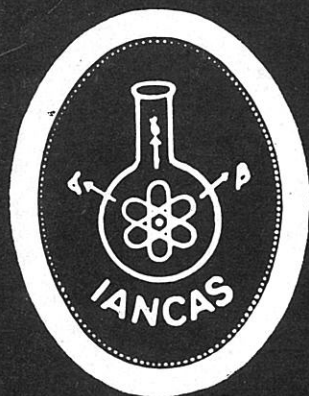


Volume 10, No. 2

June 1994



IANCAS BULLETIN

**SOLVENT EXTRACTION
NEW PERSPECTIVES**

A Publication of
**INDIAN ASSOCIATION OF NUCLEAR CHEMISTS AND
ALLIED SCIENTISTS**

PKM

Editorial

The field of solvent extraction has tremendous applications in industry and also is an interesting area for fundamental research. The challenges it provides to a chemist are nicely summed up by Dr V.K. Manchanda in **FOCUS** who has worked as Guest- editor for this issue. In optimising a solvent extraction process, the choice of a solvent is guided by a number of considerations such as extractability, selectivity etc as well as their physical properties (density, viscosity etc). Researchers also characterise the process through measurement of bulk properties. However, it will be very interesting to study the molecular interaction or molecular association process in general, say, between the metal ion, extractant and diluent in a given matrix using in situ probes such as NMR, Perturbed angular correlation (PAC), Positron annihilation Spectroscopy, X- ray based techniques such as EXAFS and Neutron Scattering. This calls for an interdisciplinary approach. Microscopic characterisation of a given system will certainly enhance our knowledge and ultimately help the process chemists.

I would like to put on record my sincere thanks to Dr V.K. Manchanda, the Guest editor for this issue. I thank all the authors, who constitute a spectrum of specialists from reputed research laboratories and academic institutions. I also thank Dr A.V.R. Reddy for his help and Shri J.K. Samuel for designing the lay out.

LANCAS has published a text book titled "Principles in Radiochemistry", details of which are given in the announcement column of this issue.

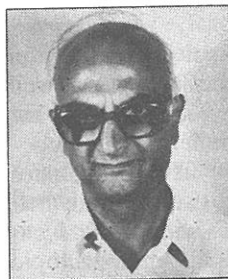
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P.K. Pujari

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Solvent Extraction Processes In Nuclear Technology



Dr S.K. Patil is presently the Head of the Process chemistry section, Fuel Chemistry Division, BARC. After graduating from University of Poona in 1958, he joined the 2nd batch of Training School, BARC and subsequently obtained his Ph D from Bombay University. A specialist in the chemistry of Actinide elements, he has contributed extensively to the chemistry of aqueous methods of fuel reprocessing which has been very useful for the separation of neptunium as a by product of the Purex process. He has a large number of publications in international journals of repute. An excellent teacher, he keeps special interest in studying the historical aspects of science and its development.

INTRODUCTION

Solvent extraction is a familiar technique to most of those working in nuclear energy. It is routinely used for the separation and purification in chemical analysis of materials as well as used on industrial scale for the production of super-pure materials vital for the realization of nuclear power. Solvent extraction of metals has a long history of more than a century. Earlier extracting agents used for analytical separations primarily were diethyl ether and some chelating extractants such as diphenyl carbazide, cupferron, dithiozone and oxine. However much of the work in solvent extraction was initiated due to special and urgent materials requirements of nuclear energy. This provided a powerful impetus to sustained investigations in solvent extraction. Nuclear technology pioneered the industrial uses of solvent extraction for the separation and production of the metals with exacting purity. Solvent extraction owes much of its present prominence to its successful applications to the separation and purification of thorium, uranium, plutonium, and other actinides, lanthanides, zirconium and niobium used in nuclear technology.

HISTORICAL

Although detailed history of solvent extraction has not been reported, Irving in his several reviews, has reported a brief history of solvent extraction. Selective extraction of uranyl nitrate by diethyl ether was reported by Peligot in 1842 and almost exactly after 100 years, in 1942, ether extraction process was used to produce high purity uranium required in the Manhattan Project, by the Mallinckrodt Chemical Works. Production of

uranium by ether extraction, thus became the first large scale application of solvent extraction process in hydrometallurgy. Upto about 1950, ether extraction was the only process for the production of nuclear grade uranium. In the historical separation of plutonium-239, the element of great importance in nuclear technology, from neutron irradiated uranyl nitrate hexahydrate ether extraction was used. In the laboratory scale separation of zirconium-hafnium using solvent extraction from aqueous thiocyanate again diethyl ether was used. Thus diethyl ether historically is the most useful extractant. However, serious limitations of ether extractions such as the use of high concentration of salting agent and especially fire hazard, have terminated its use in solvent extraction.

During the Manhattan Project a wide variety of extractants were investigated to develop solvent extraction processes for plutonium separation from irradiated fuel. Of these methyl isobutyl ketone (hexone) and dibutyl carbitol were used for some time in fuel reprocessing.

THE EXTRACTANTS IN NUCLEAR HYDROMETALLURGY

Of the large number of available or specially synthesized organophosphorus and organonitrogen extractants studied, only a few have been found suitable for industrial applications though several of them have proved very useful in analytical separations. Good selectivity and capacity, ease of stripping, immiscibility with water, different density than that of water, low viscosity, chemical and radiation stability, nonvolatility, nonflammability, nontoxicity and easy regenera-

tion for recycling are the requirements of the solvent. The extractants used can be broadly classified into three types : (i) Acidic, (ii) Neutral and (iii) Basic. Mostly the extractants, for their use, are dissolved in organic diluents to reduce viscosity. Hydrocarbon diluents, usually aliphatic, are selected on the basis of a flash point above 60C to minimize evaporation losses and fire hazard and with density of about 0.8 for easy phase separation. In some systems diluent modifier, which invariably is solvating agent such as long chain alcohol, is added to prevent the splitting of organic phase into two, commonly known as third phase formation. The addition of modifier can aid phase separation also. Efficient separation of the product metal from undesired impurities or similar metals by multistage counter current operation has made solvent extraction a very versatile technique useful for all the stages of nuclear fuel cycle. Table 1 shows the solvent extraction systems used in the production of metals for nuclear applications.

TRI-N-BUTYL PHOSPHATE (TBP)

The most important and widely used extractant for purification of metals in nuclear technology is tri-n-butyl phosphate (TBP). The first paper published in 1949, by Warf on extraction of Ce(IV) from nitric acid is an important milestone in solvent extraction. The ability of TBP to extract nitrates of uranium and other actinides was recognised as early as 1944. TBP first synthesised in 1930, was used as commercial plasticizer before 1940 and was readily available. TBP was first rejected for solvent extraction applications which in retrospect appears to be mistake. Fear that it would be excessively degraded by acid hydrolysis could probably be the reason. As use of undiluted TBP only was then considered, its high viscosity and density and the difficulty in back extraction of the extracted metals, by the methods then in use, could be other reasons for rejecting TBP. Use of diluent solved the problem of density and viscosity and TBP diluted with hexane was first used successfully for thorium extraction, at the Battelle Memorial Institute.

The group, working at ORNL developed TBP extraction process for recovery of uranium and plutonium from dissolved spent fuel and this concept became known as the "PUREX", (Plutonium Uranium Reduction Extraction) Process. The evolution of the flowsheets is described by Cole-

man and Leuze. The first plant using the Purex process for the reprocessing of nuclear fuels started operating, in November 1954, at Savannah River, and subsequently the Hanford Plant also changed from hexone process to this process in January 1956. Processes, based on TBP extraction, were also developed and successfully applied for thorium reprocessing for the production of Uranium²³³.

TBP is now employed in many hydrometallurgical processes associated with nuclear industry. It is exclusively used in uranium refining of "Yellow Cake", a uranium mill product to produce nuclear grade uranium. It is a chosen solvent for all commercial and demonstration fuel reprocessing plants for separation and purification of uranium and plutonium from fission products. The potential use of TBP for treatment of nuclear wastes resulting from reprocessing operations has also been explored. The extraction of metals from nitric acid by TBP is of utmost importance to process technologies developed for nuclear fuel cycle.

It is interesting to note that a relatively small fraction (~ 15%, i.e. 1000 T/yr) of the total quantity of TBP manufactured annually is used in hydrometallurgical processes for metal extraction. Its commercial availability relies heavily on its other applications namely as a plasticizer, anti-oxidant or catalyst and as antifoaming agent, hydraulic fluids and fire retardant. In the plenary lecture entitled "Tri-n-butyl phosphate: The universal solvent for nuclear fuel cycle" delivered in ISEC-1988, Moscow, Naylor stated that guaranteed supply, cost competitiveness, good physical properties, reasonably good chemical stability, practically no toxicity and good extraction behaviour exhibiting adequate selectivity and fast kinetics have resulted in its universal use in nuclear fuel cycle and it is difficult to replace it. Vast amount of technical data and continuously updating the bank of information indicate the predominance of this solvent. A series of volumes entitled "The Science and Technology of Tri-butyl phosphate" being published presently reveals the wide use and the importance of TBP.

ACIDIC ORGANOPHOSPHORUS EXTRACTANTS

Around 1950 the distribution ratio data for various actinides, obtained by different groups using TBP as the extractant, showed considerable

discrepancies. These were eventually traced to the presence of hydrolysis products in the TBP samples used and it became obvious that mono- and dibutyl- phosphoric acids themselves are good extractants. Subsequently a number of synthetic dialkylphosphoric acids have been studied and di-2-ethylhexylphosphoric acid (HDEHP) is most commonly used in number of processes for metal recoveries.

The basic operation in the uranium producing mills, is selective leaching of hexavalent uranium from the ore by dilute solution of sulphuric acid or of sodium carbonate-bicarbonate, the former being more widely used. For the recovery purification and concentration of uranium from the sulphuric acid leach solutions containing very low concentration of uranium (0.5 g/l to 2.0 g/l), TBP is ineffective. Brown and coworkers, at ORNL started a search for reagents that could extract uranium effectively and economically from the leach liquors. Several organic compounds were begged, bought or synthesized and tested for their potential application. HDEHP was chosen from these studies, to recover uranium from leach liquors. The process, known as Dapex process, was developed and successfully applied in the US plants. The process however, is presently not being widely used to recover uranium from sulphuric acid leach liquors.

RECOVERY OF URANIUM FROM WET-PROCESS PHOSPHORIC ACID

Wet-process phosphoric acid produced by fertilizer industry contains 50-200 mg/l of uranium and thus is a significant source of uranium. Two attractive solvent extraction processes for the recovery of uranium from the acid have been developed at ORNL. In the first process, the extractant consists of HDEHP (0.5 M) and TOPO (0.125 M) in hydrocarbon diluent. Hexavalent uranium is preferentially extracted by this solvent and the extracted U(VI) is stripped by reducing it to U(IV) by using Fe(II). The uranium produced is further purified by an additional extraction cycle where lower concentrations of HDEHP (0.3 M) and TOPO (0.075 M) are used and uranium from loaded organic phase is stripped with 0.5 M $(\text{NH}_4)_2\text{CO}_3$. In the second process, 0.3 M to 0.4 M octylphenyl phosphoric acid (a better extractant for U(IV)) is used and the extracted U(IV) is stripped by using NaClO_3 to oxidize U(IV) to

U(VI). The uranium product is further purified by HDEHP-TOPO process.

A number of plants have successfully used HDEHP/TOPO process producing 1000-2000 TW/yr, in the US. The fall in the price of uranium at present however, has made such recovery economically unviable though technically feasible.

ZIRCONIUM-HAFNIUM SEPARATION

Zirconium alloys are used as cladding and structural materials in water-cooled nuclear reactors as these alloys are highly corrosion-resistant, strong at high temperatures and nearly transparent to thermal neutrons. Zirconium in nature invariably contains 2-3% of hafnium. Zr and Hf are chemically similar having single +4, oxidation state in aqueous solutions and almost identical ionic size. The separation of Zr-Hf is, therefore, a formidable task. For nuclear applications Hf content of Zr must be reduced to 100 ppm as the former has thermal neutron capture cross-section about 600 times more than that of Zr. Applications of solvent extraction has made it possible to separate Zr from Hf on industrial scale.

Three different solvent extraction processes are presently being used to produce nuclear grade zirconium. The hexone- thiocyanate process is based on the preferential extraction of Hf(IV) as a neutral thiocyanate complex by hexone. This process is used in number of US plants which are the major producers of zirconium. TBP-nitric acid process is based on selective extraction of Zr(IV) by TBP from nitric acid. A number of plants use this process which consists of extraction of Zr(IV) from 5-6 M nitric acid by 50% TBP/Kerosene, scrubbing the organic extract with 5 M nitric acid to remove coextracted hafnium and finally back extraction of zirconium with water. Recently Zr-Hf separation from sulphate medium using tertiaryalkylamine extractant has been developed. The process, used for commercial production of nuclear grade zirconium by Nippon Mining Co., consists of extraction of Zr(IV) from 1M sulphuric acid by organic extractant containing 10% Amine + 7% Tridecanol in kerosene followed by scrubbing the organic extract, with 1 M H_2SO_4 containing pure Zr, to remove extracted Hf(IV) and finally back extracting Zr(IV) with 20% NaCl solution. The amine extraction process has some advantages over the other two processes viz. less environmental pollu-

tion, lower chemical cost and relatively less emulsion problems.

NIOBIUM AND TANTALUM

Zirconium -2.5% Nb alloy is preferred to zircaloy for permanent structural components in water-cooled nuclear reactors. High purity Nb is required for the same. Nb is separated from Ta by solvent extraction using hexone which extracts Nb and Ta from HCl, HNO₃ or H₂SO₄ containing HF. Nb is selectively back extracted with a low acidic aqueous medium. In another process first Ta is selectively extracted by 50% TBP/kerosene from 0.5 HF- 2N H₂SO₄. After complete removal of Ta, the aqueous phase (raffinate) is adjusted to 5 N HF - 9 N H₂SO₄ and Nb is extracted with 50% TBP. Extracted Nb is then stripped with demineralized water.

RARE EARTHS SEPARATION

Two rare earth elements are used in nuclear technology. Gd is used as a burnable poison and for nuclear reactors shut off purpose. Eu is used in control rods in some reactors.

The rare earths or lanthanides are known for their markedly similar chemical properties and for the difficulty in their individual separation by chemical methods. Spedding and coworkers from Ames laboratory, developed carboxylic acid elution method for separating fairly large quantities of rare earths using a strong acid cation exchange resin.

Solvent extraction methods, using extractants such as TBP, HDEHP, PC-88A, tertiary carboxylic acid (versatic acid) and quaternary ammonium compound Aliquat-336 have been developed for large scale separation of rare earths. These methods have several advantages such as the use of concentrated feed solutions, faster flow rates and ease of adaptation for continuous operation. The purity of the rare earths obtained by solvent extraction is generally not as good as that obtained by the band displacement ion exchange system. However in many applications, very high purity of rare earths is not necessary and hence the solvent extraction separation is adequate to achieve the desired purity of the rare earths. HDEHP or more recently PC-88A is used as the extractant to fractionate the rare earths into lighter, medium heavy and heavy rare earth elements. Commercial processes employed

today are highly proprietary and specific details are not available. However, production of Gd₂O₃ and Eu₂O₃ of better than 99.9% purity by solvent extraction processes has been reported.

TRANSPLUTONIUM ELEMENTS SEPARATION

Two solvent extraction processes have been developed for the group separation of lanthanides and actinides from the plutonium targets irradiated in HFIR for the production of large quantities of transplutonium elements. In the Tramex process the targets are dissolved in HCl and the resulting solution is adjusted to 10 M LiCl, 0.1 M AlCl₃ and 0.02 M HCl. Actinides are selectively extracted, rejecting lanthanides and other contaminating ions to aqueous raffinate, into 0.6 M Alamine 336, a tertiary amine. The organic extract is scrubbed with 11 M LiCl and the actinides are stripped with 8 M HCl. Actinides are further separated and purified by ion exchange chromatography. In the other process, Talspeak process, from the aqueous feed containing 1 M lactic acid which complexes actinides strongly, lanthanides are selectively extracted with 0.5 M HDEHP, the organic extract is scrubbed with 1 M lactic acid (pH = 3) containing 0.1 M Na₅ DTPA to wash down the actinides extracted to a small extent, thereby achieving complete separation of the two groups.

PARTITIONING OF HIGH ACTIVE WASTE (HAW)

High active wastes generated from nuclear fuel reprocessing contain long-lived actinide alpha emitters such as Np, Pu, Am and Cm. If these actinides are isolated from the rest of HAW, the long term radiological risks of the HAW will be reduced very effectively. Several studies have been devoted to develop solvent extraction methods for removal/recovery of the actinides from HAW with or without reducing the acidity. Laboratory studies have established that actinides can be successfully removed using common extractants such as HDEHP if the acidity is very low or TBP when Al(NO₃)₃ is added to the low acidity waste. The Japanese have shown diisodecylphosphoric acid (HDIDP) is somewhat superior to HDEHP for the same purpose.

It is, however, preferable to remove actinide from HAW without requiring acidity reduction. The Swedish have proposed a scheme which consists of three extraction cycles consisting of (i)

HDEHP extraction of U, Np and Pu from HAW containing 2 M HNO₃, (ii) TBP extraction of nitric acid and Tc and (iii) a second HDEHP extraction of lanthanides and higher actinides viz. Am and Cm.

Several bifunctional organophosphorus extractants have been intensively studied for their potential applications to removing actinides from acidic HAW. Of these, carbamoyl methylphosphonates (CMP) and carbamoylmethylphosphine oxides (CMPO) have proved to be superior to others as they are able to extract tri-, tetra- and hexavalent actinides from strong nitric acid solutions. Horwitz and coworkers, at ANL, have extensively investigated the use of octyl(phenyl)-N,N-diisobutylcarbamoyl methylphosphineoxide [Oo/D(iB)CMPO]. Its favourable properties viz. low aqueous phase solubility, high resistance to both chemical and radiolytic degradation, compatibility with various organic diluents, high affinity and capacity for all 3⁺, 4⁺ and 6⁺ actinides from both aqueous HNO₃ and HCl solutions and ease of stripping has made this reagent of choice for the TRUEX process developed for removal of actinides from HAW. In the TRUEX process, Np in HAW feed is first reduced to Np(IV) with ferrous sulphamate. All the actinides from 1-3 M HNO₃ waste solutions are extracted by 0.2- 0.25 M CMPO - 1-1.2 M TBP - hydrocarbon extractant. Besides, the lanthanides and Tc in HAW are also extracted. From the actinide loaded organic phase trivalent actinides (Am and Cm) are selectively stripped with 0.04 HNO₃ followed by stripping of tetravalent actinides (Pu and Np) using 0.05 M HNO₃ + 0.05 M HF. U(VI) and pertechnetate are removed with Na₂CO₃ during solvent washing step.

Batch and counter-current tests of the TRUEX process with various actual waste solutions have been very successful. After pilot plant tests, full plant scale TRUEX process is to be operated at Hanford.

ALKYLAMIDES EXTRACTANTS

Extractants used, for nuclear fuel reprocessing or actinide separations from HAW if are completely incinerable, it helps to limit radioactive wastes. Musikas and coworkers have explored the prospects of using N,N-dialkylamides as alternatives to TBP for fuel reprocessing and of using N,N-tetraalkyl 2-alkylpropane diamides for

actinides removal from HAW. Several amides, R₂NCOR', where R and R' are alkyl groups, have been studied. Based on the extraction data for U(VI), Pu(IV) and fission products and the solubility of U(VI) amide complex in hydrocarbon diluents, amides with R = di 2-ethylhexyl and R' = -C₃H₇, -C₅H₁₁, CH(CH₃)₂ or CH₂C(CH₃)₃ are found potentially useful for fuel reprocessing. For removal of actinides from HAW, N, N tetraalkyl, 2-alkylmalonamides are promising. The malonamides explored include (C₉H₁₇CH₃N)CO)₂CH₂, and (C₄H₉CH₃NCO)₂CHR with R = C₆H₁₃, C₂H₄O C₂H₅ and C₂H₄OC₂H₄-O-C₆H₁₃ and all these are able to extract trivalent actinides from 3-6 M HNO₃.

Musikas et al state that the use of alkylamides as alternative to TBP for fuel reprocessing offers number of advantages : (i) lower quantities of waste, (ii) simpler processes as U-Pu can be partitioned by control of nitric acid and the usual reductive partitioning can be avoided, (iii) possibility of limiting the number of purification cycles, (iv) easier U(VI) back extraction and solvent regeneration.

It is to be seen if and when amides replace TBP for fuel reprocessing.

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Table 1

Solvent Extraction Reagents in Nuclear Hydrometallurgy

Extractant Class	Name of extractant	Application
1. Acidic	HDEHP	U from ore, Actinides and Rare earths separation
	PC-88A	Rare earths separation
	Versatic acid	Rare earths separation
2. Basic	Alamine-336	U, Actinides, Zr/Hf separation
	Aliquat-336	Rare earths separation
3. Neutral	TBP	U & Th refining, Zr/Hf separation, Rare earths, Nb/Ta separation and nuclear fuel reprocessing
	Hexone	Zr/Hf separation, Nb/Ta separation
	TOPO	U recovery from H_3PO_4
	*CMP & *CMPO	Removal of actinides from HAW
	*Amides	Fuel Reprocessing and removal of actinides from HAW.

*Laboratory studies only. No plant scale application as yet.

The Role of Solvent Extraction in the Production and Purification of Uranium



Dr T.K. Mukherjee, Head, Uranium and Rare Earths Extraction Division, BARC, is a 1967 metallurgy graduate from Calcutta University and joined BARC after successful completion of 11th batch Training School course of BARC. A DIC from London, he has done his Ph.D from Bombay University. His field of interest is pyro, hydro and electrometallurgical extraction of refractory, base, nuclear metals and rare earths. He has a large number of publications and has received Best Metallurgist Award of IIM in 1990.

Shri S.K. Tangri is presently the Head, Uranium Extraction Section, Uranium and Rare Earths Extraction Division, BARC. After finishing his post graduation from Delhi University, he joined the 11th batch of BARC Training School. His field of interest is hydrometallurgy of Uranium, refractory metals and rare earths including development of solvent extraction process flowsheets using computer simulation technique. He has many publications in this field.



INTRODUCTION

The pioneering commercial application of solvent extraction (SX) was in the refining of uranium using ether for the war time Manhattan Project way back in 1940s. Since then solvent extraction has been playing pivotal role in hydrometallurgy of uranium right from processing of ores to the production of nuclear pure metal. With the advent of versatile range of organophosphorus compounds in 1950s, scope of SX widened further. SX technique got the real impetus in 1953 when tri-n-butyl phosphate (TBP), today known as the workhorse of nuclear industry replaced ether in the commercial refining of uranium. In 1955, with the availability of di-2-ethylhexyl phosphoric acid (DEHPA), a liquid cation exchanger, the use of solvent extraction was extended to the recovery of uranium and later many other metals like V, Zr, Hf and rare earths from their leach liquors. Subsequently in 1957, amines on account of their better selectivity towards uranium were extensively used for the recovery of uranium from sulphuric acid leach liquors. Later, TBP also found its industrial use in fuel reprocessing operations for the separation of U and Pu from the fission products and also for the purification of U and Pu. Thus SX, with TBP as the universal solvent, became an integral part of the nuclear fuel cycle.

Because of certain inherent advantages of SX over ion exchange (IX), today more than 80% of uranium mills throughout the world are using SX processes for treating sulphuric acid leach liquors. The significant advantage being the ease with which SX can be performed in continuous counter-current flow in mixer settlers or pulsed columns. Coupled with this are the advantages of ability to treat relatively stronger solutions, higher efficiency, higher throughputs and improved economics.

RECOVERY OF URANIUM FROM LEACH LIQUORS

Sulphuric acid leach liquor contains all types of uranium species viz. neutral UO_2SO_4 , cationic UO_2^{2+} and anionic like $[\text{UO}_2(\text{SO}_4)_2]^{2-}$ and $[\text{UO}_2(\text{SO}_4)_3]^{4-}$. Thus in principle any extractant whether anion exchanger, cation exchanger or solvating type can be used for extraction of uranium from such leach liquors. However, only liquid cation and anion exchangers are used in practise as these are relatively more efficient. The following solvent extraction processes can be employed in uranium ore processing.

Dapex Process

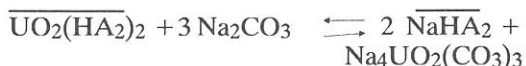
In this process sulphuric acid leach liquor is clarified to < 100 ppm of suspended solids prior

to extraction with 0.1 M DEHPA containing 0.1 M TBP or isodecanol as phase modifier in kerosene. The extraction of U(VI) proceeds via cation exchange mechanism as follows:



Since DEHPA is a liquid cation exchanger many cationic impurities like Fe^{3+} , Th^{4+} , VO^{2+} , Ti^{4+} , rare earths and molybdenum interfere in the extraction process. The major interference due to Fe^{3+} is minimised by reduction of Fe^{3+} to Fe^{2+} by contacting the leach liquor with iron.

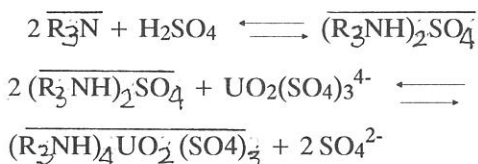
Although any strong acid e.g. 10 M HCl can also be used for stripping of uranium, preferred reagent is 1 M Na_2CO_3 which works as shown in following reaction.



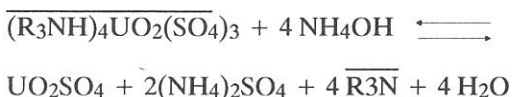
In view of non-selectivity of the reagent and slower rate of extraction, Amex process is preferred to this.

Amex Process

The process also known as the Purlex process in South Africa, uses 5% solution of Alamine 336 containing 2 to 5% isodecanol in kerosene as the extractant for uranium. Leach liquor needs clarification upto 20 ppm solids prior to extraction as amines and have a low tolerance towards suspended solids. The extraction of uranium by this solvent proceeds via following anion exchange mechanism:



Stripping of uranium from loaded extract may be done using variety of reagents like 1.0 M NaCl + 0.1 N H_2SO_4 , 0.09 M NH_4NO_3 + 0.1 M HNO_3 and 1.0 M Na_2CO_3 . Controlled pH stripping employing 1.5 M $(\text{NH}_4)_2\text{SO}_4$ + NH_4OH at pH 4.5 is most commonly employed. Stripping of uranium proceeds as per following reaction:



The schematic flow-sheet of the Amex process is shown in Fig. 1.

Eluex Process

This process also known as the Bufflex process in South Africa employs both IX and SX techniques in succession for the purification of low grade leach liquors. Low grade leach liquor is first purified and concentrated by IX using strongly basic resin. Elution is done by strong sulphuric acid to give a concentrated eluate which is then treated by Amex process employing controlled pH stripping. This process is now worldwide preferred as it gives ammonium diuranate (ADU) of higher purity particularly w.r.t. silica and rare earths.

RECOVERY OF BY-PRODUCT URANIUM FROM WET PROCESS PHOSPHORIC ACID

Wet process phosphoric acid (WPA) (25-30% P_2O_5) produced by dissolving rock phosphate in sulphuric acid is a potential source of by-product uranium. Though uranium content of this acid is rather low i.e. in the range of 50-200 ppm commercial recovery of this by-product uranium is economically viable at large P_2O_5 throughputs. Three extractant systems have been used for recovery of uranium from WPA, viz., octyl-pyrophosphoric acid system (OPPA), octyl phenyl acid phosphate system (OPAP) and di-2-ethylhexyl phosphoric acid + tri-octyl phosphine oxide system (DEHPA-TOPO). Of the three systems DEHPA-TOPO process developed by the Oak Ridge National Laboratory (ORNL), USA is the improved technology avoiding the various disadvantages of the other two processes viz, (a) poor reagent stability in case of OPPA (b) poor phase separation characteristics (c) the need to reduce uranium to the (IV) state in case of OPPA (d) the need to use an expensive HF reagent for stripping to produce only a relatively low grade UF_4 .

Pretreatment of WPA

As the crude acid contains organic humus matter, gypsum, fluorosilicates and other suspended solids, there exists the problem of crud or gunk formation at the organic/aqueous interface during extraction. To avoid these problems a pretreatment step is needed.

Pretreatment of WPA involves clarification of acid with the help of flocculation followed by

filtration to bring down the suspended solids to around 50 ppm. The organic matter is removed during passage of acid through beds of activated carbon. Temperature of WPA is reduced to 45 C before extraction when gypsum or silicates crystallize out.

DEHPA-TOPO Process

It is based on the extraction of U(VI) with a synergistic mixture of DEHPA and TOPO in kerosene. This is essentially a two cycles process in which advantage is taken of suitable phase ratios, O/A during extraction and stripping stages to give a product solution of about 20 g U₃O₈/l suitable for precipitation of ammonium uranyl carbonate (AUC). The first cycle uses 0.5 M DEHPA + 0.125 M TOPO in kerosene for extracting uranium which has been oxidised to +6 state by NaClO₃/H₂O₂ solution. The reductive stripping with merchant grade H₃PO₄ containing enough Fe²⁺ helps in re-extracting uranium from organic to aqueous phase. The strip of first cycle after suitable dilution and oxidation of U(IV) to U(VI) by NaClO₃/H₂O₂ forms the feed for the second cycle. A solvent composed of 0.3 M DEHPA + 0.075 M TOPO in kerosene is used for the second cycle. Stripping of uranium is done by 2-3 M (NH₄)₂CO₃ to recover uranium as AUC. The schematic flow-sheet of the process is shown in the Fig. 2.

Uranium & Rare Earths Extraction Division, B.A.R.C., in collaboration with Fertilizers and Chemicals Travancore has recently set up a pilot plant at Cochin based on the two cycle DEHPA-TOPO process to treat 1.0 m³ of WPA/hr. In India, total potential for byproduct uranium from WPA can go upto 200 tons/year.

Post-treatment

Post-treatment of the raffinate acid is necessary before its subsequent use in the fertilizer production as traces of entrained solvent are not desirable. This is done by enhanced coalescence, air floatation and mechanised filtration.

REFINING OF YELLOW CAKE TO PRODUCE NUCLEAR PURE URANIUM

This is the vital step of the nuclear fuel cycle where solvent extraction by TBP is used for extracting nuclear pure uranium from nitrate medium. The process involves dissolution of yellow cake in nitric acid followed by filtration to remove insoluble silica and other impurities. For the se-

lective extraction of uranium, concentration of the feed solution is adjusted to around 200-250 g U₃O₈/l and that of free nitric acid to 2N. The extraction of uranium takes place by solvation mechanism as indicated below:



The extraction of uranium depends on concentrations of uranium, nitrate and TBP as indicated by the above equation. Increase in nitrate ion concentration will help better extraction of uranium. The anions such as F⁻, SO₄²⁻, PO₄³⁻ and CO₃²⁻ which are able to complex uranyl ion can suppress extraction of uranium. Addition of Al helps in reducing the effects of F⁻ ion by forming stronger complex with F⁻. Some metals like Mo and Th may interfere in extraction. By loading uranium to almost 90% capacity of the solvent, interference due to these metals is minimised. At present, both in NFC and UMP SX is carried out in slurry extractors which have eliminated the need for clarification of crude feed solution prior to SX.

Future Challenges

Despite solvent extraction being the most widely used technique for hydrometallurgy of uranium, there are still some problem areas left. R & D efforts are being pursued to find possible solutions to these problems. Attention is drawn below to some of these areas with suggestions for possible approach to deal with them.

1. Slurry extractors are in use for treating slurries in uranium refining plants. Such slurry extractors if designed for treating leach liquor slurries would effectively improve the economics of the process.

2. Solvent losses in raffinate streams should be minimised particularly for treating large volumes of low grade leach liquors. Recent development of mixer-settlers with recycling arrangement to provide organic continuous dispersion has helped in reducing solvent losses. Another approach would be liquid membranes techniques which use very small inventory of solvents and thus minimise solvent losses.

3. There is a need for synthesising new diluents which can help in solving phase separation problems.

4. Efforts should be made to develop new mixed solvent systems with improved synergism both in kinetics and degree of extraction.

5. There is a need for development of stronger and tailor made solvents with multifunctional groups and different degrees of steric hinderance to provide versatile extraction system.

6. Liquid membrane techniques based on dynamic rather than equilibrium chemistry should be developed for recovery of uranium from merchant grade phosphoric acid.

7. The last but not the least, the economics of uranium production can be improved by eliminating certain steps in the conventional flow-sheet. This is possible by integrating milling and refining operations at the mill site. Loaded amine can be stripped by nitric acid and the strip solution directly refined by TBP at the mill site. This sort of integration will eliminate many steps like precipitation, filtration, drying, storage, transport and nitric acid dissolution of yellow cake and thus reduce the cost.

All these improvements would make SX still more versatile and cost effective technique for production and purification of uranium.

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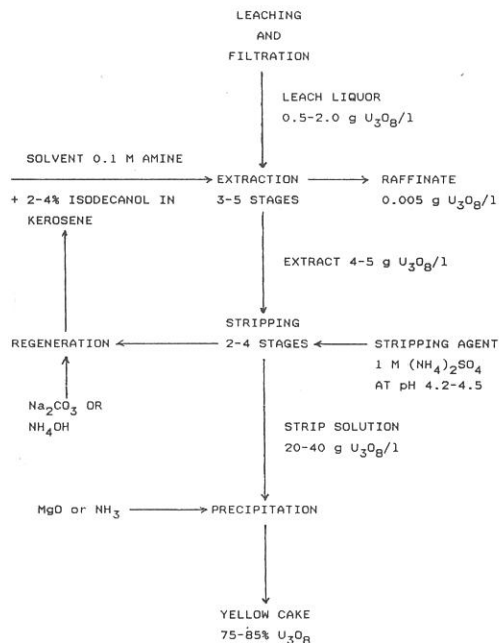


FIG 1. AMEX PROCESS

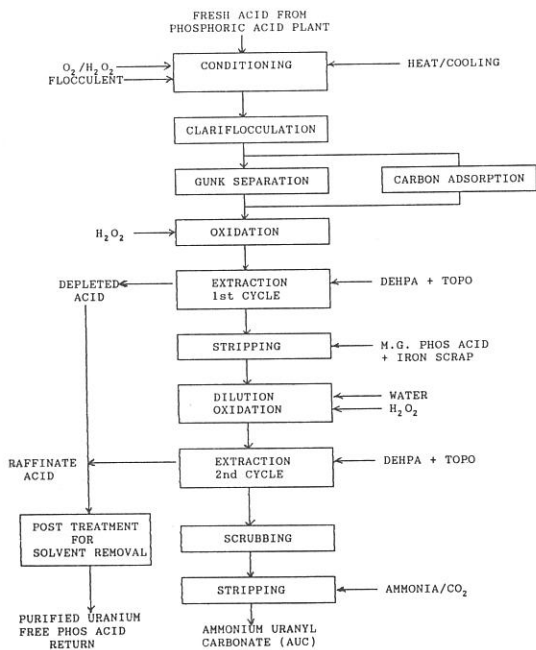


FIG. 2. DEHPA - TOPO PROCESS

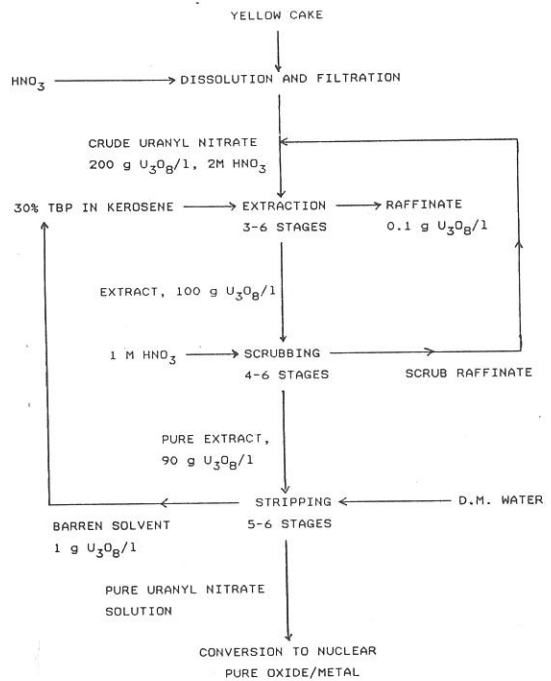


FIG. 3. TBP PROCESS FOR REFINING OF YELLOW CAKE TO NUCLEAR GRADE URANIUM

Fast Reactor Fuel Reprocessing : A Challenge For Solvent Extraction Chemist



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BACKGROUND:

The dissolution of irradiated uranium fuels in nitric acid leads to a solution containing uranium, plutonium and small quantities of the higher actinide elements (especially americium and curium), as well as various fission products. The recovery of uranium and plutonium from such irradiated fuel solution is performed by means of a solvent extraction process known as "Purex" process. In this process, Tri-n-Butyl Phosphate (TBP), dissolved in an "inert" diluent, usually a hydrocarbon such as n-dodecane, is employed as the extractant. By employing TBP, plutonium, adjusted to the tetravalent state, and U(VI) are selectively extracted, leaving behind the higher actinides (which normally exist in trivalent state). Partitioning of Pu from U is carried out by reducing Pu to Pu(III) which is not extracted by TBP.

To be used for fast reactor fuel reprocessing, the solvent must satisfy several criteria. These include, in addition to selectivity in extracting the desired actinide ions, chemical and radiation stability, poor solubility in the aqueous phase and good solubility for the metal solvate in the organic phase. The importance of these properties of the solvent is best emphasised in fast reactor fuel reprocessing. The Pu content of the irradiated fast reactor fuels can be as high as 200g/kg, about 10 times that of irradiated PHWR fuels. The fast reactor fuels are irradiated to high levels of "burn-up" (as high as 1,00,000 MWd/t, as compared to the PHWR fuels which reach a burn-up of about 10,000 MWd/t). They are reprocessed after a short cooling time of 6 to 9 months, whereas cooling times of the order of a few years is common in the case of thermal reactor fuels. As a result, the irradiated fast reactor fuel is highly

radioactive. The extractant and diluent used for reprocessing fast reactor fuels, therefore, must be capable of withstanding the high levels of radiation. Further, a higher level of decontamination from the fission products has to be achieved in the solvent extraction steps of fast reactor fuel reprocessing. For meeting this objective, the fraction of solvent which is "free" to extract metal ions has to be minimised, that is, high (U + Pu) loadings in organic phase have to be realised. This means that the solubility of the metal solvates in the organic phase also must be sufficiently high. Important areas of consideration by a process chemist engaged in fast reactor fuel reprocessing are briefly outlined in the following discussion.

Third Phase Formation:

When the TBP phase is loaded with high concentrations of the tetravalent actinide ions, the organic phase splits into two phases: the light organic phase, consisting mainly of the diluent and the heavy organic phase (the third phase) where the metal solvate is present at high concentration [1]. Apart from introducing hydrodynamic problems in the plant, this phenomenon can also have more dangerous implications: the accumulation of the third phase, containing large amounts of Pu, in a part of the plant can lead to criticality. In fast reactor fuel reprocessing, where high organic phase concentrations of Pu are encountered, it is important to design flowsheets carefully, so that the "Limiting Organic Concentration (LOC)" for third phase formation is never exceeded. This demands a detailed knowledge of the phenomenon and means to predict conditions in which it would take place.

A number of factors affect the LOC, the temperature being the most important one [2]. The concentration of the extractant, the composition of the aqueous phase and the nature of diluent used are some of the other important factors affecting the LOC. These factors are being studied in detail in our laboratory. The effect of diluent on the LOC is especially very interesting, in that even a slight branching in the alkyl groups of the hydrocarbon diluent causes an increase in the LOC [3]. Addition of small amounts of aromatic solvents or other polar solvents to organic phase leads to a significant increase in the LOC [4] (Fig.1). How these changes could be correlated with the properties of the solvent is a question yet to be fully resolved though some empirical methods have been arrived at for such correlations [3].

The higher homologues of TBP, such as Tri-n-amylyl phosphate (TAP) and Trihexyl phosphate (THP), appear to be attractive alternatives from the point of view of third phase formation. They exhibit much higher "tolerance" for the metal solvate [5,6] (Fig.2) and flowsheets with these solvents can therefore be more safely designed. In fact, TAP is reported to have been used in reprocessing of fast reactor fuels in Russia.

Use of Higher Temperatures in the Extraction Systems:

TBP extracts U(VI) better than it extracts Pu(IV) at ambient temperatures. As a result of this, during the co-extraction of U(VI) and Pu(IV), accumulation of Pu can occur in some stages of the solvent extraction cascade [7], especially while processing fuels with high Pu concentrations. This can lead to losses of Pu in the raffinate streams. One of the suggestions for avoiding this problem is the use of higher temperatures in the extraction steps. The extraction of U(VI) by TBP decreases with temperature while the extraction of Pu(IV) increases with temperature. By using an operating temperature at which the extraction of Pu(IV) is better than that of U(VI), the problem of Pu losses in the raffinate could be addressed. The concept of "Impurex" process developed in Germany [7] thus advocates the use of higher than ambient temperatures in the extraction. As has been mentioned above, the phenomenon of third phase formation could also be avoided by the use of higher temperatures. There is also evidence that decontamination from the notorious fission product, ruthenium, is better

when higher temperatures are employed during the extraction step [8]. In the context of the fast reactor fuel reprocessing, it would perhaps be worthwhile to examine the feasibility of extraction at higher temperatures, though this might add to the complexities of the plant design.

Degradation of Solvent:

The hostile environment faced by the solvent in fast reactor fuel reprocessing leads to the degradation of the extractant as well as the diluent by the combined effect of radiation as well as nitric acid. These degradation products extract and retain fission products (viz. Zr and Ru) which cause further degradation of the diluent. Very high levels of degradation lead to the formation of cruds containing fission products [9].

The primary degradation products of TBP have been identified to be Di-n-butyl Phosphoric acid (DBP) and Monobutyl Phosphoric acid (MBP). Similarly, it is known that the aliphatic hydrocarbons degrade through the formation of the nitro or nitrate derivatives [10]. A large number of studies have been performed on the mechanism of degradation [10,11]. A number of products of degradation have been identified by sophisticated techniques such as GC-MS [11]. However, the precise nature of the product that causes the retention of the fission products is yet to be unequivocally established. This would be a challenging task indeed and there is a good scope for further work in this area.

Amides are known to possess unique advantages in this regard. It has been established that the degradation products formed during degradation of amides are easily washed off by the aqueous phase, and no serious interference is therefore caused by them [12].

Aqueous Solubility:

One of the disadvantages of TBP is its aqueous solubility. (The solubility of pure TBP in water is approx. 0.4 g/l). This can pose problems when the aqueous raffinate solutions are concentrated for the purpose of waste management since methods to destroy TBP ultimately result in phosphate containing solutions. Thus, there has been an interest in the development of alternate solvents which could alleviate this problem.

The higher homologues of TBP, for example, have much less solubility in the aqueous phase than TBP (g/l[12]), on account of their higher

bulk. Long chain aliphatic amides and diamides are another group of compounds which provide an answer to the above problem. Their aqueous solubility is known to be very small; further, these compounds are completely incinerable, and do not leave any residue [12].

Partitioning of Plutonium from Uranium:

In thermal reactor fuel reprocessing, partitioning of Pu from U is carried out by first coextracting them by TBP [as Pu(IV) and U(VI)] and then reducing Pu to Pu(III) which is poorly extracted by TBP. The reduction was earlier carried out by using ferrous sulphamate. To avoid the production of active waste solutions containing high amounts of iron, ferrous has now been replaced by uranous [U(IV)] as the reductant. However, addition of externally produced U(IV) adds to the uranium to be processed, thereby reducing the throughput of the process. There is therefore a worldwide interest in schemes for partitioning where the U(IV) is generated in-situ electrolytically.

Electrolytic partitioning has been tried out for fast reactor fuels in Germany [13]. In UK, the difference in complexing behaviour of U(VI) and Pu(IV) was exploited for their separation [14]. In this scheme, sulphuric acid was used to selectively complex Pu and strip it from the TBP phase. This technique has not evoked interest in other countries perhaps in view of the corrosive nature of sulphuric acid. An even better alternative would be to have extractants which exhibit a significant difference in extractability for U(VI) and Pu(IV) so that one could devise conditions under which one or the other is retained in the organic phase preferentially. It has been claimed that some amides could permit such selective stripping without employing reducing agents [15]. Studies reported from Japan seem to indicate that the use of low temperature could be another alternative [16]. More work (especially on counter current extraction experiments) is necessary before such possibilities are established.

Alternate Solvents and Diluents:

It was earlier pointed out that TBP is not perhaps the ultimate in extractants as far as the fast reactor fuel reprocessing is concerned. The factor weighing heavily in favour of TBP is the extensive experience that has been gained with this extractant in a large number of plants all over the

world. A number of organophosphorus compounds have been examined in the past as alternatives for TBP, but none has so far reached plant scale applications even for thermal reactor fuels. However, there is still scope for considering alternate solvents for reprocessing fast reactor fuels, in view of the considerations mentioned above. The advantages of amides as well as trialkyl phosphates with higher number of carbon atoms in the alkyl chain have been highlighted in the earlier sections. However, considerable work needs to be done on these alternate extraction systems before they could be proposed for replacing TBP in the Purex process.

There appears to be a good scope for the development of alternate diluents, as well. Presently, aliphatic saturated straight chain hydrocarbons have been accepted as the ideal diluents for TBP. The diluent must be practically free from aromatic and unsaturated hydrocarbons, to minimise the degradation of the diluent. In fast reactor fuel reprocessing, where the radiation levels encountered would be high, the specifications of the diluent would be more stringent. While n-dodecane has been universally accepted as a good diluent, many plants have used a mixture of straight chain aliphatic hydrocarbons with carbon numbers in the range of 11 to 13, with equal success. The dodecane diluent used in our country has been so far imported at somewhat high cost. Recently, however, efforts in our laboratory have led to the development of an indigenous diluent (a mixture of aliphatic saturated hydrocarbons with carbon numbers 11, 12 and 13) in collaboration with a local manufacturer. It remains to be seen whether this diluent would perform well in the reprocessing plant.

Future Challenges:

The reprocessing of fast reactor fuel presents very interesting challenges to the chemist. There is tremendous scope for studies on new solvents, diluents and extraction schemes. In addition to application oriented programmes, there is considerable scope for basic research for developing a thorough understanding of the extraction systems. In this brief article, I have dealt with the issues, which are more specific to fast reactor fuel reprocessing, in general terms. The Fast Breeder Test Reactor at Kalpakkam uses uranium plutonium mixed carbide as the fuel and the development of the reprocessing scheme for this

fuel demands additional studies, which would perhaps merit a separate discussion.

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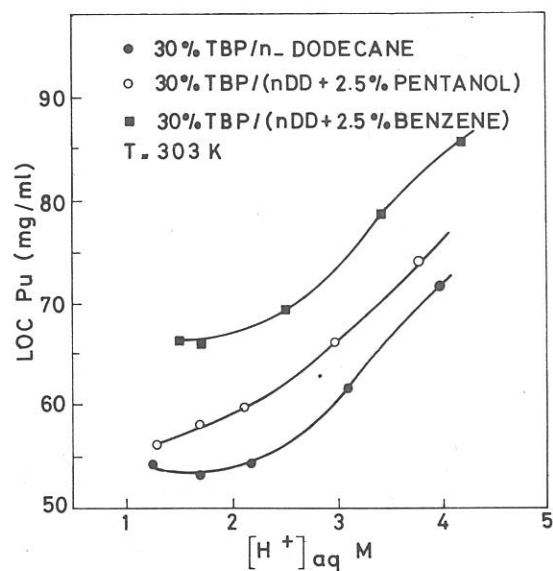


Fig. 1 Effect of polar modifiers on the LOC for third phase formation in Pu (IV) -HNO₃ - 30% TBP system.

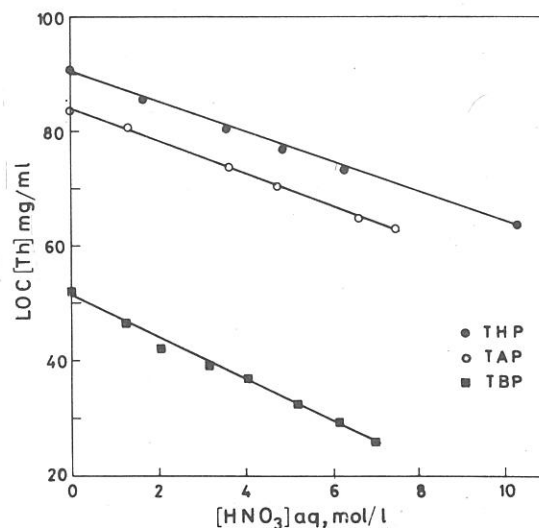


Fig. 2 Effect of increase in carbon chain length in Trialkyl phosphates on the LOC for third phase formation in the extraction of Th(IV) from nitric acid medium.

Calixarenes - New Complexing Ligands For Metal Ion Separations



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Dr. Mayuri Gandhi is working as a scientist at Regional Sophisticated Instrumentation Centre, IIT, Bombay. A specialist in environmental analytical chemistry, she has a number of publications in reputed international journals.



INTRODUCTION

In the last two decades the supramolecular chemistry has gained importance with the discovery of macrocyclic compounds like crown ethers and cryptands. Calixarenes, a new class of supramolecular compounds have features common with cyclodextrins and crown ethers and readily form guest-host complexes[1]. Calixarenes have a potential role to play in chemistry, due to ease of their availability through acid/base catalysed condensations of the resorcinol/phenol derivatives. A variety of molecular baskets could be constructed to perform the unique task of trapping the metal ions in the three dimensional network. In the years ahead, progress is anticipated in their applications in selective separation procedures.

The name calixarene was originally conceived to connote the shape of the phenol derived cyclic tetramer in the conformation in which all four aryl groups are oriented in the same direction. Subsequent work indicated the presence of more than four aryl groups in a calixarene molecule. Some typical calixarenes are shown in Fig.1 where bracketed number inserted between calix and arene. e.g. calix[6]arene indicates six aryl groups. The p- substituent is designated by name which indicate, from which phenol it is derived. e.g. p-tert-butyl-calix[6]arene indicates the compound used in synthesis was p-tert-butyl-phenol. The substituent at the methylene carbon which is introduced by the aldehyde is indicated by a prefix

C-substituent. For instance the resorcinol-derived calixarene is named as C-p-bromophenyl-calix[4]resorcinarene.

SYNTHESIS OF CALIXARENES

The condensation product of phenol formaldehyde made a great revolution, particularly in analytical chemistry as it formed the basis of the synthesis of first synthetic organic ion exchange resin. The same phenol-formaldehyde skeleton was used for the synthesis of p-tert-butyl calixarene. It was obtained by the condensation of a mixture of p-tert-butylphenol with formaldehyde in basic solution to produce thick viscous mass called 'precursor'. This precursor was refluxed with diphenyl ether to give a new product which was recrystallised to give calixarene. P-tert-butyl derivatives of calix[4]arene and calix[6]arene are obtained by condensation of p-tert-butylphenol with 37% formaldehyde while that of calix[8]arene is obtained by condensation of p-tert-butylphenol with para-formaldehyde in basic solution. The procedure of synthesis is quiet simple and high yields are generally obtained.

FUNCTIONAL GROUPS FOR COMPLEXATION

The introduction of functional groups in calixarenes is extremely important to make them suitable for complexation reactions. Calixarenes have two rims, upper rim consisting of p-tert-butyl or octyl groups and lower rim consisting of

hydroxyl groups. The 'lower rim' of phenol derived calixarene and the 'upper rim' of resorcinol derived calixarenes containing -OH groups provide excellent sites for affixing other groups. When an excess of an acylating agent is used, generally all of the hydroxyl groups are converted into ester groups. e.g. acetylation of p-tert-butyl calix[4]arene gives rise to tetra-acetate derivative. Etherification, like esterification can generally be effected on all the -OH groups of a calixarene regardless of ring size if reactive reagents are used. Commonly used method involves treatment of the calixarenes with an alkyl halide in THF-DMF solution in the presence of sodium hydride. Water soluble calixarenes are obtained by converting p-tert-butyl calixarenes to p-sulfonato calixarenes by treating with sulphuric acid under controlled conditions[1].

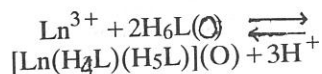
COMPLEXATION REACTIONS OF CALIXARENES WITH ALKALI METALS

The capacity of calixarenes to act as baskets is one of their most intriguing features explaining for much of the interest that they have received in recent years. Many calixarenes form complexes with organic solvents in the solid state. e.g. p-tert-butyl calix[4]arene forms complexes with chloroform, benzene, toluene, xylene, and anisole etc. The complexation of calixarenes with metals in non-aqueous solvents as well as in water is of vital interest to inorganic chemists. Izatt[2] and his co-workers observed for the first time a structural resemblance between the crown ethers, cyclodextrins and calixarenes. The complexation studies with the cyclodextrins have been directed primarily to the non-ionic molecular guests while those with the crown ethers have been mostly concerned with ionic guests. Calixarenes add to the growing list of complex forming macrocycles and it is interesting to note that they are being explored as hosts for both of these varieties of guests. Although the calixarenes are ineffective cation carriers in neutral solutions, they possess significant transport ability for alkali metals in strong basic solutions. This is in sharp contrast to 18-crown-6 compounds which are more effective in neutral media than in the basic solution. The diameters of the annuli of the calixarene mono anions are 1.0A. for the cyclic tetramer, 2.4 A. for the cyclic hexamer and 4.8 A for the cyclic octamer. Thus for complexes in which the cation and donor oxygen atoms are co-planar, the cyclic tet-

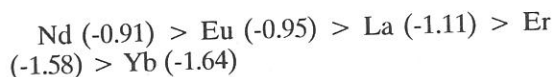
ramer has too small an opening even for metal ion like Li(I). On the other hand cyclic octamer has too large an opening to fit snugly even around metal ion like Cs(I). The cyclic hexamer behaves like crown ethers indicating a 'template effect'. Thus the importance of calixarenes arises due to (i) their role as ion carriers (low water solubility), (ii) ability to form neutral complexes with cations through loss of protons and (iii) their potential for allowing the coupling of cation transport with the reverse flux of protons. Mckerverey[3] was the first to study the extraction capabilities of cations from the aqueous phase into nonaqueous media and observed good selectivity of cations in phase transfer with different carboalkoxymethyl ether substituted calixarenes. The calix[6]arene compounds showed less affinity for sodium than for potassium with similar selectivity for rubidium and caesium.

SOLVENT EXTRACTION SEPARATIONS OF METAL IONS WITH CALIXARENES

There is a great promise for utilising carboxylic acid derivatives of p-tert-butyl calixarenes as versatile extracting agents for trivalent lanthanides[4]. By using p-tert-butyl calix(6)arene hexa carboxylic acid (H₆L), the lanthanides (Ln³⁺) were extracted from the aqueous phase at pH 2.0 to 3.5 into chloroform according to a cation exchange mechanism shown in equation (i) as 1:2 metal:ligand complexes.



The log K_{ex} corresponding to equation (i) varied as



In the presence of excess Na⁺ in the aqueous phase, this order was not changed but the lanthanides were extracted as 1:1 complexes at low extractant concentration and their extractability decreased. The use of p-tert-butyl calix(4)arene tetracarboxylic acid with a smaller cavity size results in lower distribution coefficients for all lanthanides compared to the analogous calix[6]arene. The logarithm extraction constants (defined in a manner similar to that for eqn. (i)) of the 1:2 metal: ligand complexes follow

the order $\text{Eu} (-3.29) > \text{Nd} (-3.64) > \text{Yb} (-3.69) > \text{Er} (-3.78) > \text{La} (-3.92)$. Upon addition of excess Na^+ , both extractability and selectivity increased. In addition to lanthanides, the extraction behaviour of transition elements and s-block elements has also been investigated. Para-tert-butyl calixarenes are poor extractants of alkaline earths whereas corresponding keto ether derivatives are effective extractants of alkali metals. The esterified derivative of p-tert-butylcalix[6]arene is a promising extractant for nickel, zinc, copper, while keto ether derivative of calixarene is suitable for titanium, zirconium and hafnium.

Shinkai et al. [5] demonstrated that calix[5]arene and calix[6]arene, which can be readily synthesised from cheap starting materials, serve as excellent basic skeletons for the design of pseudo planar penta or hexadentate uranophiles. Stability constant of uranyl ion with hexa acetate derivative of calix[6]arene was observed as 18.7 (log k), which is some what larger than that reported by Tabushi et al. [6] for hexaacetate derivative of 27-membered macrocyclic ligand (log k = 16.8). On the other hand, the selectivity factors of uranyl ion over other divalent metal ions are improved significantly in the case of calixarene (S.F.: $\text{UO}_2^{2+}/\text{Mg}^{2+} = 10^{17}$; $\text{UO}_2^{2+}/\text{Ni}^{2+} = 10^{15.3}$; $\text{UO}_2^{2+}/\text{Zn}^{2+} = 10^{13.1}$; $\text{UO}_2^{2+}/\text{Cu}^{2+} = 10^{12.0}$). This selectivity of uranium has attracted attention of chemists engaged in the recovery of this element from sea water where it is present only at 3.3 ppb level along with other metal ions as major constituents.

CONCLUSIONS

Calixarenes are destined to play an important role in metal ion separations in the years to come due to the ease of their synthesis from the available phenols on industrial scale. Future of supramolecular metal ion separations rests on the design and synthesis of new calixarenes. Exceptional selectivity towards uranyl ion has drawn the attention of separation chemists towards this class of ligands. Future work in this area should lead to the design of suitable ligands for further enhancement in the stability as well as selectivity not only as uranophiles but also more in general as metallo calixarenes.

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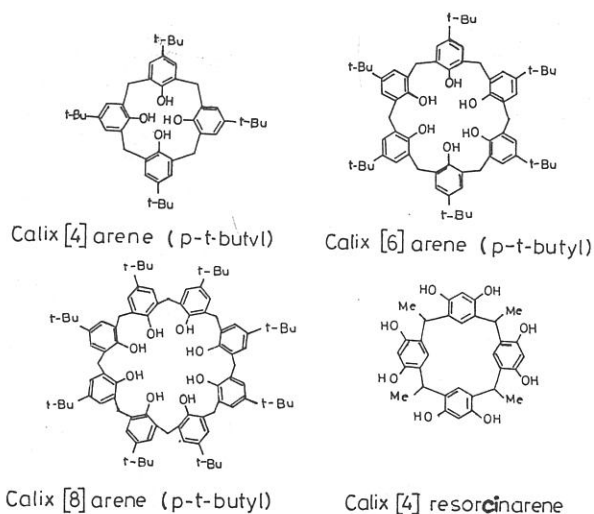


FIG.1 Different types of calixarenes

Acyl Isoxazolones : Novel Extractants Of Metals



Professor G.N. Rao, is at present Professor and Head of the Department of Chemistry at the Indian Institute of Technology, Delhi. He received his graduate and post graduate degrees from Andhra University and Ph.D. degree in 1964 from Indian Institute of Science, Bangalore. After post doctoral work in U.S.A. he joined IIT Delhi in 1968. He has a large number of publications in reputed Journals and has guided a number of research scholars. He has worked in the areas of solvent extraction, ion exchange, electro analytical chemistry, spectroscopic and thermal methods of analysis, synthesis and structural studies of coordination complexes and bio-inorganic chemistry.

Chelating ligands binding metal ions through oxygen donor atoms have been shown to be extremely useful in solvent extraction separations[1]. Among these β -diketones and in particular thenoyl trifluoroacetone (HTTA) have come to occupy a special place[2]. Acyl pyrazolones in general and 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) in particular, are efficient ligands for the extraction of metals[3,4]. Isoxazolones are similar to pyrazolones and work was initiated in our laboratories in 1985 on the use of 4-acyl isoxazolones in analysis[5].

Though 4-acyl isoxazolones are not available commercially, they can be conveniently synthesized according to the method of Korte and Storiko[6].

Extraction constant values obtained using a typical isoxazolone, 3-phenyl-4-benzoyl-5-isoxazolone (HPBI) are compared with those values reported in literature using the two well known beta diketones, 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP) and thenoyl trifluoroacetone (HTTA) in table: 1. Superiority of the ligand HPBI over the other two ligands may be rationalized on the basis of lower pka value of this reagent (1.12) as compared to that of HTTA (6.23) and HPMBP (4.10). Extraction of metals is thus expected to occur at a lower pH value with HPBI as compared to that with HTTA and subsequent work of Jyothi et al.[7,8] with La(III), Ce(III), Eu(III), U(VI) and Th(IV) clearly demonstrated this trend. Table 1 lists the extraction constant values obtained by Bangroo[9] for Nd(III) and Er(III) and by Jyothi et al [7,8] for Cu(II), Co(II), Ni(II) and Zn(II) as well as for lanthanide and actinide ions mentioned earlier.

Manchanda et al.[10,11] have reported the extraction of Np(IV), Pu(IV) and Am(III) with HPBI in toluene. It was found that Np(IV) and Pu(IV) are extracted quantitatively from 5M HClO₄ or 3 M HNO₃ with only 0.05M HPBI. The synergistic combination of 0.05 M HPBI and 0.2 M TOPO is found effective in extracting Am(III) from acidic solutions in the range 1-3 M HNO₃ [12]. Analytical separation of trace amounts of Plutonium from milligram quantities of uranium in (1:1) HCl has also been demonstrated[10].

A method for the determination of rare earth elements (La, Ce, Nd, Sm, Eu, Gd, Tb, Er and Yb) in geological samples was developed by extracting them with a mixture of 0.02 M HPBI and 0.005M Trioctyl phosphine oxide (TOPO) in toluene (in the pH range 5.5 to 6.5) after bringing the sample into solution using established methods of dissolution[9].

Investigations on the utility of the ligand, 3-phenyl-4-actyl-5-isoxazolone (HPAI) established the efficiency of the ligand as compared to HTTA in the extraction of La(III), Eu(III), Ce(III), UO₂(II), Th(IV), Co(II), Ni(II) and Zn(II)[13,14]. However, it was found that HPBI was superior to HPAI in all the systems. Structural studies on the metal complexes of HPAI and HPBI synthesized by the usual methods established the nature of the bonding in these complexes. Stoichiometry of the isolated metal complexes agrees with the nature of the complexes obtained in solvent extraction studies. Acyl isoxazolones thus seem to be very promising class of compounds as analytical reagents and the full potential of these reagents is yet to be exploited.

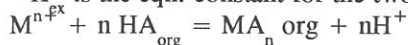
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Table 1 - Comparison of extraction constant values ($\log K_{ex}$)* of metal complexes of HPBI with those of HPMBP and HTTA

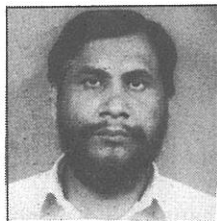
Metal	Ligand		
	HPBI	HPMBP	HTTA
Mn(II)	-6.63	-8.10	-10.07
Zn(II)	-4.36	-6.18	-8.13
Cd(II)	-4.92	-9.70	-11.40
Pb(II)	-2.06	-3.20	-5.24
Co(II)	-1.88	-7.25	-6.80
Ni(II)	-0.89	-4.22	-6.60
Cu(II)	+0.52	-0.30	-1.28
Pd(II)	-1.51	-	-3.96
La(III)	-1.95	-7.28	-9.90
Ce(III)	-1.20	-6.71	-9.60
Eu(III)	-1.05	-5.33	-8.99
UO ₂ (II)	+0.35	-1.15	-2.40
Th(IV)	+6.92	-1.00	+1.00
Nd(III)	+0.40	-5.60	-8.40
Er(III)	+0.96	-2.50	-7.80
Np(IV)	11.41	-	5.75
Pu(IV)	12.85	-	7.32
Am(III)	2.3	-2.70	-7.80

* K_{ex} is the eqn. constant for the two phase equilibrium



(where n = charge on the metal ion)

Molecular Interactions Of Extractants With Diluents



Prof. V. Chakravorty is currently the Head, Chemistry Department, Utkal University. A specialist in solvent extraction and analytical chemistry, he has a large number of publications in national and international journals.

Ms S. Mishra, co-author is a research scholar working with Dr Chakravorty.

Common extractants like tributyl phosphate (TBP), acetyl acetone (AA) and isobutyl methyl ketone (IBMK) are employed for the solvent extraction of metal ions after mixing with the suitable diluents. Such dilution helps in efficient phase dispersal, improved disengagement rate as well as better utilisation of the extractant. Thermodynamic properties such as isentropic compressibility (β_s), intermolecular free length (L_f), acoustic impedance (Z) and viscosity (η) provide information about the nature of intermolecular interactions in the binary liquid mixtures, which in turn help in predicting the behaviour of solvents in liquid-liquid extraction. β_s , L_f and Z are computed from the experimentally determined ultrasonic velocity (C) and density (ρ) of the binary liquid mixtures according to the following expressions:

$$\beta_s = 1/\rho C^2; \quad Z = \rho C; \quad L_f = K\sqrt{\beta_s}$$

where K is the temperature dependent constant. Coefficient of viscosity (η) too can be experimentally determined using Poiseuille's equation. The excess thermodynamic properties of the mixture (A^E) defined as follows are influenced by the molecular association, dissociation and complex formation.

$$A^E = A_{\text{mix}} - (f_1 A_1 + f_2 A_2)$$

where A_1 is the parameter (β_s , L_f , Z and η) for the extractant and A_2 is the same for the diluent; f_1 and f_2 are the mole fractions of the extractant and diluent respectively. The excess properties, β_s^E , Z^E and η^E are fitted to a Redlich-Kister type equation:

$$A^E = f_1 f_2 \sum_{j=1}^3 A_{j-1} (f_1 - f_2)^{j-1}$$

and the coefficients A_{j-1} are computed by a least square fit.

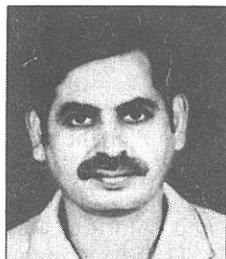
An attempt has been made by the principal author to determine experimentally the excess thermodynamic properties for several binary solutions and correlate them with their behaviour in solvent extraction. Some of these systems are briefly described here.

The formation of third phase during the extraction of actinides by TBP in a non polar diluent like kerosene or dodecane poses a problem. This can be avoided by the addition of a suitable modifier. In this connection, the binary liquid mixtures of TBP with 1-hexanol, 1-heptanol, 1-octanol and 1-decanol are investigated. The negative values of η^E , β_s^E and L_f^E as well as the positive values of Z^E and C^E for TBP/1-heptanol system indicate that the intermolecular interactions of TBP/1-heptanol solution are the strongest amongst the four solutions investigated.

In another related study, mutual correlation factor, g_{ab} , excess molar polarisation, P^E and excess free energy of mixing, F^E_{ab} were evaluated for the solution of TBP in 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol and 1-octanol employing Winkelmann-Quitze equation [1]. The trends of variations of these parameters exhibit marked dependence on the chain length of the alcohols. Work carried out in our laboratory clearly suggested that 1-heptanol is the most suitable modifier during extraction of metal ion by TBP [2]. As a consequence, this diluent helps in suppressing the formation of third phase during the extraction of actinides by TBP.

TBP, IBMK and AA are also employed as extractants in numerous analytical applications after mixing with suitable diluents. An attempt was made to evaluate physical parameters which are influenced by molecular interactions of these

Polyethylene Glycol Based Aqueous Biphasic Systems : A Novel Concept In Actinides Separations



Dr. V.K. Manchanda joined the Radiochemistry Division, BARC in 1969 after graduating from Delhi University and from Training School BARC. He was awarded Ph.D. by Bombay University in 1975 and carried out his post doctoral work at UTEP, Texas as a Fulbright scholar (1985-87). He has contributed significantly in the areas of Novel extractants of actinides, Thermodynamics and kinetics of complexes of macrocyclic ligands with lanthanides and actinides, Physico-chemical studies on actinide complexes and Chemical quality control of Pu based fuels. He has over 100 publications in various international journals and (National/ International) conferences to his credit.

INTRODUCTION

Solvent extraction is playing an increasingly important role in the recovery and purification of strategic and high tech metals of interest in chemical, space, electronics and nuclear industry. Generally speaking, two essential components of a solvent extraction process are (i) selective organophilic extractant like an organophosphorus ester, a long chain aliphatic amine or a beta diketone and (ii) a judiciously chosen diluent like kerosene, xylene or carbon tetrachloride. Though the mechanism of extraction varies with the nature of the extractant, yet a high solubility in the selected diluent is one of the pre-requisites for the development of any industrial process. Similarly, the diluent too should be non toxic, non

inflammable, non-degradable and inexpensive with desired viscosity and density for its qualification in the commercial process. These restrictions have limited the choice of solvent extraction systems which have been investigated from either basic or applied perspective so far.

Polyethylene glycol based aqueous biphasic systems offer a novel concept in metal ion separations. The major advantages of these systems are (a) the possibility of employing aqueous soluble complexing agents as selective separating agents and (b) a high molecular weight polyethylene glycol (PEG) as solvent which is inexpensive, commercially available, non toxic, non inflammable and durable.

"Molecular interactions ---"

continuation from last page

extractants with some common diluents. Viscosities and densities of four binary mixtures viz. TBP/C₆H₆, TBP/CCl₄, TBP/IBMK and TBP/AA are measured in the temperature range 25-45°C and different mole fractions of each mixture. From the experimental data, excess viscosity, Gibbs energy of activation and excess entropy are evaluated [3] and these follow the order CCl₄ > C₆H₆ > AA > IBMK which is related to the dipole induced dipole interactions. The excess thermodynamic properties have also been calculated for solutions of AA as well as IBMK in carbontetrachloride, isoamyl alcohol and benzene at various temperatures [4,5]. The greater negative values of β_s^E and L_f^E and greater positive value of η^E in CCl₄ system indicate once again stronger molecular interactions with this diluent due to the high polarisability of diluent. To conclude, carbon tetrachloride is

found to be a versatile diluent in the solvent extraction system employing TBP, AA or IBMK as the extractant.

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Most of the work reported in this direction so far, refers to the high molecular weight PEG typically represented by PEG- 2000 as the organic polymer and an aqueous solution containing inorganic salts like $(\text{NH}_4)_2\text{SO}_4$ or K_2CO_3 . Such a biphasic system is separated by centrifugation with PEG rich phase being distinctly lighter as compared to the salt rich phase and the solute of interest is unevenly distributed in these two separable phases. Each layer consists of 80% or more water on a molar basis.

PEG based aqueous biphasic systems have been used earlier for separating biomaterials. Their promise for the metal ion separation has been recognised in recent past. A very large proportion of the literature in metal ion extraction has come from Russian laboratories[1-4]. Rogers et.al[5,6] have also contributed significantly in this area during the last few years.

UNDERLYING PRINCIPLE

Phase diagram for the inorganic salt $((\text{NH}_4)_2\text{SO}_4/\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3)$ -PEG 2000 system represents the binodial below which different compositions result in a single phase and above which aqueous bi-phasic systems are observed. The shape of binodial depends on the type of polymer, its molecular weight, the nature and concentration of the inorganic salt and temperature. The approximate phase ratio can be estimated from the phase diagram. Concentrations of solutes in each phase are independent of phase volumes.

The large concentration of water in each phase allows fully hydrated species to be extracted along with water soluble aromatic chelating dyes like arsenazo III, alizarin complexone and xylenol orange as extractants. These reagents have particularly high formation constants with the actinides and partition favourably to the PEG rich phase.

Metal ion partitioning studies have borrowed many of the standard procedures like the use of radiochemical tracers from the liquid-liquid extraction in conventional systems. Distribution ratio, D , measured radiometrically is defined as the counts per minutes in the upper (PEG rich) phase divided by the counts per minute in the lower (salt rich) phase. Phase disengagement time to result in a constant height interface is comparable to that of a traditional oil/water system. Improved separation can be obtained by working at elevated temperatures. Addition of a complex-

ing dye to the system does not affect the phase disengagement significantly.

PARTITIONING OF METAL IONS IN THE PRESENCE OF WATER SOLUBLE EXTRACTANTS

Partitioning of a large number of metal ions in the periodic table employing the aqueous biphasic system has been successfully demonstrated. However, bulk of the literature in the area focusses on f-elements separation. The published data on the partitioning of these elements is from sulphate or carbonate media and chlorides and nitrates do not salt out PEGs. However, many biphasic systems can accept rather large concentrations of these ions without destroying the biphasic.

Table 1 shows that in the absence of a complexing agent, the f elements are not extracted from aqueous biphasic systems and have large distribution ratio values in the presence of aqueous complexing ligands. Extraction behaviour of actinides in the presence of a few water soluble complexing agents is summarised below from sulphate as well as carbonate media.

Sulphate Media

Table 2 shows that arsenazo III is by far the best extractant from sulphate media for all the actinide ions investigated viz. Th^{4+} , UO_2^{2+} , Pu^{4+} and Am^{3+} . All the metal ions exhibit almost identical extractant dependencies. Distribution of Am^{3+} upto 10^{-3} M of ligand towards PEG rich phase is poor.

Table 2 also shows that 10^{-3} M alizarin complexone quantitatively extract Th^{4+} and Pu^{4+} , while UO_2^{2+} and Am^{3+} are poorly extracted. Even on increasing ligand concentration to 10^{-2} M, only marginal increase in the extraction of latter ions was observed. Xylenol orange partitions actinide ions similar to the alizarin complexone at low concentrations. At higher extractant concentration, however, D_{Am} and D_{U} increases while D_{Pu} and D_{Th} tail off.

The presence of acid (3M H_2SO_4) results in the sharp decrease of extraction for all actinides. On the other hand the presence of alkali (1 M NH_4OH) affects the extraction of various actinides to different extent. It is interesting to observe (Table 2) that extraction order is almost reversed for xylenol orange in the presence of 1 M NH_4OH .

CARBONATE MEDIA

Extraction studies of f elements from carbonate media have been carried out more extensively than those from sulphate system. Methyl thymol blue, xylenol orange, hydroxy phenylimino- N,N'-diacetic acid and alizarin complexone have been employed to extract a large number of actinide ions including Am^{3+} , Cm^{3+} , Bk^{3+} , Cl^{3+} , Th^{4+} , Pu^{4+} , NpO_2^{2+} and UO_2^{2+} from K_2CO_3 , Na_2CO_3 or $(\text{NH}_4)_2\text{CO}_3/\text{PEG}-2000$ systems. These metal ions are poorly extracted by arsenazo III. Alizarin and Xylenol orange are more promising extractants from carbonate media. Distinct differences in the extraction behaviour of the actinides with alizarin in the presence of different salting out agents has been reported. Potassium carbonate has been reported to be excellent for the separation of actinide ions[5,6]. Separation factors of 220 and 630 have been reported for the $\text{Pu}^{4+}/\text{UO}_2^{2+}$ and $\text{Eu}^{3+}/\text{UO}_2^{2+}$ pairs respectively in the $\text{K}_2\text{CO}_3/\text{PEG}-2000$ system. Fig. 1 indicates that the xylenol orange extracts Am^{3+} from a K_2CO_3 system while Pu^{4+} , Th^{4+} and UO_2^{2+} show virtually no extraction at all. This is in sharp contrast to the observation in $(\text{NH}_4)_2\text{SO}_4$ system. Fig. 2 shows that in the latter case, at low xylenol orange concentration ($10^{-6}\text{M} - 10^{-4}\text{M}$) usual extraction behaviour viz. $\text{Pu}^{4+} > \text{Th}^{4+} > \text{UO}_2^{2+} > \text{Am}^{3+}$ is observed. On increasing the reagent concentration to 0.1 M, reversal in the distribution behaviour viz. $\text{Am}^{3+} > \text{Th}^{4+} > \text{UO}_2^{2+} > \text{Pu}^{4+}$ is seen.

An effective separation of the trivalent actinides from the trivalent lanthanides has also been accomplished by the addition of a masking agents to the xylenol orange/carbonate system. Generally it is observed that quantitative extraction is observed when benzene rings are present in the complexones, while aliphatic complexants can depress distribution of the f elements.

In addition to water soluble dyes, promising preliminary results have also been obtained using crown ethers for the extraction of actinides. However, no size controlled metal ion recognition to aqueous biphasic extraction is observed and UO_2^{2+} , Th^{4+} , Pu^{4+} as well as Am^{3+} show the same extractant dependence profile with 18 crown 6 indicating that this crown ether is probably not an appropriate choice for separation work. On the contrary, as expected alkali metals and alkaline earths have been selectively extracted from the aqueous biphasic system using

18 crown 6. Ionisable macrocyclic ligands (including calixarenes) hold greater promise for the actinide separation work.

PARTITIONING OF METAL IONS IN THE PRESENCE OF INORGANIC IONS

There is a second type of metal ion partitioning that finds wider applications to the softer transition and main group metals as well as some of the actinides. Inorganic anions such as SCN^- , Cl^- , Br^- and I^- have been shown to partition to the PEG rich phase. It is important to note that aqueous biphasic systems can often support the addition of these ions in concentration of 1M and above without loss of the biphasic.

Potassium phosphotungstate ($\text{K}_{10}\text{P}_2\text{W}_{17}\text{O}_{61}$) has been used as an inorganic anionic extractant for lanthanide and actinide ions. Distribution ratio values of Am^{3+} , Ce^{3+} and Pu^{4+} with $3 \times 10^{-5}\text{M}$ ligand from 14.4% $(\text{NH}_4)_2\text{SO}_4$ - PEG 2000 are 230, 64 and 4.5 respectively. PaO_2^{2+} , NpO_2^{2+} , UO_2^{2+} as well as AmO_2^{2+} are poorly extracted under these conditions. As a consequence, separation factors of Am^{3+} from these actinides are quite high (10^2 - 10^3).

The mechanism of extraction in PEG based systems utilizing these ions is unclear although interesting hypotheses based on the extraction of the metal ion as a complex anionic species/anionic polymer have been proposed[5,6].

FUTURE PERSPECTIVES

The field of aqueous biphasic extraction of metal ions shows incredible potential as it utilizes water soluble extractants and avoids the use of toxic, inflammable and expensive diluents. Available literature on actinides is mainly based on the use of complexing dyes and further work in this area should focus on finding other viable water soluble complexing agents. Metal ion recognition, a characteristic of crown ethers, cryptands and calixarenes make these complexing ligands as suitable candidates for investigations in the PEG based aqueous biphasic systems. However, aqueous complexation studies of actinides with the ligands of interest should precede their applications in biphasic systems.

Research on the mechanism of metal ion transport is vital to understand the relationship between partitioning in aqueous biphasic system and traditional extraction. The variables are currently too numerous and the understanding

currently insufficient to predict whether aqueous biphasic extraction of dissolved metal ions will ever be a basis for viable separation or recovery processes. However, this problem deserves full attention from the scientific community.

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Table I

Distribution ratio values (D_{An}) in the absence and presence of complexing ligand

Metal ion	18.8% PEG-2000/ 21.2% $(NH_4)_2SO_4$		17.5% PEG-2000 22.5% K_2CO_3	
	D^a	D^b	D^a	D^c
Th ⁴⁺	0.040	1100	0.025	0.089
Pu ⁴⁺	0.023	1030	0.022	0.080
Am ³⁺	0.013	190	0.120	46
UO ₂ ²⁺	0.082	710	0.006	0.082

- a : in the absence of complexing ligand
 b : in the presence of 5×10^{-3} M arsenazo III
 c : in the presence of 1×10^{-2} M xylenol orange

Table II

Distribution of actinide ions towards the PEG rich phase by the addition of complexing dyes in the biphasic system 18.8% PEG-2000/21.2% $(NH_4)_2SO_4$

Metal ion	D^*	Extractant Conc. (M)	D (Aqueous)	D (1M NH_4OH)	D (3M H_2SO_4)
Th ⁴⁺	0.040	Alizarin (10^{-3})	610	440	0.070
Pu ⁴⁺	0.023	Alizarin (10^{-3})	280	400	0.076
Am ³⁺	0.013	Alizarin (10^{-3})	0.10	84	0.093
UO ₂ ²⁺	0.082	Alizarin (10^{-3})	0.30	100	0.190
Th ⁴⁺	0.040	Arsenazo III (5×10^{-4})	870	14	0.086
Pu ⁴⁺	0.023	Arsenazo III (5×10^{-4})	440	4.3	0.064
Am ³⁺	0.013	Arsenazo III (5×10^{-4})	0.38	4.4	0.099
UO ₂ ²⁺	0.082	Arsenazo III (5×10^{-4})	250	17	0.200
Th ⁴⁺	0.040	Xylenol orange (10^{-3})	510	1.6	0.075
Pu ⁴⁺	0.023	Xylenol orange (10^{-3})	28	37	0.070
Am ³⁺	0.013	Xylenol orange (10^{-3})	0.02	79	0.099
UO ₂ ²⁺	0.082	Xylenol orange (10^{-3})	0.14	3.0	0.190

* in the absence of any complexing ligand

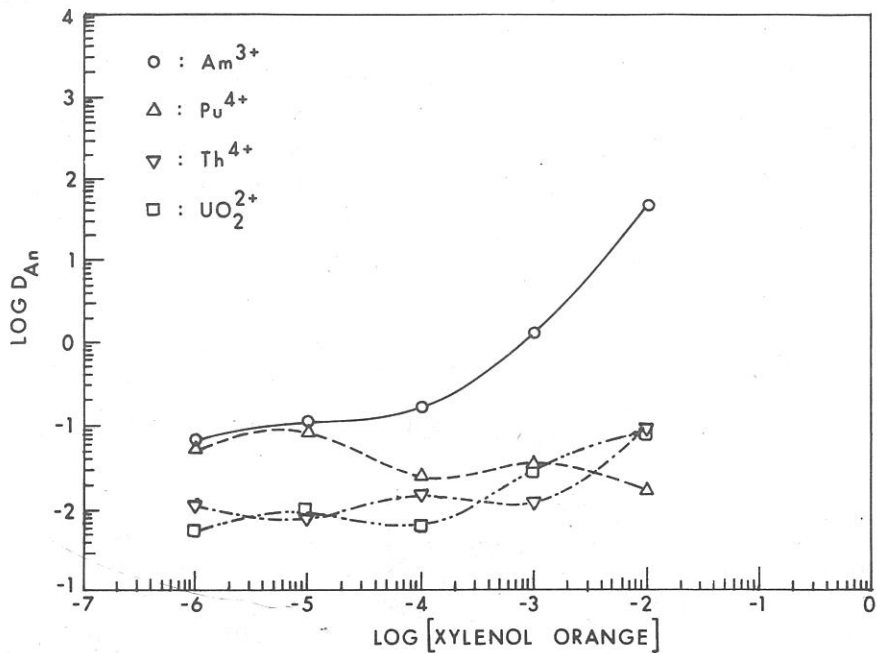


FIG.-1. VARIATION OF D FOR DIFFERENT ACTINIDE IONS WITH [XYLENOL ORANGE] FOR THE 22.5% K₂CO₃ / PEG-2000 SYSTEM

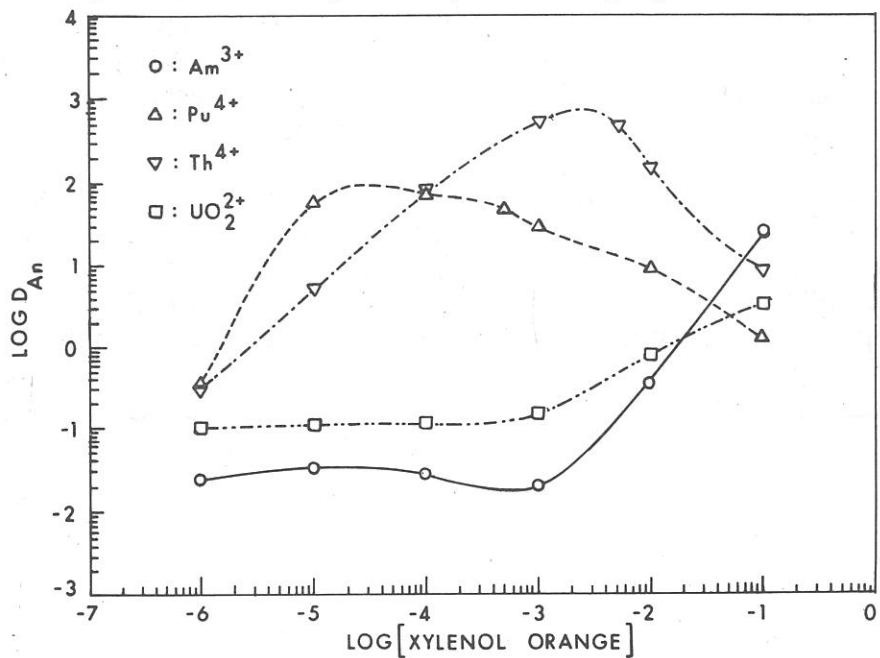


FIG.-2. VARIATION OF D FOR DIFFERENT ACTINIDE IONS WITH [XYLENOL ORANGE] FOR THE 21.2% (NH₄)₂SO₄ / PEG-2000 SYSTEM.