ⁻³	31.73	0.0437	1.404
10	3.18	1.000×10 ⁻²	9.091×10 ⁻³	49.80	0.0438	1.483

pK_a average = 1.424±0.043

2. Dissociation Constants of H₂MBP

2.1 Method of Calculation:

H₂MBP is a dibasic acid with two dissociation constants. The first dissociation constant is calculated the same as for a monobasic acid. For the second dissociation constant, this method is not applicable because the ionic strength term is different and the activity coefficients much smaller than for the first ionization process. The following method is used to calculate the second dissociation constant :

$$pK_{a2} = pH + \log \frac{2C_t - [Na^+] - [H^+] + [OH^-]}{([Na^+] - C_t + [H^+] - [OH^-])} + \frac{1.5345\sqrt{I}}{1+1.6\sqrt{I}}$$

where C_t and $([Na^+] = C_A)$ are calculated in the same way as for pK_{a1} .

Note that $[Na^+]$ is the total concentration of sodium hydroxide added, including that used in the neutralization of the stronger group.

The ionic strength $I = 2[Na^+] - C_t + 2[H^+] - [OH^-]$

Both H^+ and OH^- should be expressed as concentrations. For this purpose $[H^+] = \{H^+\} \times 10^{0.5115FS}$ where $\{H^+\}$ is calculated from pH and $FS = \frac{\sqrt{I}}{1+1.6\sqrt{I}}$.

This method is only applicable where the dissociation constants do not overlap, i.e. where $pK_{a2} - pK_{a1} > 2.7$.

2.2 Results

Tables (B.2) and (B.3) show the values of pK_{1a} and pK_{2a} for H_2MBP for several points from the pH titration curve of pure H_2MBP , Figure (3.3).

Table (B.2) Determination of pK_{a1} of H_2MBP

Titrant 0.1M NaOH (V_T) (cm) ³	pH	C_t (M)	C_A (M)	$\frac{[\text{non-protonated}]}{[\text{protonated}]}$	$\frac{0.512\sqrt{I}}{1+1.6\sqrt{I}}$	pK_{a1}
6	2.27	1.230×10^{-2}	5.660×10^{-3}	8.483	0.0471	1.388
7	2.33	1.289×10^{-2}	6.542×10^{-3}	10.318	0.0473	1.364
8	2.41	1.278×10^{-2}	7.407×10^{-3}	11.353	0.0473	1.402
9	2.49	1.266×10^{-2}	8.257×10^{-3}	14.952	0.0475	1.363
10	2.60	1.254×10^{-2}	9.091×10^{-3}	18.240	0.0475	1.386
11	2.73	1.243×10^{-2}	9.9101×10^{-3}	26.980	0.0477	1.347

pK_{a1} average = 1.375 ± 0.041

Table (B.3) Determination of pK_{a2} of H_2MBP

Titrant 0.1M NaOH V_T (cm ³)	pH	C_t (M)	C_A (M)	pK_{a2}
19	6.49	1.160×10^{-2}	1.600×10^{-2}	6.882
20	6.60	1.150×10^{-2}	1.670×10^{-2}	6.868
21	6.71	1.141×10^{-2}	1.736×10^{-2}	6.861
22	6.83	1.131×10^{-2}	1.803×10^{-2}	6.857
23	6.97	1.122×10^{-2}	1.870×10^{-2}	6.866
24	7.11	1.113×10^{-2}	1.936×10^{-2}	6.859

pK_{a2} average = 6.865 ± 0.14

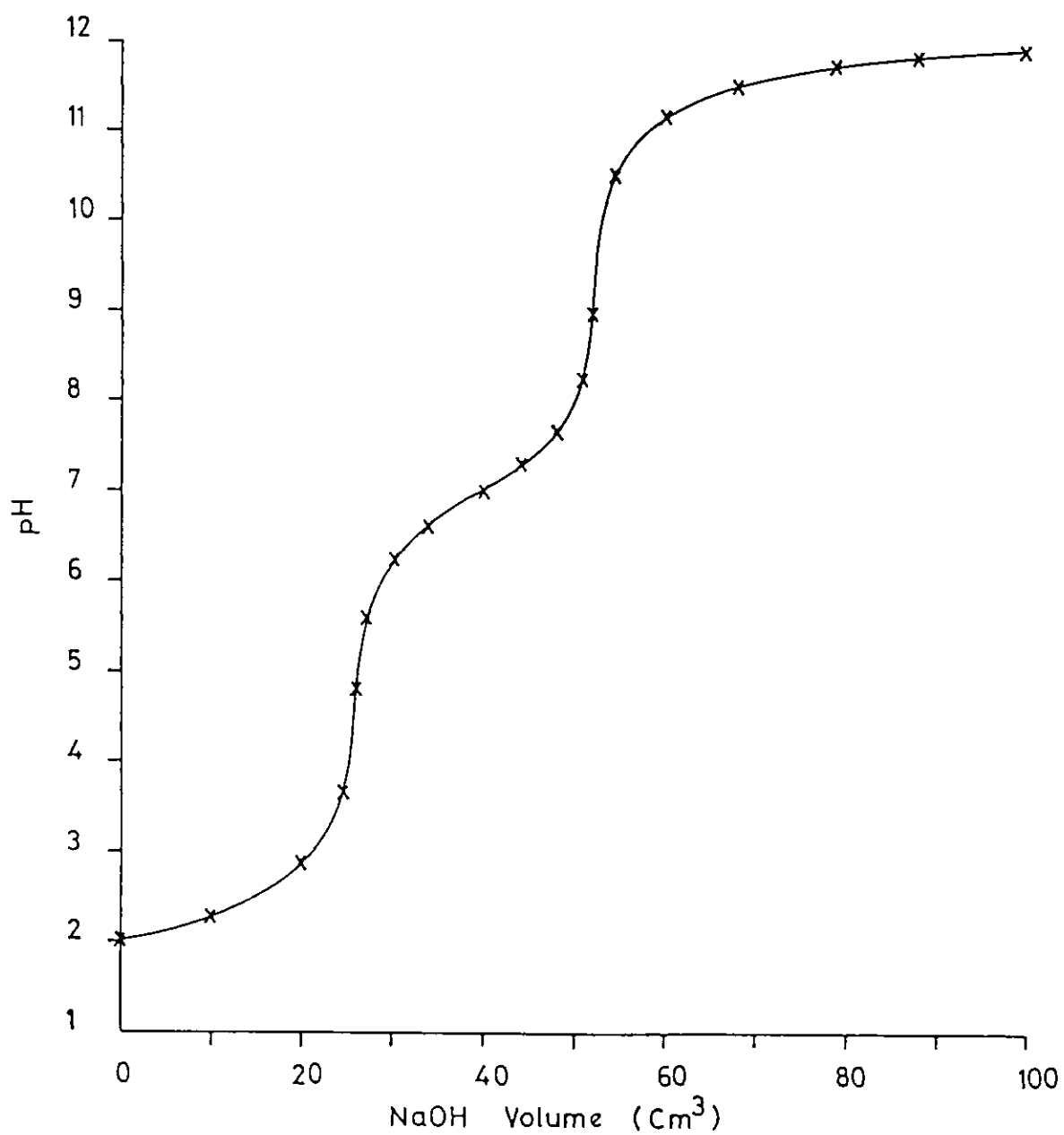
3. Dissociation Constant of H_3PO_4

In order to check the accuracy of the pH titration method used to determine the dissociation constants of HDBP and H_2MBP , the pK_{a1} for H_3PO_4 is also calculated for several points from the pH titration curve of H_3PO_4 , figure (B.1). This method is not valid for the calculation of pK_{a2} of H_3PO_4 as it is affected by the pK_{a3} of H_3PO_4 .

Table (B.4) Determination of pK_{a1} of H_3PO_4

Titrant 0.1M NaOH (V_T) (cm) ³	pH	C_t (M)	C_A (M)	$\frac{[\text{non-protonated}]}{[\text{protonated}]}$	$\frac{0.512\sqrt{I}}{1+1.6\sqrt{I}}$	pK_{a1}
14	2.40	3.906×10^{-2}	2.187×10^{-2}	2.112	0.0661	2.141
16	2.55	3.788×10^{-2}	2.424×10^{-2}	2.661	0.0671	2.192
18	2.65	3.676×10^{-2}	2.647×10^{-2}	3.792	0.0686	2.140
20	2.80	3.571×10^{-2}	2.857×10^{-2}	5.762	0.0698	2.109

pK_{a1} average = 2.146 ± 0.064



Figure(B.1) pH titration of H_3PO_4 at 25°C .

Appendix C: Distribution of HDBP, H₂MBP, H₃PO₄ and
Zirconium Between the Three Aqueous,
Organic and Solid Phases

Table (C.1) Extraction of HDBP from 3M HNO_3 solution by EOH in the presence of zirconiumInitial zirconium concentration in aqueous phase = 10^{-3} M

Initial HDBP concentration in organic phase (M)	Final HDBP concentration in organic phase (M)	Final HDBP concentration in aqueous phase (M)	Final Zr concentration in organic phase (M)	Final Zr concentration in aqueous phase (M)	Ratio [HDBP]/[Zr] in organic phase	D_{HDBP} column 2 column 3	D_{Zr} column 4 column 5
0.9185×10^{-5}	7.303×10^{-6}	1.882×10^{-6}	4.8×10^{-6}	9.952×10^{-4}	1.5	3.88	4.8×10^{-3}
5.140×10^{-5}	4.913×10^{-5}	2.274×10^{-6}	5.3×10^{-6}	9.947×10^{-4}	9	21.6	5.3×10^{-3}
1.040×10^{-4}	1.014×10^{-4}	2.593×10^{-6}	4.8×10^{-6}	9.952×10^{-4}	21	39.1	4.8×10^{-3}
4.410×10^{-4}	4.342×10^{-4}	6.805×10^{-6}	9.1×10^{-6}	9.909×10^{-4}	47	63.8	9.2×10^{-3}
0.97×10^{-3}	9.608×10^{-4}	9.15×10^{-6}	1.27×10^{-5}	9.873×10^{-4}	75	105	1.3×10^{-2}
5.14×10^{-3}	5.100×10^{-3}	4.012×10^{-5}	2.98×10^{-4}	7.014×10^{-4}	17	127.1	4.3×10^{-1}
1.23×10^{-2}	1.229×10^{-2}	6.12×10^{-5}	9.42×10^{-4}	5.8×10^{-5}	13	200	16.3

Table (C.2) Extraction of HDBP from 3M HNO_3 solution by EOM in the presence of zirconium

Initial zirconium concentration in aqueous phase = 10^{-2}M

Initial HDBP concentration in organic phase (M)	Final HDBP concentration in organic phase (M)	Final HDBP concentration in aqueous phase (M)	Equivalent HDBP concentration in solid phase (M)	Final Zr concentration in organic phase (M)	Final Zr concentration in aqueous phase (M)	Equivalent Zr concentration in solid phase (M)	Ratio [HDBP]/[Zr] in solid phase	Ratio [HDBP]/[Zr] in organic phase	D _{HDBP} column 2 column 3	D _{Zr} column 5 column 6
0.9185×10^{-5}	6.620×10^{-6}	2.56×10^{-6}	-	6.7×10^{-5}	9.933×10^{-3}	-	-	0.1	2.58	6.7×10^{-3}
5.140×10^{-5}	4.820×10^{-5}	3.20×10^{-6}	-	6.2×10^{-5}	9.938×10^{-3}	-	-	0.8	15.1	6.3×10^{-3}
1.040×10^{-4}	9.980×10^{-5}	4.21×10^{-6}	-	5.5×10^{-5}	9.945×10^{-3}	-	-	1.8	23.7	5.6×10^{-3}
4.410×10^{-4}	4.30×10^{-4}	1.10×10^{-5}	-	1.0×10^{-4}	9.900×10^{-3}	-	-	4.3	39.7	1.0×10^{-2}
0.97×10^{-3}	9.51×10^{-4}	1.92×10^{-5}	-	1.8×10^{-4}	9.820×10^{-3}	-	-	5.3	49.4	1.84×10^{-2}
5.140×10^{-3}	2.128×10^{-3}	3.53×10^{-5}	2.960×10^{-3}	1.937×10^{-3}	8.006×10^{-3}	5.700×10^{-5}	52	1.1	57	2.42×10^{-1}
1.23×10^{-2}	1.71×10^{-3}	2.22×10^{-6}	1.057×10^{-2}	4.848×10^{-4}	5.430×10^{-3}	4.085×10^{-3}	2.6	3.5	73	8.9×10^{-2}

Table (C.3) Extraction of H_2MBP from $3M HNO_3$ solution by EOH in the presence of zirconium

Initial zirconium concentration in aqueous phase = $10^{-4} M$

Initial H_2MBP concentration in organic phase (M)	Final H_2MBP concentration in organic phase (M)	Final H_2MBP concentration in aqueous phase (M)	Equivalent H_2MBP concentration in solid phase (M)	D_{H_2MBP} <u>column 2</u> <u>column 3</u>
1.54×10^{-5}	1.061×10^{-5}	4.78×10^{-6}	-	2.22
0.974×10^{-4}	6.54×10^{-5}	3.20×10^{-5}	-	2.04
1.98×10^{-4}	1.394×10^{-4}	5.86×10^{-5}	-	2.38
3.16×10^{-4}	2.150×10^{-4}	8.091×10^{-5}	1.996×10^{-5}	2.45
6.43×10^{-4}	3.87×10^{-4}	1.610×10^{-4}	9.53×10^{-5}	2.22
1.23×10^{-3}	7.93×10^{-4}	3.20×10^{-4}	1.161×10^{-4}	2.29
6.60×10^{-3}	3.63×10^{-3}	1.571×10^{-3}	1.40×10^{-3}	2.13
1.095×10^{-5}	7.37×10^{-3}	3.16×10^{-3}	4.13×10^{-4}	2.15

Table (C.4) Extraction of H_2MBP from 3M HNO_3 solution by EOH in the presence of zirconium.

Initial zirconium concentration in aqueous phase : $10^{-3}M$

Initial H_2MBP concentration in organic phase (M)	Final H_2MBP concentration in organic phase (M)	Final H_2MBP concentration in aqueous phase (M)	Equivalent H_2MBP concentration in solid phase (M)	Final Zr concentration in organic phase (M)	Final Zr concentration in aqueous phase (M)	Equivalent Zr concentration in solid phase	Ratio [H_2MBP]/[Zr] in solid phase	Ratio [H_2MBP]/[Zr] in organic phase	D_{H_2MBP} column 2 column 3	D_{Zr} column 5 column 6
1.54×10^{-5}	1.061×10^{-5}	4.78×10^{-6}	-	1.400×10^{-6}	9.986×10^{-4}	-	-	7.6	2.22	1.4×10^{-3}
5.144×10^{-5}	3.51×10^{-5}	1.633×10^{-5}	-	1.958×10^{-6}	9.980×10^{-4}	-	-	17.6	2.15	1.96×10^{-3}
0.974×10^{-4}	3.59×10^{-5}	1.300×10^{-5}	4.85×10^{-5}	8.400×10^{-7}	9.970×10^{-4}	2.200×10^{-6}	22	44	2.56	8.40×10^{-3}
6.43×10^{-4}	1.83×10^{-4}	7.21×10^{-5}	3.88×10^{-4}	3.770×10^{-5}	9.234×10^{-4}	3.890×10^{-5}	10	4.8	2.34	4.1×10^{-4}
1.23×10^{-3}	1.986×10^{-4}	8.04×10^{-5}	9.51×10^{-4}	5.870×10^{-5}	8.003×10^{-4}	1.410×10^{-4}	6.7	3.4	2.28	7.34×10^{-2}
6.60×10^{-3}	2.380×10^{-3}	1.042×10^{-3}	3.180×10^{-3}	1.000×10^{-3}	3.100×10^{-5}	9.589×10^{-4}	3.3	235	2.11	3.26×10^{-2}
1.095×10^{-2}	6.060×10^{-3}	2.69×10^{-3}	2.210×10^{-3}	2.490×10^{-5}	2.800×10^{-6}	9.723×10^{-4}	2.3	243	2.080	8.87

Table (C.5) Extraction of H_2MBP from $3M HNO_3$ solution by EOH in the presence of zirconium

Initial zirconium concentration in aqueous phase = $10^{-2}M$

Initial H_2MBP concentration in organic phase (M)	H_2MBP concentration in organic phase (M)	Final H_2MBP concentration in aqueous phase (M)	Equivalent H_2MBP concentration in solid phase (M)	Final Zr concentration in organic phase (M)	Final Zr concentration in aqueous phase (M)	Equivalent Zr concentration in solid phase (M)	Ratio [H_2MBP]/[Zr] in solid phase	Ratio [H_2MBP]/[Zr] in organic phase	D_{H_2MBP} column 2 column 3	D_{Zr} column 5 column 6
1.540×10^{-5}	1.061×10^{-5}	4.780×10^{-6}	-	3.380×10^{-5}	9.966×10^{-3}	-	-	0.31	2.22	3.40×10^{-3}
5.144×10^{-5}	4.960×10^{-5}	1.920×10^{-5}	2.73×10^{-5}	1.120×10^{-5}	9.958×10^{-3}	3.080×10^{-5}	0.88	4.4	0.238	1.12×10^{-3}
0.974×10^{-4}	2.060×10^{-6}	1.090×10^{-5}	8.44×10^{-5}	1.760×10^{-5}	9.737×10^{-3}	2.624×10^{-4}	0.32	0.11	0.174	1.80×10^{-3}
6.430×10^{-4}	8.450×10^{-6}	5.140×10^{-6}	6.290×10^{-4}	2.460×10^{-5}	9.453×10^{-3}	5.469×10^{-4}	1.15	0.34	1.364	2.60×10^{-3}
1.230×10^{-3}	8.450×10^{-6}	5.140×10^{-6}	1.216×10^{-3}	2.210×10^{-5}	9.208×10^{-3}	7.703×10^{-4}	1.58	0.38	1.364	2.40×10^{-3}
6.600×10^{-3}	8.450×10^{-6}	5.140×10^{-6}	6.586×10^{-3}	1.710×10^{-5}	6.683×10^{-3}	3.317×10^{-3}	1.98	0.49	1.364	2.56×10^{-3}
1.095×10^{-2}	3.600×10^{-5}	2.280×10^{-5}	1.089×10^{-2}	1.540×10^{-5}	3.703×10^{-3}	6.293×10^{-3}	1.73	2.3	1.420	4.15×10^{-2}

Table (C.6) Extraction of H_3PO_4 from 3M HNO_3 solution by EOH in the presence of zirconium

Initial zirconium concentration in aqueous phase = $10^{-3}M$

Initial H_3PO_4 concentration in aqueous phase (M)	Final H_3PO_4 concentration in aqueous phase (M)	Final H_3PO_4 concentration in organic phase (M)	Equivalent H_3PO_4 concentration in solid phase (M)	$D_{H_3PO_4}$ $\frac{\text{column 3}}{\text{column 2}}$
10^{-5}	9.866×10^{-6}	1.344×10^{-7}	-	1.364×10^{-2}
5×10^{-5}	4.930×10^{-5}	6.764×10^{-7}	-	1.370×10^{-2}
10^{-4}	9.860×10^{-5}	1.360×10^{-6}	-	1.380×10^{-2}
5×10^{-4}	4.908×10^{-4}	9.200×10^{-6}	-	1.874×10^{-2}
10^{-3}	9.843×10^{-4}	1.570×10^{-5}	-	1.595×10^{-2}
5×10^{-3}	3.618×10^{-3}	6.000×10^{-5}	1.322×10^{-3}	1.535×10^{-2}
10^{-2}	8.663×10^{-3}	1.448×10^{-4}	1.192×10^{-3}	1.543×10^{-2}

Table (C.7) Extraction of H_3PO_4 from 3M HNO_3 solution by EOH in the presence of zirconium.

Initial zirconium concentration in aqueous phase = $10^{-2}M$

Initial H_3PO_4 concentration in aqueous phase (M)	Final H_3PO_4 concentration in aqueous phase (M)	Final H_3PO_4 concentration in organic phase (M)	Equivalent H_3PO_4 concentration in solid phase (M)	$D_{H_3PO_4}$ $\frac{\text{column 3}}{\text{column 2}}$
10^{-5}	9.988×10^{-6}	1.167×10^{-8}	-	1.169×10^{-3}
5×10^{-5}	4.994×10^{-5}	5.484×10^{-8}	-	1.098×10^{-3}
10^{-4}	9.990×10^{-5}	1.061×10^{-7}	-	1.062×10^{-3}
5×10^{-4}	4.990×10^{-4}	2.791×10^{-7}	-	5.586×10^{-4}
10^{-3}	9.996×10^{-4}	3.860×10^{-7}	-	3.862×10^{-4}
5×10^{-3}	8.842×10^{-4}	7.600×10^{-7}	4.115×10^{-3}	7.930×10^{-4}
10^{-2}	1.154×10^{-4}	1.900×10^{-6}	9.883×10^{-3}	1.518×10^{-2}

Appendix D: Estimation of the Composition of the Streams
in Figure (9.1)

Based on the information so far available, the composition of streams in the flowsheet, figure (9.1), are estimated together with the number of the stages required in columns A, B and C.

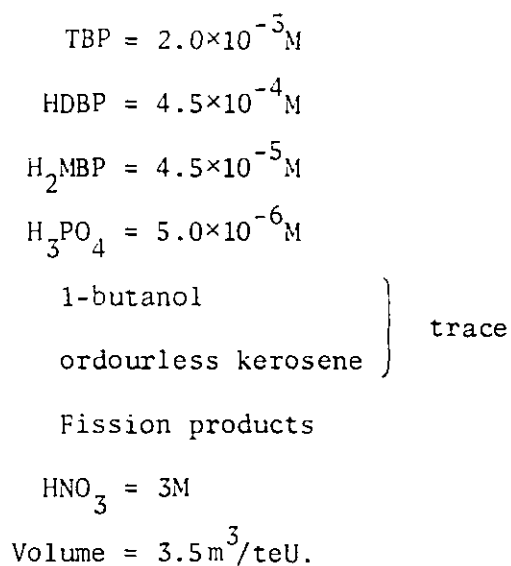
Feed Stream

The TBP content of the feed stream or the HAR depends on the amount of entrained solvent, the TBP concentration of the extractant and the composition of the HAR. during the reprocessing of the reactor fuels. The TBP content of the HAR resulting from the reprocessing of the present day fuels in U.K. reprocessing plant is estimated at about $2.5 \times 10^{-3} \text{M}$. The major contribution to the amount of HDBP present in the HAR is from the degradation of the dissolved TBP which is estimated to be about 1/5th of the total TBP ($\sim 5 \times 10^{-4} \text{M}$). The amount of H_2MBP and H_3PO_4 are estimated to be 1/10th and 1/100th of the HDBP concentration respectively.

The above estimated concentrations of the phosphate compounds in the HAR are based on the reprocessing of the present day fuels. In future when much higher burn-up fuels are expected, the HAR will contain much higher amount of the phosphate compounds. However certain modifications in the processing plants are expected for future fuel reprocessing, to reduce the radiation damage to the solvent and hence reducing the phosphate content of the HAR. One such modifications would be the replacement of the mixer-settler contactors with either pulsed column or centrifuge contactors which result in a lower contact time between the phases hence reducing the

degradation of the extractant. Therefore the estimated amount of the phosphate content of the HAR . for present day fuels may be close to what is expected in future wastes.

Apart from the organic phosphate present in the HAR there will be some 1- butanol, degradation product of the TBP, and odourless kerosene, the diluent, which must also be removed. Thus the composition of the feed stream is;



The following assumptions are made in designing column A.

1. The contactors are mixer-settlers with 80% efficiency.
2. The total phosphate content of the HAR . to be reduced to about 10^{-5}M which ensures that no precipitate will be formed with the metal ions present in the HAR.
5. The overall efficiency of column A is taken as about 65% because : (a) the extracting power of the solvent is reduced as the result of the radiation damage and (b) the presence of zirconium in the HAR ($\sim 10^{-2} \text{M}$) reduces the transfer of HDBP into the organic phase at low HDBP concentrations.

Column A $\equiv$ 3 stages , solvent = $3.5\text{m}^3/\text{teU}$

Stream 1A

TBP = $2.53 \times 10^{-9} \text{M}$
HDBP = $3.373 \times 10^{-8} \text{M}$
 H_2MBP = $5.520 \times 10^{-6} \text{M}$
 H_3PO_4 = $4.915 \times 10^{-6} \text{M}$
 HNO_3 = 2.5M
Fission products
EOH
Volume = $3.5\text{m}^3/\text{teU}$

Stream 1F

TBP = 2.534×10^{-9}
HDBP = 3.373×10^{-8}
 H_2MBP = 5.520×10^{-6}
 H_3PO_4 = 4.915×10^{-6}
 HNO_3 = 2.5M
Fission products
Volume = $3.5\text{m}^3/\text{teU}$

Stream 2A (solvent)

TBP = 1.999×10^{-3}
HDBP = 4.499×10^{-4}
 H_2MBP = 3.948×10^{-5}
 H_3PO_4 = 4.497×10^{-8}
 HNO_3 = 0.5 M
1 - butanol
odourless kerosene
Volume $< 3.5\text{m}^3/\text{teU}$

Column B $\equiv$ 2 stages, $H_2O = 3.5m^3/teU$

Stream 2B (solvent)

TBP = 1.999×10^{-3}
HDBP = $4.430 \times 10^{-4}M$
 $H_2MBP = 1.928 \times 10^{-5}$
 $H_3PO_4 = 2.0 \times 10^{-11}$
1 - butanol
odourless kerosene
Volume $< 3.5m^3/teU$

Stream 1B

HDBP = 6.9×10^{-6}
 $H_2MBP = 2.03 \times 10^{-5}M$
 $H_3PO_4 = 4.495 \times 10^{-8}$
 $HNO_3 \sim 0.5M$
EOH
Volume = $3.5m^3/teU$

Column C = 3 stages , $Na_2CO_3 = (0.1M) 3.5m^3/teU$

Stream 2C (solvent)

TBP = $1.999 \times 10^{-3}M$
1 - butanol
ordourless kerosene
degraded products
Volume $< 3.5m^3/teU$

Stream 1C

HDBP = $4.430 \times 10^{-4}M$
 $H_2MBP = 1.928 \times 10^{-5}$
 $H_3PO_4 = 2 \times 10^{-11}$
EOH
Volume = $3.5m^3/teU$

Stream 1D

$$\text{HDBP} = 2.2495 \times 10^{-4} \text{ M}$$

$$\text{H}_2\text{MBP} = 1.974 \times 10^{-5}$$

$$\text{H}_3\text{PO}_4 = 2.2485 \times 10^{-8}$$

$$\text{HNO}_3 \sim 0.25 \text{ M}$$

EOH

$$\text{Volume} = 7.0 \text{ m}^3 / \text{teU}$$

Stream 1E

$$\text{TBP} = 1.999 \times 10^{-3} \text{ M}$$

1 - butanol

odourless kerosene

degraded products

Stream 2D

$$\text{HDBP} = 2.2495 \times 10^{-4} \text{ M}$$

$$\text{H}_2\text{MBP} = 1.974 \times 10^{-5} \text{ M}$$

$$\text{H}_3\text{PO}_4 = 2.2485 \times 10^{-8}$$

$$\text{HNO}_3 \sim 0.25$$

$$\text{Volume} = 7.0 \text{ m}^3 / \text{teU}$$

Stream 2E

Pure Solvent

Appendix E: List and Sources of Chemicals

Name	Source	Specification
Acetone	B.D.H. Chemicals	99%
Ammonium molybdate	B.D.H. Chemicals	99%
Arsenazo(III)	B.D.H. Chemicals	-
Barium nitrate	Hopkin & Williams	99.5%
Caesium nitrate	B.D.H. Chemicals	99%
Cerous nitrate	B.D.H. Chemicals	99%
Di-n-butyl phosphate	Eastman Kodak Company	Crude mixture of di and mono-n-butyl phosphate
Diethyl ether	B.D.H. Chemicals	99%
2-Ethylhexan-1-ol	B.D.H. Chemicals	99%
Ferric nitrate	B.D.H. Chemicals	98%
Glycerol	Koch-Light Laboratories Ltd	Pure
Kerosene	Shell Chemicals U.K. Ltd	See table (6.7)
4-Methylpentan-2-One	B.D.H. Chemicals	99%
Molybdic acid	B.D.H. Chemicals	85%
Nitric acid	B.D.H. Chemicals	69 - 71%
Orthophosphoric acid	B.D.H. Chemicals	85%
Phenolphthalein	B.D.H. Chemicals	1% Solution in propan-2-ol
Phosphorous-32	Amercham Radiochemical Centre	As orthophosphate in dilute HCl, pH 2-3, carrier free
Perchloric acid	B.D.H. Chemicals	71 - 73%
Sodium carbonate	B.D.H. Chemicals	98.5%
Sodium hydroxide	B.D.H. Chemicals	98.0%
Sodium hydroxide	B.D.H. Chemicals	0.1M standard solution
Sodium hydroxide	B.D.H. Chemicals	1.0M (free from carbonate)
Sodium nitrate	B.D.H. Chemicals	98%
Stannous chloride	B.D.H. Chemicals	97%
Sulphuric acid	B.D.H. Chemicals	98%
Tri-n-butyl phosphate	Fiscon Laboratory Reagent	-
Uranyl nitrate	B.D.H. Chemicals	99%
Zirconium nitrate	B.D.H. Chemicals	-
Zirconium sulphate	B.D.H. Chemicals	-