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SOLVENT EXTRACTION PROPERTIES OF DITERTIARYPHOSPHINE DIOXIDES

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CONTENTS

ABBREVIATIONS

MDPO	1,1-methylenebis(diphenylphosphine oxide)
EDPO	1,2-dimethylenebis(diphenylphosphine oxide)
PDPO	1,3-trimethylenebis(diphenylphosphine oxide)
BDPO	1,4-tetramethylenebis(diphenylphosphine oxide)
HDPO	1,6-hexamethylenebis(diphenylphosphine oxide)
MBDPO	1,1-methylenebis(dibutylphosphine oxide)
EBDPO	1,2-dimethylenebis(dibutylphosphine oxide)
PBDPO	1,3-trimethylenebis(di-2-ethylbutylphosphine oxide)
MEDPO	1,1-methylenebis(di-2-ethylbutylphosphine oxide)
MCDPO	1,1-methylenebis(dicyclohexylphosphine oxide)

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MODPO	1,1-methylenebis(di-octyl-phosphine oxide)
EODPO	1,2-dimethylenebis(di-octyl-phosphine oxide)
PODPO	1,3-trimethylenebis(dioctylphosphine oxide)
MHDPO	1,1-methylenebis(di-n-hexylphosphine oxide)
EHDPO	1,2-dimethylenebis(di-n-hexylphosphine oxide)
PHDPO	1,3-trimethylenebis(di-n-hexylphosphine oxide)
BHDPO	1,4-tetramethylenebis(di-n-hexylphosphine oxide)
ADPO	1,2-acetylenebis(diphenylphosphine oxide)
VDPO	1,2-vinylenebis(diphenylphosphine oxide)
TOPO	Trioctylphosphine oxide

A. INTRODUCTION

The extraction of a metal ion by different extracting reagents is an important area of research having practical utility. For example, due to the growing production of transplutonium elements (TPE) and to progress in atomic power energetics, the problem of TPE extraction from highly acidic media is becoming vitally important. Organophosphorus compounds such as trialkylphosphates, phosphine oxides etc., constitute a class of ligands which have been intensively used [1–54]. Furthermore, bidentate neutral organophosphorus compounds have proved better extractants than monodentate ones probably due to chelate effect [55,56]. These have recently attracted still more interest as it has been found that some of them can be used for removing long lived TPE from waste nuclear fuel element solutions in order to eliminate the potential danger brought about by TPE accumulation and regeneration [57].

In this review, we intend to present extraction properties of bidentate organophosphorus compounds, namely ditertiaryphosphine dioxides (**I–III**): $R_2P(O)(CH_2)_nP(O)R_2$ (**I**), $Ph_2P(O)CH{=}CHP(O)Ph_2$ (**II**), $Ph_2P(O)C{\equiv}CP(O)Ph_2$ (**III**), where R may be an alkyl or aryl group which may be the same or different and *n* varies from one to six. Apart from a consideration of the chelate effect of these ligands, the correlation between the extraction of a metal ion and the chain length of $-CH_2-$ groups is examined, together with the effect of a substituent on phosphorus, etc. The synergistic effect of these ligands in the extraction of metal ions with other reagents has been included.

Before discussing the details of the extraction properties, two of the most important factors that must be considered in the partition of inorganic salts between water and an organic solvent are: (i) differences in the free energies of solvation in each phase of the two-phase system for both cations; and (ii) the complex forming abilities of the anions. Considering free energies of solvation, perchlorate should be capable of being well-extracted because this anion is large and symmetrical with a small charge. With its symmetry and size favouring charge delocalisation, the perchlorate ion is able to form ion pairs in the organic phase. Another factor favouring the extraction of perchlorate salts is their high activity in concentrated solutions. This may cause the overall free energy change to be highly negative for the transfer of the salt from the aqueous to the organic phase and thus extraction may be good. However, the complexing ability of perchlorate is negligible and if the organic extractant is unable to satisfy the coordination requirements of the metal cation, water molecules will be coordinated. This would tend to decrease extraction since it would make the cation more hydrophilic, off-setting to some extent the hydrophobic qualities introduced by coordination of the organic ligand.

B. METHODS OF PREPARATION OF LIGANDS

Various ligands have been prepared by adding 30% H_2O_2 solution to an appropriate ditertiaryphosphine in acetone followed by refluxing and crystallisation from a suitable solvent [58–60]. The oxidation in some cases has also been carried out in benzene [61,62]. $KMnO_4$ in acetone also acts as an oxidant [63].

Alternatively, the ligand MBDPO has been prepared from the reaction of 1,1-methylenebis(dichlorophosphine oxide) with a two fold excess of n-butylmagnesium chloride in benzene [64,65].

The ligands, EDPO, PDPO, BDPO and HDPO have also been prepared via the formation of a quaternary salt [66]. This method is particularly useful for PDPO preparation. (For detailed properties of ligands used see refs. 59, 61, 64–79.)

C. GENERAL PROCEDURE OF EXTRACTION

The ligands being soluble in most organic solvents have been taken in a suitable solvent such as benzene, 1,2-dichlorobenzene, chloroform etc. The solvent has been chosen in such a way that its miscibility with water was very small. For extractions at high temperature, a mixture of polyphenyls was used. Ligand solutions of different concentrations have been employed for extraction of a metal ion from aqueous acidic solution. After shaking well, the organic layer is separated and analysed for composition using conventional techniques or (in some cases) radiometry. Studies like IR, UV etc. have been carried out in many cases for the characterisation of composition of complex species.

D. EXTRACTIONS OF METAL IONS

A list of metals which have been extracted using these particular ligands is given in Table 1.

The general equation for the extraction is

$$M^{a+}_{(m)} + aX^{-}_{(m)} + pL_{(o)} \rightleftharpoons MX_aL_{p(o)}$$

and that for the equilibrium constant is

$$K_M = \frac{[MXaLp]_{(o)}}{[M]_{(m)}[X]^{a}_{(m)}[L]^{p}_{(o)}}$$

where o refers to the organic phase and m to the mineral phase. Since the concentration of X^- remains constant, we can have

$$K'_M = \frac{[MX_aL_p](o)}{[M]_{(m)}[L]^{p}_{(o)}} \tag{1}$$

(i) Transition metal ions (d-block elements)

The ligand EODPO extracts Sc(III) and Fe(III) from aqueous HNO_3 solutions [80,81]. It is found that the distribution coefficient of Sc(III)

TABLE 1

Metal ions extracted

Metal ion	Metal ion
Sc(III)	Ce(III)
Fe(III)	Pr(III)
Co(II)	Nd(III)
Y(III)	Sm(III)
Zr(IV)	Pm(III)
Hf(IV)	Eu(III)
Nb(III)	Tm(III)
Ta(III)	Th(IV)
Zn(II)	Pa(V)
Al(III)	U(VI)
Ca(II)	Pu(IV)
	Am(III)
	Cf(III)
	Bk(III)
	Cm(III)

between acid solutions and a 0.02 M solution of the ligand in benzene increases sharply from about 30 to nearly 80 when the acid concentration is increased from 0 to 0.5 M l^{-1} but decreases at higher acid concentrations to about 10 for 4–8 M acid solutions. Also at a constant acid concentration (1 M), the distribution coefficient increases with increasing ligand concentration. Sc(III) is probably extracted into the organic phase as $Sc(NO_3)_3 \cdot 2L$. EODPO is a most effective extractant for Sc(III) compared to monodentate trioctylphosphine oxide. Similarly Fe(III) is extracted using 0.1 M concentration of the ligand in benzene. It was observed that Fe(III) cannot be extracted from 1 M phosphoric acid.

Co(II) has been extracted from a eutectic of molten $LiNO_3$-KNO_3 at 160°C using the ligands, EDPO, PDPO, BDPO and HDPO in a mixture of biphenyl, *o*-terphenyl and *m*-terphenyl [66]. This ion is extracted as $Co(NO_3)_2L$, the order of extraction being EDPO < PDPO < HDPO < BDPO (see Table 4).

The ligand MODPO extracts Y(III) from its HNO_3 solution with 1.6–6% kerosene solution of the ligand [82]. The extraction depends on concentrations of HNO_3, NH_4NO_3 and the starting concentration of the metal ion in the aqueous solution.

Zr(IV) and Hf(IV) have been extracted from $HClO_4$ and H_2SO_4 using MHDPO extractant in a solvent like *o*-dichlorobenzene [83,84]. The extraction depends on the concentrations of H^+, SO_4^{2-} and ClO_4^- as well as on the concentration of the ligands (Tables 2 and 3). The complex species of the type, $M(OH)L_3$, MSO_4L_2 and $M(ClO_4)_4 \cdot 2HL$ (M = Zr, Hf; HL = MHDPO) are probably formed. The extraction from HNO_3 follows a similar pattern [85]. Nb[III] and Ta(III) have also been extracted from H_2SO_4 and HNO_3 with MHDPO [86]. The presence of the species, $M(OH)_4L \cdot HL_n$ and $M(OH)_3L_2$ ($n = 1,2$) in the organic phase has been indicated in case of

TABLE 2

The extraction of Hf with MHDPO

[MHDPO]=2×10^{-3} M		[MHDPO]=5×10^{-3} M		Ref.
[Hf]M	D	[Hf]M	D	
15×10^{-4}	18	15×10^{-4}	680	83
78×10^{-5}	42	78×10^{-4}	343	83
39×10^{-5}	94	39×10^{-5}	186	83
19×10^{-5}	106	19×10^{-5}	431	83
91×10^{-6}	107	91×10^{-6}	652	83
53×10^{-6}	110	53×10^{-6}	648	83

TABLE 3

The extraction of Hf with 10^{-3} M MHDPO

$[HClO_4]$M	D	$[HClO_4]$M	D	Ref.
10	16	45	99	83
20	83	55	370	83
30	216	65	450	83
35	144	75	700	83

H_2SO_4, while the complexes of composition 1:2 (M:L) are formed in case of HNO_3. The extraction in HNO_3 is greater than in H_2SO_4 and depends on acid concentration.

(ii) Main group ions

There is very little information on the extraction of main group metal ions. Only Al(III), Ca(II) and Zn(II) have been extracted. Using the ligand MHDPO in *o*-dichlorobenzene, Ferguson and Banks [84] have extracted alkaline earth metal ions from $HClO_4$ solution. The extracted species were of composition, 1:3 (metal:ligand). However, these ions could not be extracted quantitatively. Smirnov et al. [80] have also extracted Ca(II) and Al(III) from aqueous $HClO_4$ with a benzene solution of EODPO. It was noticed that, like Fe(III), H_3PO_4 suppresses their extraction. Zn(II) has been extracted synergically using pivaloyltrifluoroacetone or benzoyltrifluoroacetone with MDPO or EDPO [87,88]. ZnR_2L type of chelates were formed.

(iii) Lanthanides and actinides

Using the solutions of the ligands, EDPO, PDPO, BDPO and HDPO in a mixture of biphenyl, *o*-terphenyl and *m*-terphenyl (terphenylene OMD), the extraction of '4*f*' elements, Pr(III), Eu(III) and Tm(III) and '5*f*' elements, Am(III), Cm(III) and Cf(III) has been carried out from molten alkali nitrates, $LiNO_3$–KNO_3 at 160°C [66,89–91]. The lanthanides were extracted as $M(NO_3)_3L_2$ and actinides as $M(NO_3)_3L_2$ (except HDPO) and $M(NO_3)_3$EDPO. It may be noted here that HDPO did not extract actinides under the experimental conditions used. The values of the extraction constants are given in Table 4.

The order of extraction of these elements is:
Pr, Tm: HDPO < PDPO < EDPO < BDPO
Eu: PDPO < HDPO < EDPO < BDPO

TABLE 4

Extraction constants (K'_M)

M	EDPO	PDPO	BDPO	HDPO	TOPO	Ref.
Co	31 ± 1	39 ± 3	130 ± 7	124 ± 7		43
Pr	$(30 \pm 1)10^4$	$(20 \pm 2)10^4$	$(63 \pm 5)10^4$	$(15 \pm 3)10^4$		43
Eu	$(32 \pm 2)10^5$	$(40 \pm 5)10^4$	$(37 \pm 3)10^5$	$(11 \pm 3)10^5$		43
Tm	$(17 \pm 1)10^6$	$(53 \pm 3)10^5$	$(32 \pm 2)10^6$	$(40 \pm 3)10^5$		43
Am	2.1 ± 0.3	9.1 ± 0.6	4.3 ± 0.4		0.28 ± 0.03	91
Cm	1.9 ± 0.3	25 ± 2	11.5 ± 1		0.24 ± 0.03	91
Cf	4.4 ± 0.05	4.6 ± 0.5	4.6 ± 0.5		0.10 ± 0.02	91

Am, Cm: PDPO > BDPO > EDPO
Cf: PDPO ≃ BDPO ~ EDPO
For these ligands, the values of K'_M obtained for actinides are much lower than the values obtained for lanthanides. The great difference of behaviour between the elements in these two inner transition series allows quantitative separation of elements of the '4*f*' and '5*f*' series. For instance, the separation factor between Eu(III) and Am(III) is more than 10^4 in the case of BDPO. For lanthanides, the ligand BDPO has been found to be an excellent extractant from the molten state. In general, however, all these are very good extractants for lanthanides. In contrast Co(II) was extracted poorly.

The ligand BODPO (in benzene) extracts Ce(III) from HNO_3 and $HNO_3H_3PO_4$ acid mixture media [80,92]. The extraction increases with increasing HNO_3 concentration up to 3 M because the acid prevents the dissociation and hydrolysis of $Ce(NO_3)_3$. The distribution coefficient reaches a maximum of 5.2 and 800 at 1 M and 3 M HNO_3 concentrations in the aqueous phase. The decrease above 3 M is attributed to the fact that the acid itself is extracted into the organic phase. The compound is extracted as $Ce(NO_3)_3L_2$ from HNO_3 and $Ce(NO_3)_3$ 1.5 L from an HNO_3–H_3PO_4 mixture.

Eu(III) and Am(III) have been extracted from $HClO_4$ medium using the ligands, $R_2P(O)(CH_2)P(O)R'_2$ (R = R' = Ph; R = Ph, R' = octyl; R = R' = octyl) [93,94]. The extracted species are of composition, $ML_m(ClO_4)_3$ ($m = 2, 3$). The extraction constants for Am(III) trisolvates are 10^{15}, 2×10^{14} and 10^{13} respectively (aryl; arylalkyl; and alkyl), while disolvate extraction constants are four orders of magnitude lower. The selectivity coefficient, $\beta_{Am/Eu}$ for MDPO is 6–8. Increasing chain length from CH_2 to $(CH_2)_2$ lowers extraction constants by 4–5 orders of magnitude for MDPO.

Extraction of Eu(III) from aqueous perchlorate and chloride media into benzene solution by benzoyltrifluoroacetone (HTTA) in the presence of MDPO and EDPO and into cyclohexane solution by thenoyltrifluoroacetone (HTTA) in the presence of MHDPO, PHDPO and BHDPO is enhanced [87,95,96]. Eu(III) is extracted as $Eu(TTA)_3L$ (L = MDPO, EDPO, HTTA = benzoyltrifluoroacetone, medium $HClO_4$; and L = MHDPO, PHDPO and BHDPO, HTTA = thenoyltrifluoroacetone, medium HCl) and $[Eu(TTA)(MHDPO)_3](ClO_4)_2$ (HTTA = thenoyltrifluoroacetone). This study is based on the fact that Eu(III) is very poorly extracted by HTTA in the absence of a synergist. The concentration of $Eu(TTA)_3$ in the organic phase will be very small in comparison to that of the octacoordinated mixed complex and will contribute very little to the percentage extraction of Eu(III). Moreover, the extraction becomes possible at lower pH in the presence of phosphine oxide ligands. The percentage of Eu(III) extracted reaches 100 when a stoichiometric amount of organophosphorus compound is added.

TABLE 5

The equilibrium constants for Eu(III) complexes

System	*K*	Ref.
Eu(III), Cl/HTTA, MHDPO	$(1.05 \pm 0.24)10^5$	96
Eu(III), Cl/HTTA, PHDPO	$(2.08 \pm 0.34)10^5$	96
Eu(III), Cl/HTTA, BHDPO	$(8.19 \pm 0.84)10^5$	96
Eu(III), ClO_4/HTTA, MHDPO	$(1.21 \pm 0.37)10^{14}$	96

It is significant to note that *K* (Table 5) increases with increasing length of the bridge between the phosphoryl groups. This order is that which would be expected because the basicity of the phosphoryl groups should increase in the same order. The stability of the 1:1 adducts is in the order BHDPO > PHDPO > MHDPO. It appears likely that chelation to larger Eu(III) is more suited when the number of CH_2 groups connecting two (PO) groups is four. In the case of perchlorate medium, two TTA^- ligands have been displaced in favour of the formation of an ion association complex. The loss of chelation energy has apparently been compensated by the formation of a more stable complex containing three MHDPO ligands.

The extractions of Pr(III), Nd(III), Sm(III), Tm(III) and U(VI) from aqueous HCl, HNO_3 and $HClO_4$ acid media have been carried out with the ligands, MHDPO, EHDPO, PHDPO and BHDPO in 1,2-dichlorobenzene [97–101]. For the extraction of U(VI) from HNO_3 medium, the distribution ratios indicate the order of increasing effectiveness as extractants: MHDPO < BHDPO < PHDPO < EHDPO. The similarity in extraction behaviour of the ligands is due in part to coordinating tendencies of the NO_3 anion. The decrease in distribution ratio with increasing acid concentration is probably best explained by the competition of undissociated HNO_3 molecules for the donor sites of the ligands. The formation of $UO_2(NO_3)L$ is indicated which has coordinated NO_3 groups. Higher solvate formation (1:2) has also been noted in some cases. The extraction of U(VI) from HCl medium is similar to that from HNO_3. Very low distribution ratios were obtained for extractions from very low concentrations of acid with rapid increases to maximum values at 5 M HCl. This maximum is attributed to the formation of a neutral dichloro complex of U(VI) which should be more readily extracted than a positively charged cation [102,103].

The extraction of U(VI) from $HClO_4$ falls into two categories: (i) MHDPO and EHDPO exhibit very high distribution ratios (generally $> 10^3$) and (ii) PHDPO and BHDPO exhibit intermediate values (generally < 30). In comparison, TOPO has a very low affinity for U(VI) perchlorate (< 2). The nature of complexes is 1:2 (metal:ligand). It is apparent that these ligands are good extractants of U(VI) from nitrate and chloride media while only MHDPO and EHDPO are powerful extractants from perchlorate medium. Extractions of Pr(III), Nd(III), Sm(III) and Tm(III) follow trends similar to U(VI) from HNO_3 and $HClO_4$ media. However, the extractions from HCl were quite poor for all the compounds ($K_d < 0.201$ for maximum acid concentration of 7 M). Comparing the individual lanthanides using the same extractant, separation factors were generally quite low with the only factors of any magnitude being obtained for Tm(III) in the presence of the other three lanthanides from 5–7 M HNO_3 using MHDPO and EHDPO (separation factors 10–15).

It was also observed in the extraction of Pm(III), Pr(III), Sm(III) and U(VI) that the replacement of alkyl groups (e.g. butyl, hexyl and octyl groups) on phosphorus by phenyl groups results in large increases in extraction [82,104,105].

The extraction ability of diphosphine dioxides, $[CH_2P(O)Ar_2]_2$, increases with increase in their basicity as for example, observed in case of uranyl nitrate. (Ar group contains substituents like n-BuO, *m*- and *p*-MeO, *m*- and *p*-Me, H, *m*- and *p*-Cl, *m*- and *p*-Br, *m*- and *p*-CF_3 [106,107].)

Th(IV) extraction is quantitative with the ligands MHDPO and MEDPO from HNO_3 medium [108]. The species $Th(NO_3)_4 \cdot 2L$ predominates at higher ligand concentration. Similarly, Pu(III), Pu(IV), Pu(VI) and Pa(V) have been extracted with a number of ligands such as MBDPO, EBDPO, MODPO, MDPO, EODPO etc. as well as *cis*- and *trans*-VDPO, ADPO (using their chloroform solution) from HNO_3 medium [109–111]. The *cis*-VDPO and ligands having phenyl substituents have greater extraction capacity as compared to other ligands. The increase in the number of CH_2 groups decreases extraction ability.

The transplutonium elements (TPE) (Am, Cm, Bk, Cf, Es) U and Eu have been extracted from 1 to 15 M HNO_3 solutions with a number of bidentate organophosphorus ligands [57,109–116]. The effect of reagent structure on their extraction capacity and selectivity has been observed. For instance, let us take MDPO and trace the effect of modifications in its structure on the extraction ability with respect to TPE and Eu. As the bridge elongates to two CH_2 units, e.g. EDPO, the distribution coefficients decrease approximately by a factor of 10^3. The substitution of the ethylene bridge by a vinylene bridge i.e. in *cis*-VDPO, arrests the PO groups in the *cis* position and brings about a thousandfold increase in the distribution coefficients. If the PO groups are bound together by a vinylene bridge arresting them in the *trans* position i.e. *trans*-VDPO or by an acetylenic bridge, ADPO, the reagents stop behaving as bidentates and the distribution coefficients decrease sharply.

The introduction of CH_3– groups into *p*-positions of benzene rings attached to the phosphorus atoms in *cis*-VDPO make the reagent more basic and more nucleophilic and thus $(p\text{-CH}_3\text{C}_6\text{H}_4)_2\text{P(O)CH}=\text{CHP(O)}(p\text{-CH}_3\text{C}_6\text{H}_4)_2$ is a somewhat better extractant of TPE and Eu. It may be noted here that these facts refer primarily to extraction from solutions where the nitric acid concentration is less than 5 M. For instance, the distribution coefficients of all the elements by extraction from 14–15 M HNO_3 with the help of EDPO reagent do not differ as greatly from those observed with the reagents *cis*-VDPO and its tolyl analog as in moderately acidic media. In particular, the distribution coefficient for extraction with EDPO reagent is almost the same as that by extraction with *cis*-VDPO and exceeds that with its tolyl analog.

The substitution of hydrogen in the methylene bridge of MDPO by other atoms or groups such as Cl, allyl, n-dodecyl and vinylidene has been found to decrease the extraction capacity in all cases. Further, the replacement of phenyl by alkoxyl, $ClCH_2CH_2$, alkyl, $PhCH_2$ etc. where direct Ph–PO bonding cannot occur, decreases complex stability, i.e. the extraction is poor.

It has been found that the best extractant of trivalent transplutonium elements is MDPO. This reagent can be used for quantitative group extraction from nitric acid solutions containing nitrates and concentrating of TPE solutions containing 1–15 M HNO_3 and arbitrary amounts of Li, Al, Na or NH_4 nitrates. Table 6 gives some examples of Am concentrating up to a hundredfold.

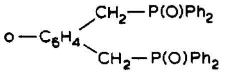
The selectivity of the reagent depends on the structure of the bridge between the PO groups, provided the substituents on phosphorus remain the same [117]. It is known that the reagent selectivity is significantly influenced by fragments preventing individual groups from free rotation and more or less arresting functional group positions and therefore controlling the size of the chelate ring. In a series of compounds with the same functional groups

TABLE 6

Americium extraction from HNO_3 solutions by 0.1 M $CHCl_3$ solution of the MDPO reagent

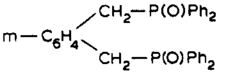
Org/aq.	Extraction %				Ref.
	1 M HNO_3	3 M HNO_3	1 M HNO_3/ 1 M $Al(NO_3)_3$	1 M HNO_3/ 1.8 M $Al(NO_3)_3$	
1:10				99.9	57
1:20	94.9		98.6	93	57
1:50	92.0	98.5	97.0		57
1:100		98.0	93.0	89.0	57

and the same substituents to the phosphorus atoms, the selectivity of dioxides containing flexible saturated bridges (MDPO and EDPO) differed from that of dioxides with non-rigid groups (*cis*-VDPO and its tolyl analog) which restrict the freedom of mutual orientation of PO groups. The latter reagents are relatively more selective with respect to berkelium; in the extraction from concentrated nitric acid, the factor of Bk/Cm separation reaches 10. A similar effect can be provided by introducing substituents into the CH_2 bridge of MDPO; thus in all the cases the factors of TPE separation both from each other and from Eu are increasing in diluted (3 M) as well as in conc. HNO_3. The only exclusion is extraction by the chloro derivative (i.e. MDPO containing Cl in place of H in the CH_2 bridge) from 15 M HNO_3 when the distribution coefficients of all the TPE are the same. Incidentally this reagent displays appreciable selectivity with respect to Am extraction from 1–5 M HNO_3; the factor of Cm/Am separation is about 5 and that of Am/Eu separation is about 7.5.



$$o\text{—}C_6H_4\begin{matrix}\diagup CH_2\text{—}P(O)Ph_2\\ \diagdown CH_2\text{—}P(O)Ph_2\end{matrix}$$

(IV)



$$m\text{—}C_6H_4\begin{matrix}\diagup CH_2\text{—}P(O)Ph_2\\ \diagdown CH_2\text{—}P(O)Ph_2\end{matrix}$$

(V)

A related ligand (**IV**) in which the functional groups are in the *o*-position is highly selective to U(VI), the U/Am separation factor reaching about 10^5. The reagent (**V**) provides a relatively high Am/Eu ratio [57]. It appears that TPE and Eu complex formation with this reagent occurs essentially on account of PO groups in mutual *m*-positions, and this is responsible for the high factors of TPE separation from each other and of Eu separation from Am. The ability of reagent (**IV**) to extract Am(III) proved about 3×10^3 times weaker than that of reagent (**V**). U(VI) extraction by the reagent (**IV**) is highly selective.

It may be noted that the ligands (**IV**) and (**V**) provide for relatively high factors of the TPE separation from each other and of Am from Eu also in moderately acidic media (3 M HNO_3) whereas the reagents containing nonsubstituted linear bridges display good selectivity only in highly acidic media ($>$ 10 M HNO_3).

A significant synergistic effect has been observed in Am(III) extraction from 0.1 M HNO_3 by mixtures of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) and MDPO, *cis*- and *trans*-VDPO in chloroform and dichloroethane [118]. The mixtures of PMBP with MDPO and *cis*-VDPO make it possible to extract Am(III) quantitatively from 0.1–1 M HNO_3. The distribution coefficients are higher in dichloroethane as compared to those in chloroform. The synergistic effect decreases with increase in the concentration of nitric acid.

The extraction of Am in different oxidation states and also of Cm, Eu and Ce from H_3PO_4 solutions by MDPO has been reported recently [119].

Trivalent actinides and lanthanides are extracted only in the presence of $S_2O_8^{2-}$. Am(IV) is reduced by MDPO to Am(III) and then transferred to the organic phase. Am(VI) is not extracted quantitatively from 1 M H_3PO_4. Separation of Am and Ce can be accomplished by controlling the extractant and H_3PO_4 concentration.

E. FACTORS CONTROLLING EXTRACTION AND CONCLUSIONS

From the foregoing survey, it is apparent that these ligands have been utilised chiefly for the extraction studies of lanthanides and actinides. The reason for this difference appears to be due to greater extraction and separation difficulties encountered in lanthanides and actinides as compared to other metal ions. Moreover, there has not been any extensive use of these types of ligand for synthesis and characterisation of complexes as is evident from a recent survey [120]. It is believed that in due course, more and more metal ions will be brought under the purview of extraction studies after their greater success in lanthanides and actinides where these ligands have shown ability to extract quantitatively a number of metal ions. The full scale use of these compounds in TPE extraction from nuclear acidic waste solutions seems very likely in the future. Since the structure of the reagents may be widely varied, one may hope that it will be possible to develop highly selective extractants capable of TPE separation from each other as well as from rare earth elements.

(i) Effect of a substituent on phosphorus on extraction

The replacement of a phenyl group by alkyl groups (or groups related to it) such as butyl, hexyl, octyl, $ClCH_2CH_2$, $PhCH_2$, etc. decreases extraction of metal ion, notwithstanding the fact that an alkyl group enhances the basicity of the ligands. The difference is caused by the chemical nature of the phenyl group and is known as aryl stabilisation. Aryl stabilisation is attributed to an entropy effect explained below.

When a ligand bearing phenyl substituents approaches a metal ion in the aqueous acidic medium, the metal ion may not come in immediate contact with the donor end of the ligand, i.e. PO group. It is possible that phenyl groups which have highly polarisable π-electron density may first come in contact with the metal and there will be some loose interaction between the metal and π-electrons before the donor end of the ligand could bind with the metal. However, if on the other hand the substituent is an alkyl one, there is no similar interaction possible. Thus there will be a greater increase in entropy of the system when the metal–ligand interaction takes place in the case of phenyl ligands as compared to alkyl ligands.

Also the introduction of an electron withdrawing substituent in phenyl leads to a decrease in the extraction while an electron releasing group or a group having a positive inductive effect increases the extraction, seen as for example in the tolyl analog of *cis*-VDPO.

(ii) Effect of number of (CH_2) units between PO groups on extraction

There appears to be no clear cut correlation between the number of $-CH_2-$ groups connecting two phosphoryl groups and extraction. In general, the increase in number of $-CH_2-$ groups leads to a decrease in the extent of extraction. It gives MDPO and *cis*-VDPO an important position with respect to their extraction properties. The greater extraction in the case of MDPO is attributed to the greater stability of the chelated complex having a six membered ring, while in EDPO, PDPO etc. the chelate ring formed is bigger and thus unstable. Now, the greater extraction in the case of *cis*-VDPO is attributed to both fixation of PO groups on the same side and the presence of a double bond connecting the PO groups. The double bond will have an effect similar to a phenyl substituent while approaching a metal ion.

However, in the synergistic extraction of Eu(III) by MHDPO, PHDPO and BHDPO, K increases with increasing length of the bridge between the phosphoryl groups. The stability of the adducts is in the order: BHDPO > PHDPO > MHDPO. The reversal in the order is probably due to change in softness of Eu(III) after binding to benzoyltrifluoroacetone and thenoyltrifluoroacetone. Hence Eu(III) has become more soft and prefers to bind the relatively soft base BHDPO.

(iii) Effect of chelation on extraction

It has been observed that, due to its chelation properties, a bidentate ligand is a far better extractant than a monodentate one. As pointed out above, a bidentate ligand having one CH_2 group separating phosphoryl groups is a better extractant in general than the one having a larger number of CH_2 groups. It is obviously due to the greater stability of a six membered ring formed on chelation to a metal ion, as for example, in the case of MDPO or its analog. Main group ions could not be extracted quantitatively as compared to transition metal ions and this is attributed to more stable chelates being formed by the latter ions, probably due to larger effective nuclear charge on *d*-block elements. It is worth mentioning here that lanthanides or actinides have been more effectively extracted than even transition metal ions. This leads to the conclusion that the interaction between the oxygen of PO groups and a lanthanide or actinide ion is stronger than with other metal ions. This is probably due to preference of hard oxygen to bind with harder '4*f*' and '5*f*' elements. However, a π-accepting ligand would have formed stable complexes with transition metal ions for well known reasons.

(iv) Specificity of a ligand

To illustrate specificity of a ligand, let us consider ligands of the type (IV) which have functional groups in the *o*-position. Type (IV) ligands are highly selective to U(VI) because the U/Am separation factor reaches 10^5 which is not possible in the case of other ligands. In contrast the ligand (V) is more selective for Am(III) and is 3×10^3 times better than the ligand (IV). This is clearly due to size difference of the two ions. U(VI) is much smaller than Am(III) and thus the ligand (IV) is capable of more effective encapsulation as compared to ligand (V) which is more effective in chelating Am(III). Similarly, the greater effectiveness of *cis*-VDPO is chiefly due to fixation of PO groups in the *cis*-position.

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