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SOME ASPECTS OF SYNERGISTIC EXTRACTION OF ACTINIDES AND LANTHANIDES FROM MIXED AQUEOUS-ORGANIC MEDIA

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REVIEWS

ABSTRACT

Various aspects of the synergistic extraction and separation of actinides and lanthanides from mixed aqueous-organic solutions (polar media) have been reviewed. Notable recent developments as well as its current status in solvent extraction system.s where the aqueous acidic phase contains an organic solvent which is completely miscible with water, are presented briefly. In general, extraction increases in the presence of an organic component. The less polar the additive, the higher is the tendency to form neutral metal complexes which ultimately brings about an increase in the extraction. In a polar media, synergism has mostly been observed, though antagonism is not uncommon. An attempt has been made to classify the factors that play an important role in polar phase extractions. Also, their influence particularly on the extractability of actinides and lanthanides is discussed. The discussion is limited to the factors affecting the extraction equilibria, effect of dielectric constant of the polar medium, solvation of the extracting agent and to the composition and stability of the metal complex in the organic phase.

Hydroxyl (OH^-) bearing organic additives, e.g. alcohols and solvents not containing the hydroxyl group such as acetone, dimethylsulphoxide, tetrahydrofuran, amides and acetonitrile etc. are the two major classes of organic additives considered in these studies. Generally, synergistic effect in extraction of the ion-association (TBP, TOPO, sulphxoides etc.) or anion exchange (amines etc.) type is relatively more pronounced compared to other extractions. A tabular summary concerning extraction of actinides and lanthanides from polar media is appended for ready reference.

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I INTRODUCTION

Mixed aqueous-organic media have attracted much attention only recently in solvent extraction of systems that contain in the aqueous phase, an organic solvent completely miscible with water. Since the amount of water coextracted with the metal salt affects its distribution, the partial replacement of water by an organic component will therefore affect its extraction behaviour. It is reported(1-7) that the extraction of some metal salts is influenced to different extents which may help in useful interseparations. Such mixed media have been for a long time in general use in ion-exchange studies and separations(8-12), nevertheless their application in extractions has been infrequent. However, several potential applications of such systems in chemical and radiochemical separations have been suggested. For example, separation of silver and mercury and also silver and selenium, which previously seemed not feasible from pure mineral acid solutions was made possible from mixed media(13). Furthermore, such synergic effect is certainly valuable from analytical point of view, since it is one of the factors affecting extraction and hence increases the range and choice of extraction conditions. Although the increase of acidity or salting out agent's concentration may also significantly effect extraction and separation, use of organic additives may be more convenient and/or suitable for many reasons. Thus the application of highly acidic solutions is generally unfavourable and that of salting out agents sometimes inconvenient since it is difficult to eliminate them from the aqueous phase. Organic solvents e.g. acetone, alcohols etc. on the other hand, can easily be distilled off. Alternatively extraction data in mixed media are also essential for combined ion exchange, extraction separation procedures in such media.

A complete understanding of the role of organic additives is still open to criticism. At present, little information is available on the effect on metal extraction by the addition of a polar solvent to a non-polar one. Despite this, their studies nevertheless are useful even from the practical point of view. Addition of alcohol significantly improves the separation of uranium, thorium and protactinium on extraction by tri-n-octylamine(14). Likewise, the presence of ethanol or acetone reduces the number of stages required for separation and purer products are obtained. Furthermore, oil or gel formation at the interface is prevented by decreasing the difference between polarities of the two phases; either by adding a liquid less polar than water (eg. acetone) to the aqueous phase or by using more polar solvents as the diluent for the extractant(15).

Recently an attempt has been made to review the present-day state of the extraction chemistry of inorganic substances from aqueous-organic media(16). The chemistry of such synergic systems involving actinides as well as lanthanides is, however, sparse and scattered too. Table 1 gives a summary of polar phase extractions of these elements by different extractants. The aim of this article is to review briefly the progress made in the field of extractive separations of these elements from polar phases and list out the underlying principles involved in such systems.

II ORGANIC ADDITIVES

Physical properties

Some relevent physical characteristics of the organic additives that have been frequently employed for polar phase extraction studies are summarized in Table 2. An essential requirement for such organic solvents is that they should be soluble in water in all proportions. Roughly, they fall into two categories: (i) hydroxyl (OH^-) bearing organic additives, (e.g. alcohols), (ii) solvents not containing the hydroxyl group (acetone, DMSO, THF, CH_3CN, dioxane, amides, pyridine).

Mutual solubility and swelling of the organic phase

Detailed account of mutual solubility of the various components as well as the swelling of the organic phase seem to have not been reported except in one instance(1). At concentrations of alcohol of about 30% and less in polar phase, the change in volumes of phases has been found to be of the same order as in the case of pure aqueous mineral acid solutions. At higher alcohol concentrations the swelling of the organic phase becomes noticeable with long chain alcohols (propanol and butanol). In other words, swelling increases with increasing chain length and dielectric constant of the alcohol. Swelling also increases with the percentage of alcohol added. It depends further on the nature of the extractant as well as the diluent employed too. Sometimes only one phase is formed when the concentration of alcohol is increased above a certain limit. The concentration of alcohol above which one phase is formed decreases with increase in chain length of the alcohol.

Relative permitivity of equilibrium organic phases

Studies on relative permitivity of equilibrium organic phases have been reported only in the case of alcohols used in polar phase extractions(3). Owing to partial miscibility of a weak polar organic phase and a polar aqueous-alcoholic phase a certain amount of alcohol is transferred into the organic phase. In view of higher permitivity of alcohols (CH_3OH 31.5, C_2H_5OH 24.3, C_3H_7OH 20.1, 2-C_3H_7OH 18.3, all at 25° (see ref. 31) changes in the relative permitivity of the organic phase may be expected. Hala et al(3) studied the dependence of the relative permitivity of the equilibrium benzene phase on the initial alcohol concentration, and found it increased with the total alcohol concentration following the order : $CH_3OH < C_2H_3OH <$ 2-$C_3H_7OH <$ 1-C_3H_7OH even though the relative permitivity of alcohols decreases in this series. It is caused by the sequence of solubility of alcohols in the equilibrium organic phase.

III POLAR PHASE EXTRACTION OF ACTINIDES

Thorium

Extraction of thorium from 3.9 M HNO_3 medium with 0.3 M TLA has been investigated in the presence of alcoholic additives for improved extractability$^{(1)}$. Values of E for Th in 50% ethanol and 10% isopropanol were 10 and 2.5 respectively while that from pure acid medium it was 0.35. Furthermore, separation of thorium from selenium, silver, cobalt and zinc in the presence of 10% isopropanol was found to be much more effective than from pure aqueous solutions. Most important being the separation of iron from thorium which was only possible on the addition of 10% isopropanol.

Alian and others$^{(14)}$ recommended the use of alcoholic and acetonic solutions for the separation of thorium-234 (UX_1) from uranium(VI) by extraction with trioctylamine from 4.8 M HCl medium. Maximum yield of about 98% could be easily achieved from mixed aqueous organic media. Another noteworthy feature of this method is that the loaded extractant can be used as a cow for ^{234}Th whereby the latter can be miled intermittantly.

Schmid and Kenndler$^{(17)}$ examined the influence of methanol and ethanol introduced to the aqueous nitric acid phase on the extraction of Th(IV) with Aliquat-336 and TLA. Noticeable change in the extraction coefficient of thorium was explained by the shift of the equilibrium of the metal nitrate complexes and by the enhanced extraction of acid too.

Haggag et al(18) found a marked enhancement on the extraction of Th with a liquid cation exchanger solvent, HDEHP, by the addition of alcohols and acetone. Synergic enhancement obtained from halide and sulphate media was of the order of about 100.

A distribution study was carried out on the extraction behaviour of Th(IV) and other elements using 5% TOPO in xylene from mixed solvents(19). Extractability of Th from 3.6 M HCl polar medium followed the trend : methanol > ethanol > isopropanol > acetone.

Extraction and separation of Th(IV) from alcoholic and acetonic solutions of HCl and H_2SO_4 with HDEHP has been suggested(4). U-Th separation can be achieved by successive extraction from 11 M HCl or 4.5 M HCl in presence of 50% ethanol. Addition of isopropanol to the aqueous acidic phase has been recommended to achieve Ce(III)-Th(IV) separation. This study gave no definite conclusions about the composition of the extractable complex which may be due to the formation of mixed complexes having different compositions depending upon the ionic strength of the aqueous solution.

Protactinium

Work on protactinium extraction is particularly interesting because of its production in reactors using thorium and also because of its complicated aqueous chemistry. Thus protactinium exists in the form of various hydroxo rather than simple metallic or oxo complexes in HCl and HNO_3 solutions(20,21). Allen et al(1) reported the extraction of Pa from HCl as well as HNO_3 media with trilaurylamine, tributyl phosphate and isobutyl methyl ketone in the presence of water-miscible alcohols and acetone. These additives were found to increase considerably the extraction of Pa with all the extractants. However, the influence was relatively less in the case of TTA. In mixtures of an acid with various alcohols, the influence depended on the alcohol concentration, the acidity and on the chain length and dielectric constant of the alcohol introduced in the extraction system. Fig.1 shows the results of varying amounts of alcohols and acetone on the value of E for protactinium extraction from 2.9 M HCl by 0.3 M TLA in xylene.

Alian and coworkers$^{(14)}$ further extended the use of trioctylamine in the polar phase extraction of ^{234}Pa (UX_2) from uranyl salt in ~ 5 M HCl medium and devised a rapid method for the continuous milking of ^{234m}Pa. As a solvent, a 10% TOA in benzene was employed. The separation of ^{234m}Pa in a pure state, as developed for a polar medium, is valuable for dead time, disintegration and half life measurements.

Uranium

Alian and coworkers$^{(14)}$ have attempted the synergistic extraction of macro amounts of uranium by successive batch extraction with 10% TOA in benzene from partially nonaqueous media. Uranium extraction considerably increased in the presence of organic liquids such as alcohols, acetone etc. This enhancement has been attributed to the decrease of hydration in presence of these liquids which favour the formation of the negatively charged extractable uranyl chloride complexes. The data on uranium extraction in presence of ethanol and acetone showed that the U partition ratio $\gtrsim$ 50. The effect of alcohols and acetone clearly increased with the decrease of dielectric constant of the organic additive.

Shabana and Hafez$^{(2)}$ investigated the effect of water-miscible alcohols and acetone on the extraction of U(VI) with 30% TBP in kerosene from 1.1 M HCl as well as 0.5 M HNO_3 solutions. Their results showed that its extraction from both acids increased with the increase of acetone concentration and the decrease of alcohol concentration. The effect of additives in nitric acid case was generally more pronounced that in the case of HCl. Acetone gave the most useful effect. Thus in 1.1 M HCl, E for uranium increased from 0.85 to ~ 5 and, in 0.5 M HNO_3 it increased from 3 to 6. At low additive concentration, the dehydration effect due to the presence of additives should lead to an increase in the metal extraction. With the increase of the additive concentrations, the extraction of acid increases (Table 3) leading to a drop in metal extraction, as in the case of isopropanol. However, the effect of alcohols decreased in the order : methanol $<$ ethanol $<$ isopropanol which is parallel to their dielectric constants (Table 2). On the other hand, U(VI) extraction considerably increased with increasing acetone concentration in the polar phase . Log-log plots of E vs TBP concentration gave slopes of nearly 2 in both acids thereby suggesting that the nature of species is not influenced by the presence of additives. Uranyl chloride as well as uranyl nitrate are extracted by TBP as the neutral solvates $UO_2Cl_2.2$ TBP and $UO_2(NO_3)_2.2$ TBP respectively$^{(32,33)}$.

Shabana and Ruf$^{(22)}$ explored the effect of some organic components, viz.methanol, dioxane, and acetone on the extractability of uranium(VI) with Aliquat-336. Here, the distribution coefficient of U(VI) was markedly affected by replacement of water with these substances and the extractability varied in the order : methanol $\angle$ dioxane $\angle$ acetone similar to that observed in extraction of plutonium. Extraction behaviour of uranium(VI) from pure nitric acid solutions was in line to that from partially non aqueous solutions. Higher E values being about 4 times more than from pure acid solutions, were obtained by introducing the organic solvents particularly at low nitric acid concentrations. Linear relationship found between E and extractant concentration at 4 M HNO_3 solution in absence or presence of 50% organic additives in the polar phase, was attributed to the existence of the singly charged anion, $[UO_2(NO_3)_3]^-$. Moreover, the presence of the organic solvents used is presumed to have no effect on the extraction mechanism but only on the magnitude of the extraction coefficient. The stripping of hexavalent uranium from loaded organic phase was accomplished without any problem by successive washings with dilute nitric acid solutions (less than 0.4 M HNO_3). Application of 5% TOPO in xylene has also been recommended in its polar phase extraction$^{(19)}$.

Recently, extraction and separation of U(VI) from Ce(III) or Th(IV) from different mixed media with HDEHP has been achieved$^{(4)}$. Ce(III) could be eliminated from U(VI) at 4.5 M HCl or H_2SO_4 solutions as well as at 2.5 M HCl in presence of 50% ethanol which, however, was more plausible.

Neptunium

Alian and associates(23) extended the use of TLA in the polar phase extraction of neptunium from HNO_3 as well as HCl solutions. Extraction of neptunium from HNO_3 medium was slightly influenced by alcoholic and acetonic additives, while the effect was considerable in case of extraction from HCl solutions. For example, E for Np(IV) was 0.1 in pure aqueous 4.2 M HCl and was greater than 10 in a solution of 4.2 M HCl in 40% acetone for extraction into TLA. The presence of these components in the aq. phase brought about an increase of nitric acid extraction. The effect increased in the order : methanol $<$ ethanol $<$ isopropanol $<$ acetone. The effect also increased with the increase of the proportion of the organic additive present. This difference in additives effect could be explained in view of the results on the extraction of the acid itself. HNO_3, being highly extractable in the presence of additives, competes with the metallic species for the available solvent molecules and thus compensates the dehydration effect of additives which tend to increase extraction. The latter effect predominates in case of chloride extraction.

Under similar conditions, the effect of additives in TBP extraction is generally lower than in the case of TLA extraction. Log-log plots of E vs $[\text{TLA}]_{org}$ have slopes of about 1.6, irrespective of the alcohol concentration in the aq. phase. This suggests that the nature of Np(VI) extraction is not much influenced by the presence of alcohols. Np(V) extraction considerably increased with increasing acetone concentration in the polar phase, while alcohols had only a slight effect.

Shabana and Ruf(19) performed a distribution study on the extraction behaviour of Np(IV) from mixed HCl-organic media using 5% TOPO in xylene. Higher extractability of Np(IV) in presence of 50% alcohols has been attributed to the fact that in such solutions the hydration shell of the metal ion is destroyed and the specific interaction of the cation with the extractant can become more pronounced. At similar organic additive contents the sequence of E for Np(IV) was found as acetone > iso-propanol > ethanol > methanol which is in accordance with their dielectric constants. Straight lines with slopes of about 2 obtained for Np(IV) in presence or absence of organic additives implied that their presence causes no chemical effect on the extraction mechanism but only a physical one which affect the magnitude of extraction coefficient. Use of TOA (7.5%) as well as HDEHP (0.75 M) has also been reported for the polar phase extraction of Np(IV)(24). Recently, Shabana(25) extended the application of a quarternary amine (TCMA) for its extraction.

Plutonium

As an extension of their previous study on plutonium extraction from mixed aqueous media to achieve its separation from uranium(26) Shabana and Ruf(5) carried out systematic studies on the extraction behaviour of Pu(IV) with Aliquat-336 in xylene from partially non-aqueous solutions. Data was obtained for its extraction from various nitric acid concentrations in the presence of 50% (v/v) methanol, acetone and dioxane. Extractability increased following the trend methanol < dioxane < acetone, and the maximum extractability shifted towards lower acidity in presence of organic additives. This was ascribed to the enhancement of acid activity by replacement of water with organic additives. E of Pu at 4 M HNO_3 was two times higher in presence of acetone as compared with that in pure acid solution. Another similar study indicated that Pu(IV) could be easily separated from Am(III) and Cm(III) with 30% Aliquat-336 in xylene at intermediate nitric acid concentrations from alcoholic and acetonic mixed solutions(27). Furthermore, the mutual separation of Am(III) and Cm(III) may be also achieved. Maximum extractability of Pu(IV) also shifted towards lower nitric acid molarity and it increased with organic additive concentration (Fig.3). Here formic or acetic acid served as stripping agents.

Extraction behaviour of plutonium(IV) from nitric acid media by two long chain aliphatic sulphoxides, namely di-n-hexylsulphoxide (DHSO) and di-n-octylsulphoxide (DOSO) has been investigated by us recently (28a) in the presence of several water-miscible organic liquids. Methanol, ethanol, n-and isopropanol, dioxane, acetone as well as acetonitrile were used as the organic components of the polar phase. These additives affected the extraction to varying degrees and E of Pu(IV) increased in the order : dioxane $\angle$ methanol $\angle$ ethanol $\angle$ acetone $\angle$ acetonitrile (Fig.4). Extractability of plutonium increased 2-3 fold with increasing concentration (upto 20%) of acetonitrile, acetone, methanol and ethanol while it diminished with increasing concentration of n-and isopropanol. At high concentration of the former, the synergism changed into antagonism.

Volume changes are supposed to be the cause of antagonism in the case of n- and isopropanol(3). Among these organic additives maximum enhancement in Pu(IV) extraction was observed in the presence of acetonitrile (Table 4). The relative increase in extraction was found to be more at lower sulphoxide concentrations. At higher HNO_3 concentrations, Pu(IV) extraction was relatively less influenced by introducing organic component in the polar phase, whereas higher E values were obtained by adding organic solvents particularly at low acid concentrations. Maximum extractability was obtained at relatively lower acidity in presence of an organic additive (Fig.5). This has been attributed to the increase of effective acid concentration in the polar phase by replacement of water with an organic solvent.

Americium/Curium

Shabana and Ruf(27) studied the distribution of Am(III) as well as Cm(III) from nitric acid-organic solvent mixtures employing 30% Aliquat-336 in xylene as the extractant. Fig.2 shows that extraction of both the elements increased considerably in presence of 50% acetone, though it decreased with increasing nitric acid concentration. Mutual separation of Am(III) and Cm(III) is reported to be possible at low acid concentrations by such polar phase extraction.

Recently, extraction behaviour of Am(III) from aqueous nitrate media by three long chain aliphatic sulphoxides has been investigated in the presence of alcohols, dioxane, acetone as well as acetonitrile in the polar phase(28b). Extractability of Am increased 5-10 fold with increasing concentration of some of these additives except higher alcohols. Essentially quantitative extraction (> 95%) could easily be obtained in the presence of acetone or acetonitrile from HNO_3 concentration in the range between 0.01M - 1M containing 2.5M $Ca(NO_3)_2$ as the salting-out agent.

IV. POLAR PHASE EXTRACTION OF LANTHANIDES

Alian and Born(29) studied the liquid-liquid extraction of Ce(III) and Tb(III) from a polar medium with the well known liquid cation exchanger, bis (ethyl, 2-hexyl) phosphoric acid (HDEHP) from varying HNO_3, HCl and $HClO_4$ media. Extraction of both the elements was found to decrease significantly in presence of 10-50% acetone. Maximum synergistic effect for Tb(III) extraction was, however, encountered from dilute nitric acid solutions.

Extraction and separation of Ce(III) from mixed hydrochloric acid-organic solutions using 5% TOPO in xylene as the extracting agent merit mention here(19).

Shabana and Ruf(4) devised elegant methods for the mutual separation of U(VI) - Ce(III) as well as Th(IV) - Ce(III) using different mixed media with HDEHP. Ce(III) could be eliminated from U(VI) at 4.5M HCl or H_2SO_4 solutions and at 2.5M HCl in presence of 50% ethanol being more plausible. Th(IV) could be easily separated from Ce(III) on the addition of isopropanol. Here, addition of this solvent to the aqueous phase used was recommended to achieve Ce(III)-Th(IV) separation.

Nedden and associates(30) examined in detail the influence of some organic additives, viz. ketone, carboxylic acid, alcohol or phenol on extraction of Eu(III) by different organophosphorus acids. The aqueous phase consisted of a 1M (H, Na) ClO_4 solution of pH1, benzene being the diluent. Only metal complexes formed with di-acidic extracting agents exhibited an increase in extraction, by a factor as large as 100, while those formed with mono-acidic ones showed antagonistic effects. This difference was attributed to the presence of free P-OH groups on the complexes formed by di-acidic extracting agents. In the region of medium alcohol concentration, a sharp decrease in europium extraction was observed for all the organophosphorus extractants. When the alcohol content exceeded 50%, the dielectric constant of the organic phase increased appreciably and an increase in the extraction of metal cation was observed. This phenomenon has been explained by the enhanced extraction of mixed complexes of the type:

$$Eu(ClO_4)_x \cdot (AH)_{3-x} \; (x = 0 \rightarrow 3).$$

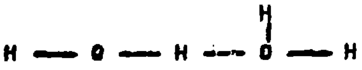
Data suggested that the variation in E of the metal cation is due to a solvent effect rather than to the metal cation, as indicated by the perfect parallelism of the two extraction curves of Eu(III) and Gd(III).

V. THEORETICAL CONSIDERATIONS

Both synergism as well as antagonism are commonly encountered in extractions from polar phases. Presence of completely water-miscible organic solvents in the aqueous phase mostly enhances the extraction of metal cations with different extracting agents and sometimes suppresses their extraction too. Existing data suggest that several factors are involved, and partly their effects neutralise each other. Theoretical interpretation of various parameters that play prominent role in polar phase extractions is more difficult because of insufficient data on the properties of electrolytes in mixed media. The influence of organic additives can be related to a number of mutually related factors. Thus, these may influence complex formation, solvation and ionic and molecular interaction in the aqueous phase. Partition of water-miscible liquids between organic and aqueous phases may also influence complex formation in the organic phase.

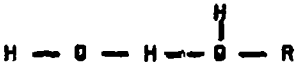
In consequence to replacement of water by an organic additive, hydrated metal cation in the aqueous phase gets gradually dehydrated(34). This results in a parallel increase of ionic interaction, and hence of association in polar media. Stability of the negatively charged chloro complexes in solution was reported to be sufficiently enhanced on addition of water-miscible organic components(35-42). Evidently it must bring about a synergic effect in extraction of the ion-association (TBP, sulphoxide extraction etc.) or anion-exchange (TLA, TOA extraction etc.) type. This synergism can be attributed to the fact that dissociation of electrolytes decreases in the presence of organic substances with lower dielectric constants. This should cause a distinct enhancement in the degree of extraction of the types mentioned.

Intermolecular association, also referred to as 'molecular compound' formation through a hydrogen bond is present between two or more water molecules, a water molecule and a molecule of any other hydroxylic compound, or two molecules of the latter$^{(43)}$. Thus a mixture of water and alcohol probably contains compounds such as:



$H - O - H \cdots \overset{H}{\overset{|}{O}} - H$

(I)



$H - O - H \cdots \overset{H}{\overset{|}{O}} - R$

(II)

$R - O - H \cdots \overset{H}{\overset{|}{O}} - R$

(III)

and a mixture of water and a ketone contains, besides compound (I), the compound $H - O - H \cdots OCR_2$(IV). The tendency of formation and comparative stability of complexes I, II, III and IV has some influence on ion-association in the polar phase and hence on the extraction.

In a recent review$^{(16)}$, Hale examined the various factors that play some role in extractions from mixed solutions in order to evaluate their possible contributions. These are;

(i) Changes in the structure of water

(ii) Changes in ion association

(iii) Solubility of extracted metal complexes in the polar phase

(iv) Changes in ionic strength resulting from volume changes

(v) Organic phase effects

An increase of metal ion extractability can be expected in cases where the organic additive of the polar phase promotes the structure of water$^{(16)}$. The structure - making effect has been observed in aqueous solutions containing small amounts of alcohols$^{(44-48)}$ acetone$^{(48)}$ and dioxane$^{(49)}$ and also in water-tetrahydrofuran with high THF contents$^{(50)}$. This effect played no role in the extraction of Cs^+ ion-pairs from mixed solvents$^{(7)}$, whereas higher concentration of alcohols(46,47) and dioxane(49) as well as those of DMSO over the whole concentration range(51) are deemed to act as structure-breakers, whereby the energy gain from WSEIP (water structure-enforced ion-pairing) was eliminated. Obviously, it was considered as one of the reasons for the observed diminished extractability of Ce^+ ion-pairs from mixed media. Probably it also played some role in extractions from water-urea mixtures, since urea is known to be a structure-breaker(52).

According to Nedden et al(30), a complete interpretation of polar phase extractions should include three more main factors besides the solvation of the extracting agent: (i) the dielectric constant of the organic phase which influences the stability of the complexes so that the metal extraction should diminish when the dielectric constant increases, (ii) specific interactions between the second solvent and the extracting agent on one side and the metal complexes on the other side. Here solvation modifies the partition ratio of the extractant which happens to be a supplementary reason influencing the distribution of the cation; and (iii) a change in the stoichiometry of the extracted metal complexes.

Briefly speaking, several other factors which also influence extraction, such as the ionic radii, ionic charge and ionic strength, all of which are being altered in the presence of organic additives(53), should also be taken into account while examining polar phase extractions.

VI. ACKNOWLEDGEMENT:

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TABLE 1

Synergistic Extraction of Actinides and Lanthanides from Mixed Aqueous - Organic Solutions with Different Extractants - A Summary

Element	Extractant	Aqueous acidic medium	S.E.*	Ref.
Th	TLA	HNO_3 (3.9 M)	25	1
	TOA	HCl (4.8 M)	-	14
	Aliquat-336, TLA	HNO_3		17
	HDEHP, TBP	HCl, H_2SO_4	>100	18
	TOPO	HCl (3.6M)	-	19
	HDEHP	HCl, H_2SO_4		4
Pa	TLA, TBP, IBMK, TTA	HNO_3, HCl	100	21
	TOA	HCl (5 M)		14
U	TOA	HCl	50	14
	TBP	HCl (1.1M); HNO_3(0.5M)	5	2
	Aliquat-336	HNO_3 (4 M)	4	22
	TOPO	HCl	-	19
	HDEHP	HCl, H_2SO_4	-	4
Np	TLA, TBP	HNO_3, HCl	100	23
	TOPO	HCl	-	19
	TOA, HDEHP	HCl (7 M)		24
	TCMA	HNO_3	-	25
Pu	Aliquat-336	HNO_3	-	26
	Aliquat-336	HNO_3	2	5,27
	Sulphoxides	HNO_3	5	28 a
Am/Cm	Aliquat-336	HNO_3	-	27
Am	Sulphoxides	HNO_3	>100	28 b
Ce	HDEHP	HNO_3, HCl, $HClO_4$		29
	TOPO	HCl		19
	HDEHP	HCl, H_2SO_4		4
Eu	Organophosphorus acids	$HClO_4$(pH-1)	100	30
Tb	HDEHP	HNO_3		29

* Approximate enhancement in the value of distribution coefficient (E) observed in the polar phase when compared to that obtained from pure acid solutions.

TABLE 2

Physical Characteristics of Organic Additives Frequently Studied in Polar Phase Extractions

Organic additive	Density[a]	Dielectric constant[a]
Water	0.997	78.54
Dimethyl sulphoxide	1.096	46.68
N, N-Dimethylacetamide	0.937	37.78
Ethylene glycol	1.110	37.70
Acetonitrile	0.777	37.50[b]
N, N-Dimethylformami	0.944	36.71
Methanol	0.787	32.70
Ethanol	0.785	24.55
Acetone	0.784	20.70
n-Propanol	0.800	20.33
iso-Propanol	0.781	19.92
iso-Butanol	0.803	16.56
Pyridine	0.978	12.40[c]
Tetrahydrofuran	0.889[b]	7.58
Dioxane	1.028	2.21

a, Values taken from "Organic Solvents" by J.A. Riddick and W.A. Bunger, 3rd Edn., Wiley - Interscience, New York, 1970. All values correspond to 25°C, unless stated otherwise.

b, At 20°C

c, At 21°C.

TABLE 3

Extraction of HCl, HNO_3 and H_2SO_4 with 50% TBP in Xylene in Presence of Organic Additives

Additive in polar phase (%)	Initial Acid Concentration								
	2.9 M HNO_3			6.2 M HCl			6M H_2SO_4		
	$[HNO_3]_a$	$[HNO_3]_o$	D	$[HCl]_a$	$[HCl]_o$	D	$[H_2SO_4]_a$	$[H_2SO_4]_o$	D
Water	2.066	0.818	0.40	5.751	0.393	0.07	5.573	0.442	0.08
Methanol									
10	2.066	0.828	0.40	5.849	0.396	0.07	5.633	0.490	0.09
20	2.010	0.860	0.43	5.835	0.562	0.10	5.626	0.594	0.11
30	2.055	0.891	0.43	5.841	0.682	0.12	5.618	0.695	0.12
40	2.085	0.925	0.45	5.772	0.803	0.14	5.514	0.861	0.16
50	2.100	0.950	0.45	5.640	0.969	0.17	5.557	0.918	0.17
Ethanol									
10	2.051	0.873	0.43	5.847	0.534	0.09	5.666	0.561	0.10
20	2.035	0.899	0.44	5.835	0.707	0.12	5.732	0.789	0.14
30	2.041	0.933	0.46	5.950	0.967	0.16	5.647	1.053	0.19
40	2.120	0.955	0.47	5.808	1.360	0.23	5.466	1.441	0.26
50	2.136	1.044	0.49	5.126	1.935	0.38	4.788	1.909	0.40
Isopropanol									
10	2.055	0.891	0.43	5.834	0.651	0.11	5.758	0.639	0.11
20	2.030	0.895	0.44	5.950	0.908	0.15	5.867	0.958	0.16
30	2.026	1.003	0.50	6.360	1.006	0.17	5.896	1.301	0.22
40	2.126	1.075	0.51	5.796	1.845	0.32	5.635	1.918	0.34
Acetone									
10	2.097	0.864	0.41	5.890	0.582	0.10	5.714	0.577	0.10
20	2.082	0.870	0.42	5.950	0.735	0.12	5.851	0.708	0.12
30	2.183	0.951	0.43	5.896	0.996	0.17	5.860	0.857	0.15
40	2.273	0.985	0.43	6.020	1.216	0.20	5.804	1.076	0.19
50	2.283	1.031	0.45	5.843	1.595	0.27	5.120	1.292	0.23

TABLE 4

Effect of Organic Additives on the Extraction of Pu(IV) from 1.8M HNO_3 and 4.6M HNO_3 with 0.2 M sulphoxides

Aqueous (Polar) phase	Extraction coefficient, E 1.8M HNO_3		4.6M HNO_3	
	DOSO	DHSO	DOSO	DHSO
Pure Aqueous	3.31	3.27	4.49	4.52
20% Acetonitrile	6.16	5.64	8.50	7.61
20% Acetone	5.01	4.78	5.63	6.03
20% Dioxane	4.18	3.26	4.88	5.15
20% Ethanol	4.48	3.15	6.62	6.39
20% Methanol	4.01	3.03	6.05	5.24
20% n-Propanol	2.97	1.87	3.20	3.13
20% iso-Propanol	1.76	1.44	1.42	1.56

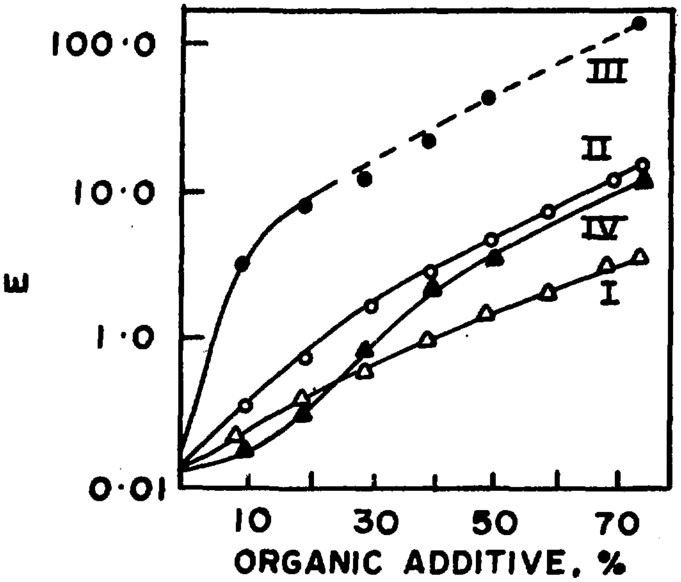

FIG.-1. EFFECT OF ORGANIC ADDITIVS ON E FOR EXTRACTION OF Pa WITH 0·3M TLA IN XYLENE FROM 2·9M HCl

I – METHANOL ; II – ETHANOL

III – ISOPROPANOL ; IV – ACETONE

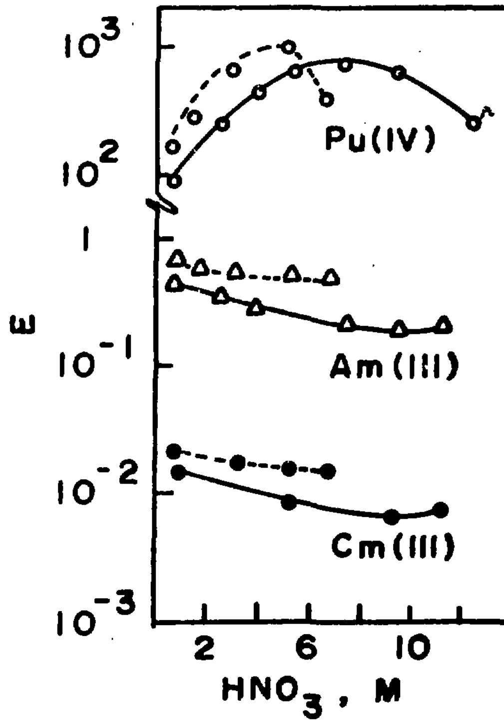

FIG.-2. EXTRACTION OF Pu(IV), Am(III) AND Cm(III) WITH 30% ALIQUAT-336 IN XYLENE AS A FUNCTION OF HNO_3. CONCENTRATION IN ABSENCE AND PRESENCE OF 50% ACETONE (THE DOTTED LINES REPRESENT THE EXTRACTION IN PRESENCE OF ACETONE)

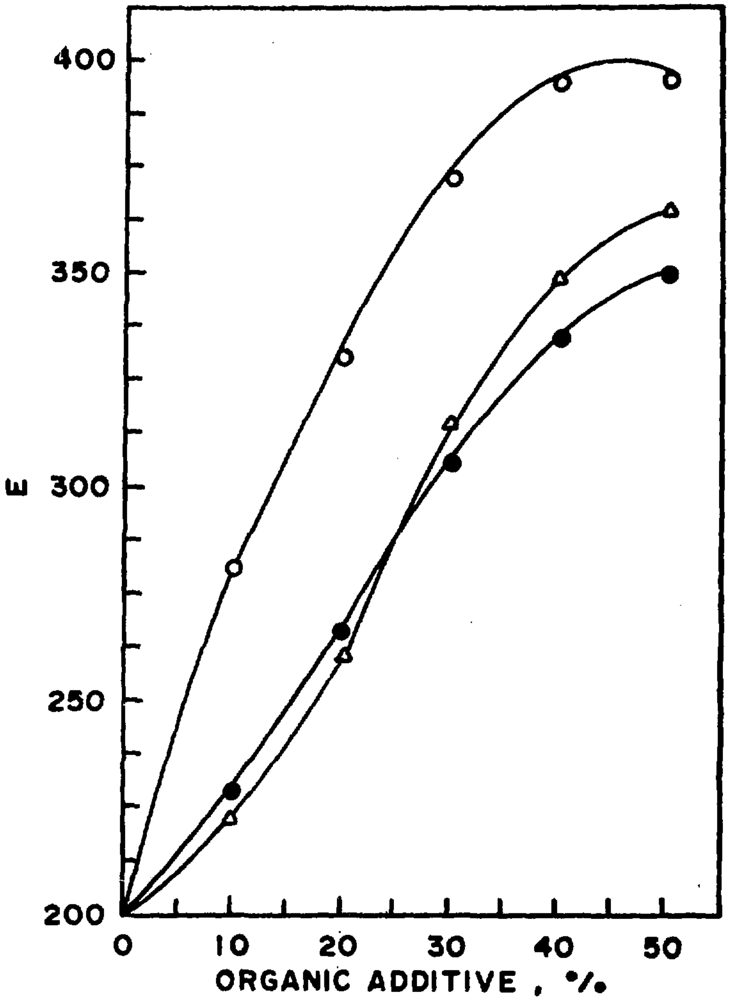

FIG.-3. EFFECT OF ORGANIC ADDITIVES ON THE EXTRACTION OF Pu(IV) WITH 30 % ALIQUAT-336 FROM 2M HNO_3 SOLUTION

●——● METHANOL
△——△ ETHANOL
○——○ ACETONE

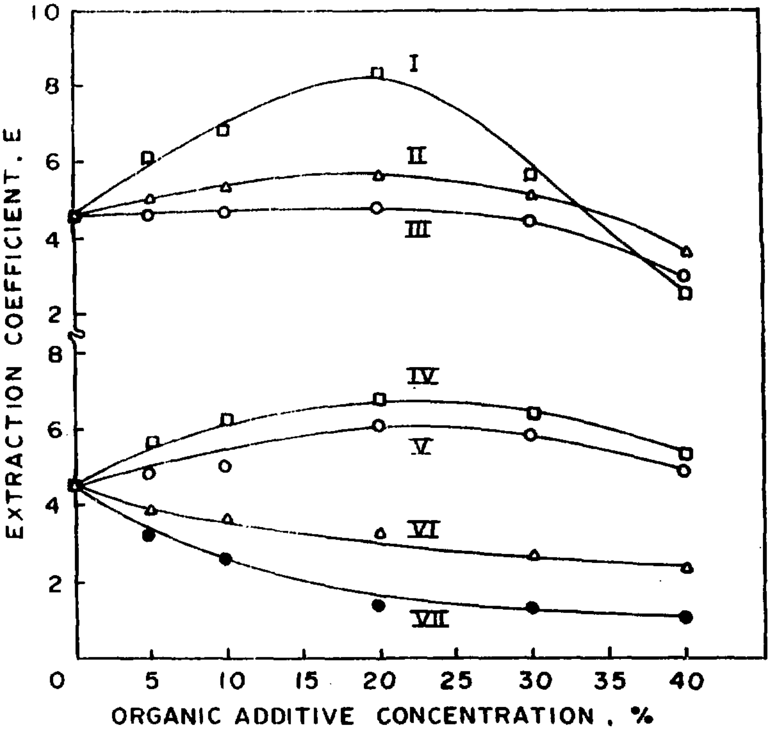

FIG.-4. EFFECT OF ORGANIC ADDITIVES ON EXTRACTION OF Pu(IV) FROM 4.6 M HNO_3 WITH 0.2 M DOSO IN SOLVESSO-100.
I-ACETONITRILE; II-ACETONE; III-DIOXANE; IV-ETHANOL; V-METHANOL; VI-n-PROPANOL; VII-ISOPROPANOL.

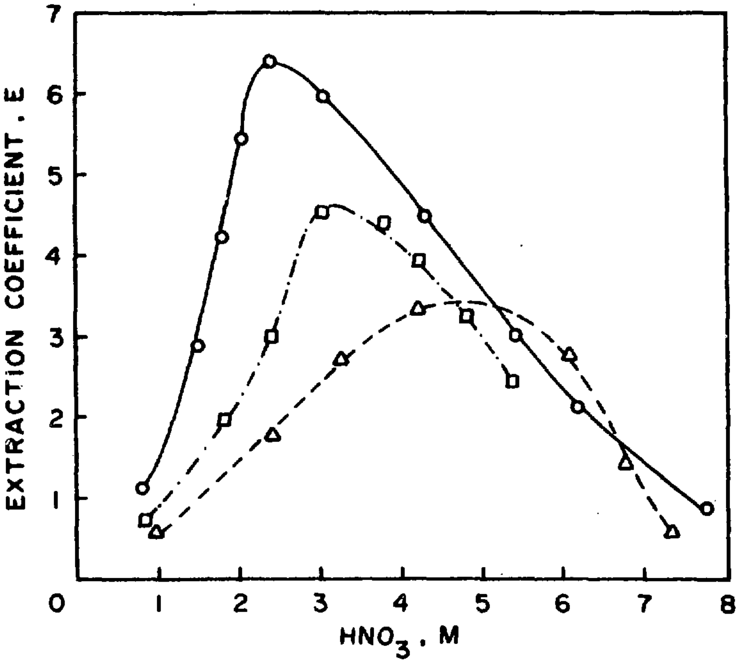

FIG.- 5 :- Effect of HNO$_3$ concentration on the extraction of Pu(IV) with 0.1M DOSO/Solvesso-100

from (-△-) pure nitric acid solutions

(-□-) solutions containing 20% (v/v) methanol

(-○-) solutions containing 20% (v/v) acetonitrile.