Review

Amides and diamides as promising extractants in the back end of the nuclear fuel cycle: an overview

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Abstract

An overview of the work carried out on the development of amides/diamides as alternate extractants in the back end of fuel cycle has been given. Whereas a straight chain amide, viz. *N,N*-dihexyl octanamide (DHOA) is a promising alternate to tri-*n*-butyl phosphate (TBP) in the reprocessing of irradiated uranium-based fuels, a branched chain amide, viz. *N,N*-di(2-ethylhexyl) isobutyramide (D2EHIBA) has been found suitable for the selective recovery of ^{233}U from irradiated Th. DHOA has been found to extract Pu more efficiently than TBP under uranium loading conditions. On the other hand, significant improvement in the separation of ^{233}U from Th and fission products has been achieved by employing 0.5 M D2EHIBA in *n*-dodecane as compared to that of 5% TBP (the THOREX solvent). Stripping behaviour of U for DHOA and D2EHIBA is better than that of TBP. *N,N′,N,N′*-dimethyl dibutyl tetradecyl malonamide (DMDBTDMA) has been evaluated for the partitioning of minor actinides (MA) from high-level nuclear waste with large uranium content (∼20 g/l). Designed amide ligands, viz. D2EHIBA showed improved separation of the desired actinide constituents like Pu (mainly ^{239}Pu) and ^{233}U over the fission products and the major matrix elements like U and Th.
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1. Introduction

Nuclear power constitutes ∼16% of the total power produced worldwide (3500 GWe). In all, 30 countries are engaged in this activity with ∼400 nuclear reactors in operation. Spent fuel produced till 1997 was 200,000 tonnes and it is expected to touch 340,000 tonnes by the year 2010 [1]. However, out of this only about 80,000 tonnes has been reprocessed so far. To sustain nuclear power programme beyond the availability of naturally occurring ^{235}U, it is imperative to follow closed fuel cycle option. Future of nuclear energy depends a great deal on the availability

of man-made isotopes like ^{239}Pu and ^{233}U. These fissile isotopes are produced in nuclear reactors in low concentrations (usually in range 0.1–1.0%) along with other actinide isotopes and a large number of fission products, which cover more than half the elements of the periodic table. The challenging task of recovery and purification of Pu from irradiated U and of ^{233}U from irradiated Th is accomplished presently by the well-known PUREX and THOREX processes, respectively [2–14]. Both of these processes employ organophosphorous compound, viz. tri-*n*-butyl phosphate (TBP) in long chain aliphatic hydrocarbon, viz. *n*-dodecane as solvent.

Though TBP-based PUREX process has been the workhorse of nuclear fuel reprocessing industry for the last four and a half decade yet a few drawbacks associated with the use of TBP have caused concern to the separation scientists and technologists [15–25]. The main problems of TBP are (i) its vulnerability to high radiation field and deleterious nature of its degradation products (mainly monobutyl phosphoric acid, H_2MBP and dibutyl phosphoric acid, HDBP) affecting the product recovery particularly with respect to fission products like Zr and Ru, retention of Pu in the organic phase and the rate of separation of the two phases; (ii) relatively lower distribution coefficient of Pu(IV) as compared to that of U(VI); (iii) its solubility towards aqueous phase; and (iv) non-incinerable nature of the spent solvent yielding large volumes of secondary radioactive waste. These shortcomings may pose a serious challenge particularly during the reprocessing of short cooled mixed oxide (MOX) thermal reactor as well as fast reactor fuels with the larger Pu content and significantly higher burn up.

The separation of U from irradiated bulk Th, on the other hand, is quite challenging in view of the non variable oxidation state of Th (unlike that of Pu), poor solubility of $Th(NO_3)_4$·3TBP species in diluent leading to the third phase during the co-extraction of uranium and thorium [26]. There is also the limitation of the decontamination factor (DF) of U with respect to Th and Pa. In addition, there is a specific problem of the handling of irradiated Th (while reprocessing as well as during fuel fabrication) due to the presence of ^{232}U (precursor of hard gamma emitting decay products), which is a radiological hazard, and the loss of ^{233}Pa (in view of its long half life, 27 days) inside the reactor due to neutron absorption. Innovative approaches

in fuel reprocessing are called for to overcome at least some of these problems.

In nuclear fuel reprocessing, the advantages of *N,N*-dialkyl aliphatic amides were identified since the work of Siddall [27]. These extractants offer several advantages over organophosphorous compounds especially with respect to the (i) innocuous nature of their degradation products, viz. carboxylic acids/amines; and (ii) the possibility to incinerate the used solvent leading to reduced volume of secondary waste [27–31]. In addition, the physico-chemical properties of this class of ligands can be tuned by the judicious choice of alkyl groups. In the last decade, many investigations have been conducted on the improvement of amide structures in order to secure the best extracting properties. Interesting molecular modeling studies have also been reported to understand the influence of amide structure on the extraction of metal ions [32,33]. Most of the work reported earlier on amides referred to either aromatic or substituted aliphatic hydrocarbons employed as diluents. However, these diluents are not suitable for commercial scale reprocessing due to their poor radiation and chemical stability in the presence of nitric acid as well as their tendency to form a three-phase system [34,35]. Recently, a systematic attempt has been made to investigate (a) linear dialkyl amides as alternate to TBP (as in PUREX process) for the recovery and purification of Pu; and (b) branched chain dialkyl amides as alternate to TBP (as in THOREX process) for the recovery and purification of U [36–46].

Steady growth of global fuel reprocessing activities (6000 tHM per annum) implies a vital role for the radiochemists not only in developing efficient procedures for the separation and purification of actinides but also in devising safe procedures for the management of nuclear waste arising at different stages of the PUREX process [47–49]. High-level waste (HLW) comprising of the concentrate of the raffinate of the co-extraction cycle (with over 95% of the total radioactivity produced in the burn up process in reactor) need to be isolated from the biosphere. There is a consensus among the waste management technologists that the safest route to achieve this, is to deposit it in a stable geological formation after it's immobilization in suitable glass/Synroc matrix. It ensures that any risk from exposure due to accidental intervention or natural disturbance is minimized.

In view of the high cost involved and the need for continuous surveillance, several countries are considering modifying their reprocessing schemes to partition (isolate) long-lived actinides from HLW. Since the volume of the actinide oxides (which retain major fraction of the radio toxicity of HLW) is significantly lower as compared to the other metal oxides present in HLW, such an approach is expected to reduce the cost of immobilization as well as of disposal (in geological repository) and surveillance significantly. Thus there is a need to develop procedures for the separation of long-lived isotopes of minor actinides (MA) and fission products from the high active aqueous raffinate streams of co-extraction cycle of PUREX process, commonly referred to as actinide-partitioning (AP). The separated minor actinides need to be kept in retrievable long-term storage facilities as such or in conditioned thermodynamically stable phase depending on which of the commonly discussed options, viz. transmutation-recycle in MOX fuels/transmutation–incineration in special targets or deposition in deep repositories, is proposed to be exercised in future. Duration of the storage for a century is recommended to allow for the decay of ^{244}Cm,

which apart from being an intense heat/neutron source may lead to the formation of long-lived ^{245}Cm. It is desirable to free the MA fraction from nuclides of high neutron absorption cross-section if partitioning is to be followed by transmutation. Possibility of the isolation of some pure radionuclides as valuable by-products makes actinide-partitioning a further attractive strategy for HLW treatment. Application of universal fuel reprocessing extractant like TBP for actinide-partitioning is not possible without producing waste streams with high salt content. Thus there is a need to develop versatile reagents capable of partitioning actinides under the prevailing conditions of HLW. USA, France, Japan and China are among the leading nations with R&D programmes (in this area) employing different extractants, viz. dihexyl-*N,N*-diethylcarbamoylmethyl phosphonates (DHDECMP), octyl(phenyl)-*N,N*-diisobutylcarbamoyl methyl phosphine oxide (CMPO) (Fig. 1), *N,N′,N,N′*-dimethyl dibutyl tetra decyl malonamide (DMDBT-DMA), trialkyl phosphine oxide (TRPO), and diisodecyl phosphoric acid (DIDPA) [50–59]. In view of their ability to extract trivalent actinides like Am(III) and Cm(III) from HLW at ∼3 M HNO$_3$,
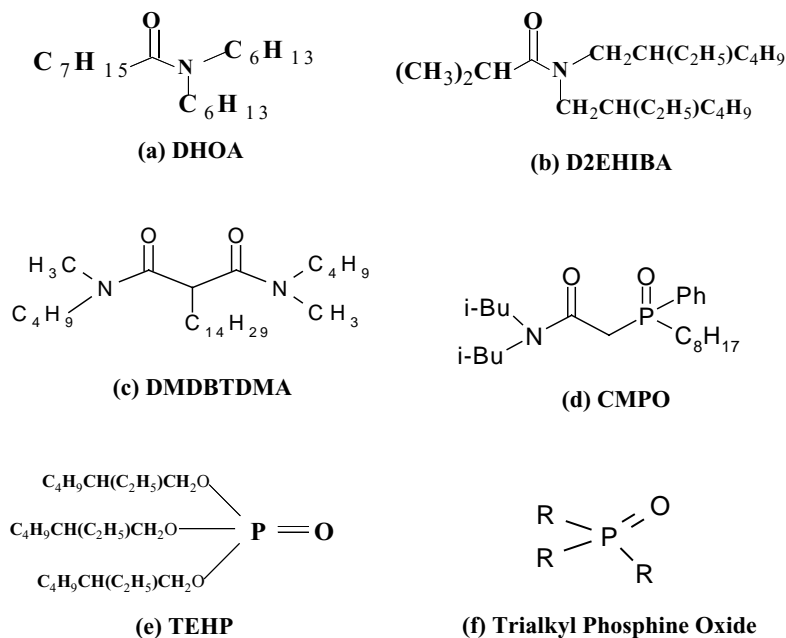

Fig. 1. Structure formulae of various extractants.

CMPO and DMDBTDMA deserve particular attention. Processes using these reagents are referred to as TRUEX and DIAMEX, respectively. TRUEX process was developed by separation chemistry group of Argonne National Lab, USA, during the eighties [50]. The TRUEX extractant is usually 0.2 M CMPO + 1.2 M TBP in paraffinic hydrocarbon (n-dodecane). High distribution ratio (D) values of tri-, tetra-, and hexavalent actinides from the solutions of moderate acid concentration and good selectivity over several fission products and high chemical stability are key features of this solvent. Various TRUEX process demonstrations have been carried out on waste solutions of different origins (acidic/alkaline) [58–65].

DIAMEX process on the other hand is being developed by CEA, France [52,53]. Salient features of this process are the use of completely incinerable extractant (leading to reduced secondary waste), ease of synthesis and elimination of a step of prior uranium removal. This work has gained momentum in recent years, in view of the support of the European Atomic Energy Community [52]. The chemical properties of malonamides are influenced by the nature of substituents on the nitrogen and central methylene carbon atom. Systematic solvent extractions as well as crystallographic studies have been carried out to understand the mechanism of extraction of metal ions from nitric acid medium using substituted malonamides as extractants [66]. The relationship between metal extraction from aqueous nitric acid solution, basicity and the structure of the malonamide has also been investigated. Highest metal ion extraction was reported for the ligands with the lowest basicity. The introduction of phenyl substituents on the nitrogen in malonamides or the replacement of carbon of the central atom chain by ether oxygen decreases the basicity and thus increases the metal extraction [67]. Various research groups have also investigated the extraction of lanthanides(III) and actinides with diglycolamides, which have an ether oxygen between two amide groups [68–74]. These studies have been focused on the effect of alkyl substituents, aqueous phase acidity on the extraction behaviour of lanthanides and actinides.

A detailed account of the work carried out at Bhabha Atomic Research Centre (BARC), India, on nuclear fuel reprocessing of U/Th-based fuels as well as on actinide-partitioning employing amides and diamides as extractants, respectively, is summarised in this review.

2. Results and discussion

2.1. N,N-dialkyl amides as extractants in nuclear fuel reprocessing

2.1.1. Straight chain amides: promising extractants for U-based fuels

Work was initiated to design, synthesise and characterise dialkyl amides followed by their investigation of the extraction behaviour of U(VI), Pu(IV), Am(III) and fission products like Cs(I), Sr(II), Eu(III), Zr(IV) and Ru(III) from nitric acid medium employing n-dodecane as the diluent. The physical and chemical properties of these amides are influenced strongly by the nature of alkyl groups. N,N-Dihexyl derivatives of hexanamide (DHHA), octanamide (DHOA) and decanamide (DHDA) were found to be promising amongst a large number of extractants studied. These ligands readily dissolved in n-dodecane and did not form third phase with nitric acid (up to 7 M). The nature of extracted species formed in the organic phase, the corresponding two-phase extraction constants, the influence of U loading on third phase formation and on distribution data, and the effect of gamma irradiation as well as of temperature have been investigated [36–40]. Laboratory batch studies as well as mixer settler studies were performed in further details with DHOA and compared with those of TBP. This is the first ever attempt to evaluate DHOA/n-dodecane system as a process diluent [38].

2.1.1.1. Synthesis. The extractants employed in this work were amongst a score of amides synthesised in our laboratory by the reaction shown in Eq. (1). Amides were purified by vacuum distillation. Overall yield of the synthesised product was 80–90%. Characterisation of the ligands obtained after vacuum distillation was done by elemental analysis and IR/PMR spectral analysis [36–40].
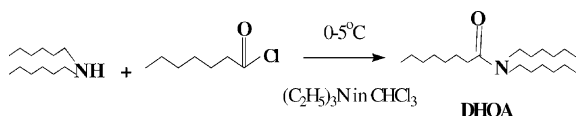
$$\tag{1}$$

Similarly *N,N*-dihexyl derivatives of hexanamide (DHHA) and decanamide (DHDA) were synthesised using hexanoyl and decanoyl chlorides. Their purity was ascertained by the determination of amide contents through non-aqueous potentiometric titration [75]. Acid uptake values (K_H) of these amides vary in the order DHHA (0.17) < DHOA (0.18) < DHDA (0.20). The corresponding value of TBP is 0.16. HNO_3 concentration at which third phase is formed with 1 M amide/*n*-dodecane solution vary in the range 7 M (DHHA) to 10 M (DHDA). Kilogram quantities of DHOA and DHHA were synthesised and employed for the mixer settler runs to investigate their potential as alternate extractants to TBP in the PUREX process.

2.1.1.2. Nature of extracted species. From moderately acidic solutions, U(VI) and Pu(IV) are extracted by the amides via solvation similar to TBP. The extracted species are identified as $UO_2(NO_3)_2 \cdot 2A$ and $Pu(NO_3)_4 \cdot 2A$ (where A: amide). The extraction constant (log K_{ex}) values obtained for these solvated species are 1.43 (DHHA), 1.49 (DHOA) and 1.47 (DHDA) for U(VI) and 3.62 (DHHA), 3.55 (DHOA) and 3.51 (DHDA) for Pu(IV). At higher nitric acid concentrations, the amides undergo protonation (HAmide)$^+$ and extract U(VI) and Pu(IV) as ion-pairs of the type $[UO_2(NO_3)_3{}^-]$ $[HAmide^+]$ and $[Pu(NO_3)_4{}^{2-}]$ $[HAmide^+]_2$. Thus, the amides differ from TBP with respect to the nature of extracted species of U(VI) at high acidity.

2.1.1.3. Comparison of the distribution behaviour of amides and TBP towards U(VI) and Pu(IV). At trace level concentrations, the *D* values of Pu(IV) with 1 M solutions of DHHA, DHOA, DHDA, and TBP in *n*-dodecane at 3.5 M HNO_3 (usual feed acidity in PUREX process) are found to be 41.2, 38.2, 32.6 and 19.2, respectively. At 50% uranium saturation of the organic phase, the corresponding *D* values of Pu(IV) are 9.2, 7.3, 5.8 and 2.1. It is evident from these data that all the three amides used in the present work extract Pu(IV) more efficiently than TBP, both at trace level concentration as well as under uranium loading conditions. The *D* values of U(VI) at trace level concentration with 1 M solutions of DHHA, DHOA, DHDA and TBP in *n*-dodecane at 3.5 M HNO_3 are found to be 13.5, 13.9, 13.6 and 29.6, respectively. At 50% uranium saturation of the organic phase, the
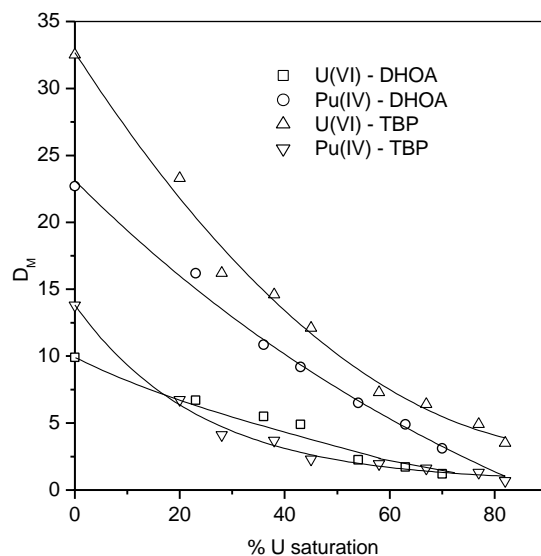

Fig. 2. Variation of distribution coefficients of U(VI) and Pu(IV) from 3 M HNO_3 into 1 M DHOA/30% TBP in *n*-dodecane with uranium saturation at 25 °C.

corresponding *D* values are 4.2, 4.3, 4.0 and 11.4, respectively. The distribution data of U(VI) and Pu(IV) obtained at 3 M HNO_3 as a function of uranium saturation of the organic phase (1 M DHOA or 30% TBP in *n*-dodecane) are plotted in Fig. 2. The *D* values of U(VI) and Pu(IV) decreased continuously with uranium saturation. It is of particular interest to note that at a given value of uranium saturation of the organic phase, D_{Pu} value for DHOA is much higher than the corresponding value for TBP. Distribution ratio values for 60% U saturation (commonly employed in some reprocessing plants at co-extraction stage) for the two solvents are (i) $D_{Pu(IV) \cdot DHOA}$: 5.6; (ii) $D_{Pu(IV) \cdot TBP}$: 1.8; (iii) $D_{U(VI) \cdot DHOA}$: 2.1; and (iv) $D_{U(VI) \cdot TBP}$: 7.0. It is obvious that larger number of contacts are needed for the quantitative extraction of Pu(IV) with 30% TBP as compared to 1 M DHOA. The *D* values of Pu(IV) under plutonium loading conditions (5 g/l) are found to be 19.4 (DHHA), 18.6 (DHOA), 14.9 (DHDA) and 8.9 (TBP). It is clear that DHOA is a better extractant of Pu(IV) as compared to TBP under loading conditions of U as well as Pu which may lead to reduced losses of Pu towards the aqueous raffinate stream. The lower *D* values of U(VI) with the amides as compared to TBP facilitate its easier stripping from the loaded organic phase.

2.1.1.4. Limiting organic concentration (LOC) of U with amides. Merits of amides over TBP like complete incinerability, benign nature of degradation products and higher extraction of Pu (mentioned above) are partially offset by rather low solubility of uranyl nitrate solvates of amides into aliphatic hydrocarbon type diluents. The concentration of uranium in the solution, resulting from the dissolution of irradiated thermal reactor fuel in nitric acid, is usually maintained at 300–350 g/l, which is much higher as compared to plutonium (∼1 g/l). Due to the limited solubility of U(VI) solvates, third phase formation can appear in the amide extraction system under high uranium loading conditions [36]. The LOC data of U(VI) for 1 M DHHA and 1 M DHOA in *n*-dodecane obtained as a function of equilibrium nitric acid concentration of the aqueous phase (1–8 M) at 25 °C are presented in Fig. 3. It can be seen that the LOC value for both the amides decreases regularly with nitric acid molarity in the aqueous phase. Moreover, the LOC values for DHOA over the entire acidity range studied are significantly higher than those for DHHA. The LOC

value ranges from 88.4 g/l (at 1 M HNO_3) to 20.9 g/l (at 6.6 M HNO_3) for DHHA and 103.3 g/l (at 1 M HNO_3) to 40.3 g/l (at 7.7 M HNO_3) for DHOA. The effect of nitric acid on the LOC of uranium was explained as due to the competition of amide for HNO_3 and $UO_2(NO_3)_2$ molecules. Uranium loading capacities of 1 M solutions of the amides in *n*-dodecane at 3.0 M HNO_3 are evaluated to be 69.1 g/l for DHHA; 96.1 g/l for DHOA. Apart from the influence of nitric acid, the influence of $NaNO_3$, temperature and ionic strength was also studied on the limiting organic concentration of uranium. The LOC value increases continuously with amide concentration for both DHHA and DHOA. However considering $UO_2(NO_3)_2 \cdot 2A$ as the extracted species, percent of U saturation of the organic phase does not change significantly with the ligand concentration. In case of DHHA, it varies between 56.2 and 59.8% and in the case of DHOA, it varies between 80.3 and 81.3% while varying the ligand concentration in the range 0.5–1.25 M. In view of the higher LOC value of DHOA, further work was pursued with this ligand only.
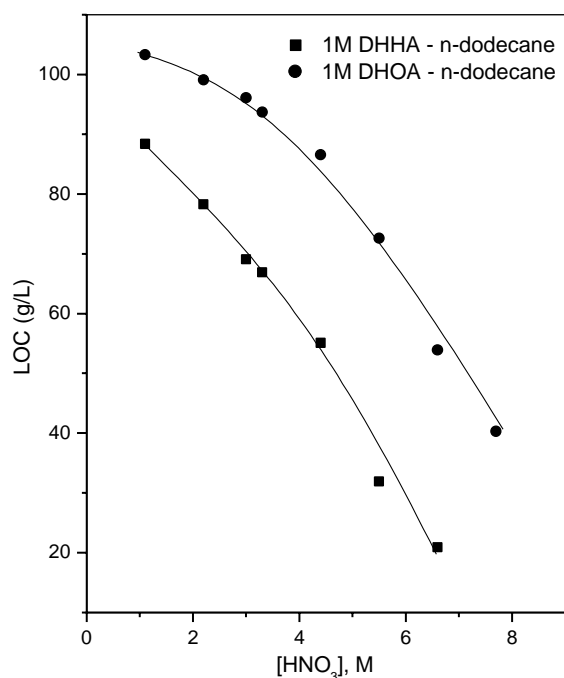
2.1.1.5. Effect of uranium saturation of DHOA on the extraction of U(VI), Pu(IV), Am(III) and Zr(IV). The distribution behaviour of U(VI), Pu(IV), Am(III) and Zr(IV) with 1 M DHOA in the presence of 97.3 g/l of uranium in the aqueous phase was also studied as a function of nitric acid concentration. The data presented in Fig. 4 show that both U(VI) and Pu(IV) are extracted efficiently, whereas the extraction of Am(III) and Zr(IV) is very poor throughout the acidity range (1–6 M) investigated, suggesting reasonably high separation factors (SF) for plutonium and uranium from these two metal ions. Another important observation is that D_{Pu} values are higher than the D_U values in the nitric acid concentration range of 2.5–6 M.

2.1.1.6. Distribution behaviour of fission products. The distribution ratio (*D*) data obtained for Zr(IV) and Ce(III) with 1.1 M DHOA and 1.1 M TBP in *n*-dodecane at varying nitric acid concentration (1–6 M) indicate that both DHOA and TBP extract Zr(IV) better than Ce(III) throughout the acidity range indicated (Figs. 5 and 6). This can be attributed to the higher ionic potential of Zr(IV) than that of Ce(III). However, the extraction of these elements with DHOA is much lower as compared to TBP. The extraction of
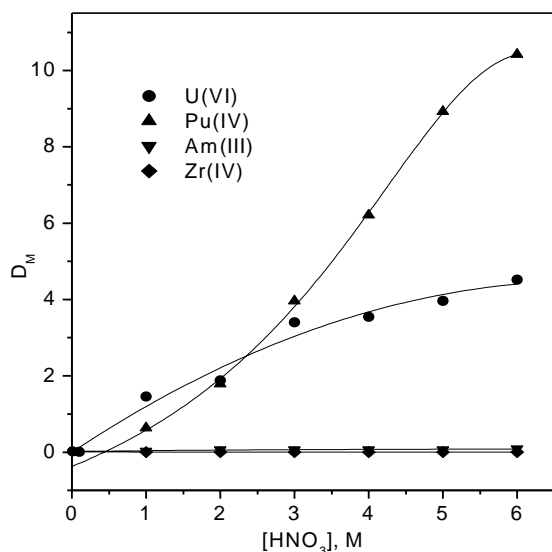

Fig. 3. LOC of U(VI) as a function of acidity: organic phase, 1 M amide solution in *n*-dodecane; temperature, 25 °C.

Fig. 4. Variation of D_M with varying concentrations of HNO_3 at macro concentrations of U(VI) (97.3 g/l): organic phase, 1 M DHOA in n-dodecane; temperature, 25 °C.
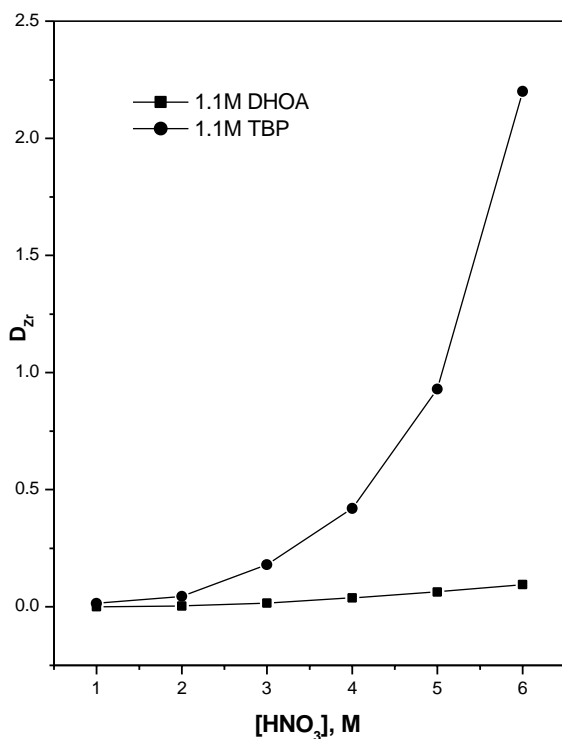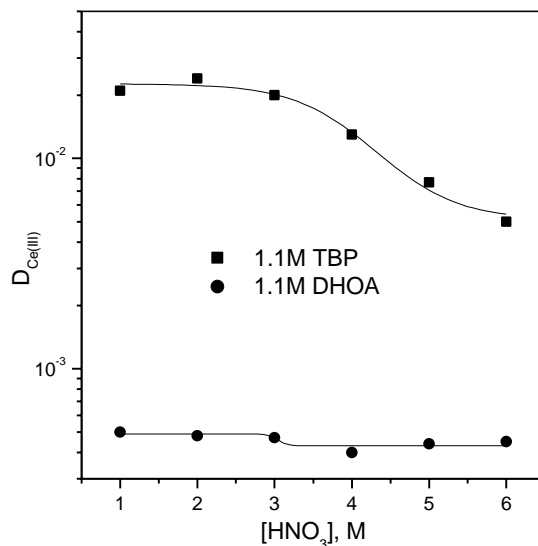

Fig. 6. Variation of $D_{Ce(III)}$ with nitric acid concentration: organic phase, 1 M DHOA in n-dodecane; temperature, 25 °C.

Zr(IV) and Ce(III) with DHOA between 2 and 4 M HNO_3 is lower by a factor of ∼10 and ∼40, respectively, as against TBP. The extraction behaviour of Ru was found to be influenced significantly by the conditioning of the aqueous phase. The extraction of Ru was negligible ($D_{Ru} < 10^{-3}$) with both the extractants from nitric acid in the range (1–6 M). However, there is a significant enhancement in the extraction of Ru for both DHOA and TBP, when the extraction is carried out from the aqueous phase prepared from the stock solution that was heated with 10 M HNO_3. This increase can be attributed to the formation of $RuNO^{3+}$ ions in the aqueous phase, which forms the extractable species. It is of interest to note that D_{Ru} is considerably lower for DHOA as compared to that of TBP between 0.5 and 3 M HNO_3 and thereafter there is no significant difference up to 6 M HNO_3. At 3 M HNO_3, the extraction of Ru with DHOA is approximately five times lower as compared to TBP under heating and N_2O_4 purging conditions.

2.1.1.7. Radiolytic degradation. The infrared investigations have revealed that the main degradation products of the amides are carboxylic acids ($\nu_{C=0} = 1720 \, cm^{-1}$) and amines ($\nu_{N-H} = 3420 \, cm^{-1}$). These degradation products are easily washable with dilute acid/water, unlike those of TBP which need alkali
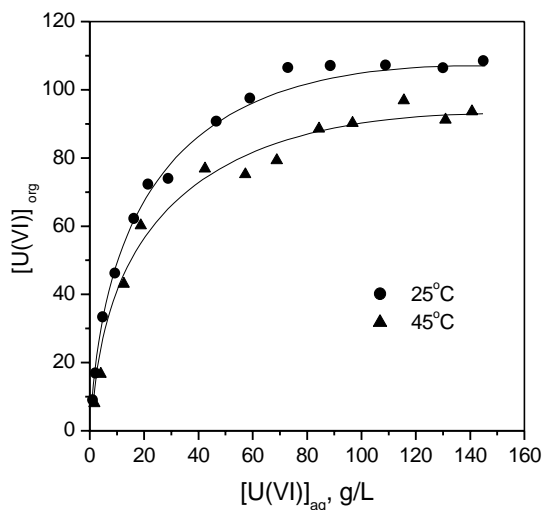

Fig. 5. Variation of $D_{Zr(IV)}$ with nitric acid concentration: organic phase, 1 M DHOA in n-dodecane; temperature, 25 °C.

Fig. 7. Extraction isotherms of uranium at 25 and 45 °C using 1 M DHOA in *n*-dodecane: [HNO$_3$] = 3 M.

wash (1 M Na$_2$CO$_3$) leading to higher volume of secondary waste. The DF values of U and Pu with respect to Ru(III) employing irradiated amides as extractants are comparable to the corresponding values with TBP [40]. However, amides are found to be particularly promising for their selectivity over Eu(III) and Zr(IV) from irradiated solutions as compared to TBP. Typically the DF values at 3×10^5 Gy with 30% TBP are ~7 (U/Zr) and ~12 (Pu/Zr) which are enhanced about five-fold with 1 M DHOA.

2.1.1.8. Effect of temperature on the extraction of macro amounts of uranium. Fig. 7 shows the extraction isotherms of the system U(VI)/3 M HNO$_3$/1 M DHOA/*n*-dodecane at 25 and 45 °C. As expected D_U decreases sharply with percent of U saturation of the organic phase as well as with increase of temperature. D_U value lies in the range 2–3 for 60% U saturation, recommended for process applications in view of the LOC values determined by us earlier. Thus it appears possible to carry out quantitative extraction of U from PUREX feed (~300 g/l) in three to four stages provided suitable volume ratio for organic and aqueous phases is chosen. It was verified in the present work by the results given in the following section on mixer settler studies.

2.1.1.9. Mixer settler studies. To explore the use of DHOA in fuel reprocessing as an alternate to TBP, mixer settler studies were carried out with both the extractants under identical experimental conditions.

Extraction cycle. In the mixer settler studies, concentration of uranium and of nitric acid in the feed for the extraction cycle was maintained close to the conditions prevailing in the PUREX process, viz. 260.7 g/l U and 3.07 M HNO$_3$ (initial concentration). Extractant was 1.1 M DHOA in *n*-paraffin hydrocarbon (NPH). Organic-to-aqueous phase ratio (O/A) was 3 (aqueous flow rate: 1.5 ml/min; organic flow rate: 4.5 ml/min). Concentrations of uranium and HNO$_3$ in organic EXIT sample at equilibrium (after six bed volumes) were 88.6 g/l and 0.43 M HNO$_3$, respectively. On the other hand, aqueous EXIT samples contained <0.1 g/l of uranium throughout suggesting quantitative extraction of U even after one bed volume was passed. Acidity of the aqueous EXIT samples under equilibrium condition was ~1.9 M. It is observed that the composition of EXIT organic stream as well as EXIT aqueous stream is similar to that of 30% TBP with respect to uranium concentration as well as acid concentration. On the other hand, stage analysis data in Fig. 8(a) depicts some differences in the behaviour of two extractants. Aqueous uranium concentration for DHOA system is lower but acidity is higher as compared to TBP system at stage 1 as well as at stage 2. Whereas approximately 215 g/l of uranium is transferred from aqueous phase to organic phase at first stage for DHOA, the corresponding figure for TBP is approximately 180 g/l.

Stripping cycle. Concentration of uranium in feed was maintained as 87.7 g/l and of [HNO$_3$] as 0.43 M and the strippant was 0.01 M HNO$_3$. O/A was maintained as 1:1.3 for TBP as well as DHOA system. Flow rate of organic phase was 4.0 ml/min and that of aqueous phase as 5.2 ml/min for DHOA. EXIT samples collected after passing three bed volumes showed quantitative stripping of uranium from organic phase and equilibrium was observed after four bed volumes were passed. Aqueous uranium concentration showed a steady value of 68 g/l and acidity of approximately 0.4 M. Stage analysis data shows that stripping is more efficient for DHOA system (Fig. 8(b)). Whereas quantitative stripping (>99.9%) was observed with this ligand at stage 6, only 74 % stripping could be achieved
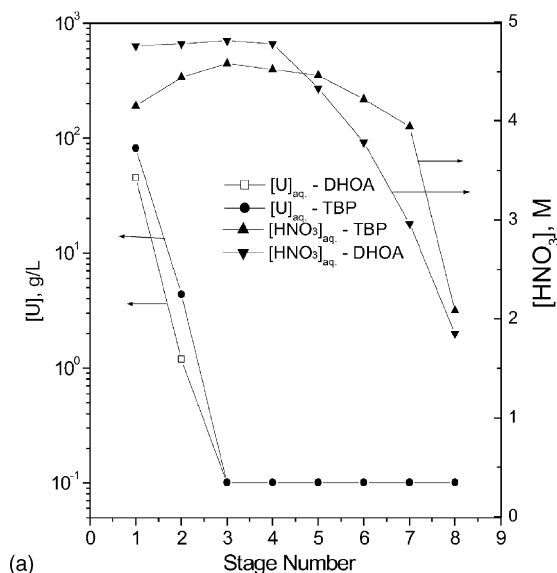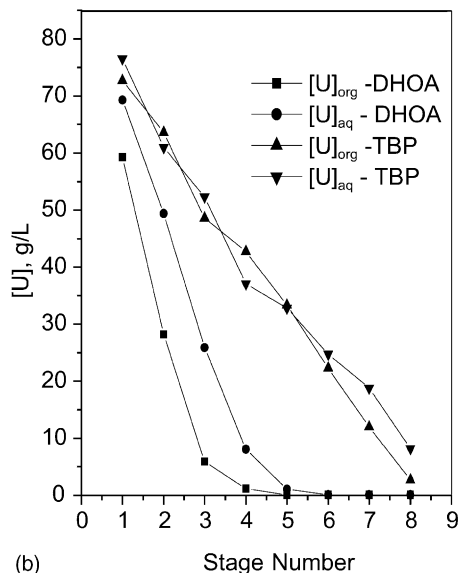
Fig. 8. Stage analysis data of (a) the aqueous phase for extraction cycle and (b) the organic phase for stripping cycle for 1.1 M DHOA and 30% TBP in NPH as diluent.

for TBP system for the corresponding stage. After eight stages of mixer settler, <97% of stripping was seen in the case of TBP. About 2.6 g/l of uranium was present in the EXIT organic samples for TBP but <0.1 g/l for DHOA at equilibrium.

2.2. Branched chain N,N-dialkyl amides: promising class of extractants for the separation of ^{233}U from irradiated thorium

In our laboratory, large number of N,N-dialkyl amides were synthesised (following the reaction shown by Eq. (1) and evaluated for their extraction behaviour towards U(VI) and Th(IV) from nitric acid medium (Table 1) [41–44]. Branched chain N,N-dialkyl amides (nos. 1–5 in Table 1) hold great promise towards process applications for the recovery of ^{233}U from irradiated thorium. Branching in the alkyl chain adjacent to the carbonyl group suppresses the thorium extraction considerably due to the steric hindrance exerted by the amide molecules on coordination to Th(IV) surrounded by four nitrate ions.

Attempts were made to arrive at the conditions suitable for the separation of ^{233}U from Th(IV), Pa(V) and fission products employing di(2-ethylhexyl) isobutyramide (D2EHIBA, a typical branched amide) in n-dodecane as diluent. D2EHIBA was chosen in view of its lower viscosity as compared to the other branched amides. No third phase was observed while equilibrating 1 M solution of D2EHIBA in n-dodecane with either 10 M HNO$_3$ or with 200 g/l Th(IV) solutions at 4 M HNO$_3$ (V_O/V_A:1). The third phase is formed with 1 M TBP even at 1 M HNO$_3$ in the presence of 200 g/l of Th.

Fig. 9 reveals that in the presence of thorium (~200 g/l), efficient separation of ^{233}U could be achieved from Th(IV) and Pa(V) in the acidity range 1–4 M HNO$_3$ by 1 M D2EHIBA in n-dodecane. Negligible extraction of fission products (D: ~10^{-3}) such as Zr(IV), Ce(III), Eu(III), Sr(II), Cs(I) and the structural material, Fe(III) over a wide range of nitric acid concentrations (1–6 M) suggested that an efficient fission product decontamination of product ^{233}U could be achieved. Preferential extraction of U over Pa, in

Table 1

Evaluation of *N,N*-dialkyl amides for the separation of ^{233}U from irradiated ^{232}Th: concentration of the extractant, 1 M; aqueous phase, 4 M HNO_3; diluent, *n*-dodecane; temperature, 25 °C; SF, D_U/D_{Th} (using ^{233}U/^{234}Th tracers only)

$$\begin{array}{c} O \\ \parallel \\ R-C-N \end{array} \begin{array}{c} R' \\ R' \end{array}$$
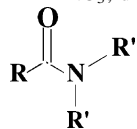
| SN	Amide	R	R′	D_U	D_{Th}	SF
1	D2EHIBA	$(CH_3)_2CH$	$C_4H_9CH(C_2H_5)CH_2$	3.70	1.0×10^{-2}	370
2	D2EHPVA	$(CH_3)_3C$	$C_4H_9CH(C_2H_5)CH_2$	2.85	8.04×10^{-3}	353
3	DIB2EHA	$CH_3(CH_2)_3CH(C_2H_5)$	$(CH_3)_2CHCH_2$	4.70	1.34×10^{-2}	351
4	DOIBA	$(CH_3)_2CH$	C_8H_{17}	5.84	1.42×10^{-2}	411
5	DO2EHA	$CH_3(CH_2)_3CH(C_2H_5)$	C_8H_{17}	6.58	1.85×10^{-2}	356
6	D2EHBA	C_3H_7	$C_4H_9CH(C_2H_5)CH_2$	8.36	6.01×10^{-2}	139
7	D2EHPRA	CH_3CH_2	$C_4H_9CH(C_2H_5)CH_2$	9.7	0.1	97
8	DHOA	C_7H_{15}	C_6H_{13}	12.40	0.59	21
9	DHDA	C_9H_{19}	C_6H_{13}	11.62	0.45	26
10	DBDA	C_9H_{19}	C_4H_9	11.48	0.96	12
11	DHHA	C_5H_{11}	C_6H_{13}	12.80	0.80	16
12	TBP	–	–	40	4	10

SN: serial number.
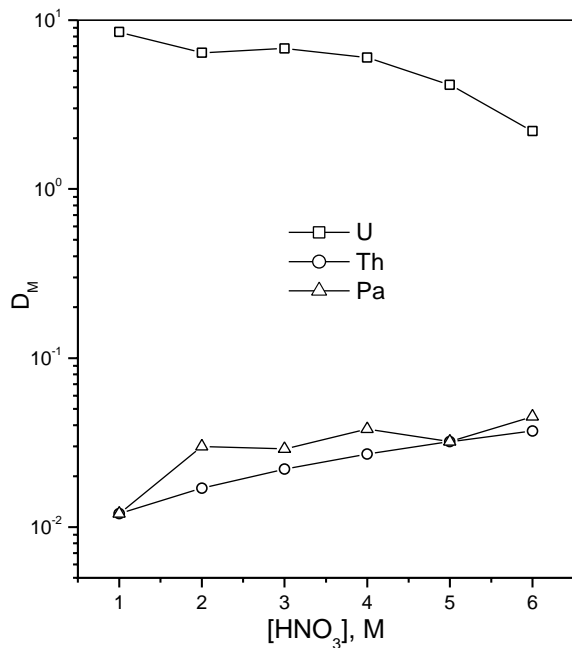
Fig. 9. Extraction behaviour of Th(IV), Pa(V) and U(VI) as a function of nitric acid concentration: [Th], ~200 g/l; [U(VI)], 10^{-4} M; [Pa(V)], ~10^{-10} M; extractant, 1 M D2EHIBA in *n*-dodecane. Temperature: 25 °C.

principle can be employed for the decontamination of ^{233}U from ^{232}U in a two-stage extraction cycle. In the first stage (with cooling period sufficient for ^{232}Pa decay, $T_{1/2} = 1.3$ days), mixture of ^{233}U and ^{232}U can be separated leaving a part of ^{233}Pa, Th and fission products in the raffinate. In the second stage (with cooling period sufficient for ^{233}Pa decay, $T_{1/2} = 27$ days), ^{233}U can be separated from Th and fission products.

Table 2 compares the distribution data of U(VI) and Th(IV) with TBP, TEHP (tris-(2-ethylhexyl) phosphate; a branched chain phosphate), DHHA (a linear *N,N*-dialkyl amide) and D2EHIBA (a branched chain *N,N*-dialkyl amide) under identical conditions.

Table 2

Extraction behaviour of linear and branched chain extractants towards U-Th separation: [Th], 200 g/l; [U], ~10^{-4} M; [HNO_3] = 4 M; diluent, *n*-dodecane; temperature, 25 °C

Extractant	[Ligand] (M)	D_U	D_{Th}	D_U/D_{Th}
TBP	0.18	2.4	2.3×10^{-2}	100
TEHP	0.18	6.2	3.5×10^{-2}	180
DHHA	0.18	0.4	1.7×10^{-3}	240
D2EHIBA	0.18	1.2	4.0×10^{-4}	3000
	0.5	*4.0*	*2.4×10^{-3}*	*1670*
	1.0	6.0	2.7×10^{-2}	220

Separation factor value of 3000 for 0.18 M D2EHIBA is significantly larger than the corresponding value of other extractants [43]. However, 0.18 M D2EHIBA has a limited process application in view of its low D_U value (1.2). On the other hand, 1 M D2EHIBA has a reasonable value of D_U (6.0) but relatively lower SF value (222). A solution of 0.5 M D2EHIBA in *n*-dodecane was therefore chosen as a candidate for process applications in view of the significant enhancement in the SF values (D_U/D_{Th}:1670 at 4 M HNO$_3$) as well as sufficiently high D_U value (4.0 at 4 M HNO$_3$). Also, density (g/cm^3) and viscosity (cP) in the case of 0.5 M D2EHIBA (0.768, 1.59) compare favourably with those of 5% TBP (0.739, 1.40) suggesting that the former could be explored further for process applications [46]. Presence of fluoride ion (used during dissolution step) suppressed the extraction of Th thereby enhancing the SF of uranium over thorium.

2.2.1. Degradation behaviour

Acid hydrolysis as well as gamma radiolysis of 0.5 M D2EHIBA in *n*-dodecane (pre-equilibrated with 4 M HNO$_3$) was compared with that of 5% (0.18 M) TBP. Whereas no change was observed in the amide content as well as in the distribution data of uranium due to acid hydrolysis, there was a continuous decrease in amide content and D_U value due to radiolytic degradation of D2EHIBA (Fig. 10). A similar decrease in D_U was observed in the case of 5% TBP. Stripping behaviour of irradiated 0.5 M D2EHIBA was found to be better than that of 5% TBP solution. Whereas three contacts were found to be adequate for quantitative stripping (>99.9%) of U in the former case, a white solid appeared at the interface in the latter case which was confirmed (by IR spectral studies) as due to Th-DBP (dibutyl phosphate) complex.

2.2.2. Mixer settler studies

2.2.2.1. Extraction cycle. To explore the applicability of D2EHIBA in the reprocessing of irradiated Th-based fuels as an alternate to TBP, twelve stage mixer settler runs were carried out employing both the extractants, viz. 0.5 M D2EHIBA and 5% TBP solutions in *n*-dodecane. Aqueous feed solution composition (initial) during these runs was: [Th] = 207 g/l, [U] = 202 mg/l, [HNO$_3$] = ~4 M, [HF] = ~0.01 M and [Al(NO$_3$)$_3$] = ~0.1 M. Flow rate of the organic
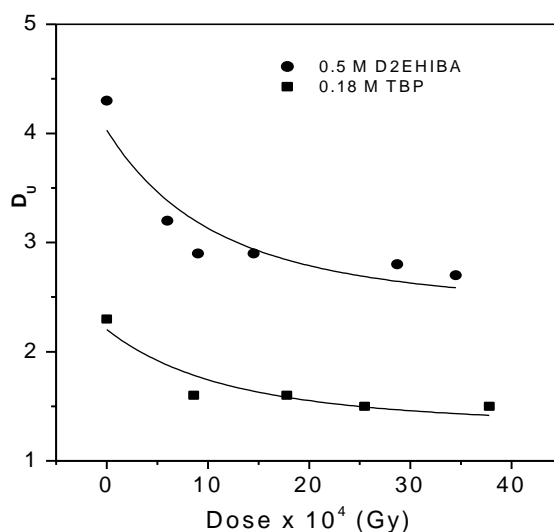

Fig. 10. Effect of radiolytic degradation on D_U: aqueous phase, ^{233}U (~10^{-4}M) + 200 g/l Th at 4 M HNO$_3$.

and aqueous phases was maintained as 4–5 ml/min. Overall O/A was maintained as 1 during extraction cycle. The aqueous EXIT samples contained ~2 mg/l U suggesting that quantitative extraction (>99%) of uranium from the feed solution. Final composition (at equilibrium) of the loaded organic phase was: [U] = 200 mg/l; [Th] = 180 mg/l and [HNO$_3$] = 0.36 M. On the other in case of 5% TBP under identical conditions, the concentrations of uranium, thorium and nitric acid in the consolidated loaded organic phase were ~219 mg/l, 5.9 g/l and 0.17 M, respectively, after passing two bed volumes. Interestingly, the aqueous raffinate contained ~11 mg/l U suggesting only ~95% extraction of uranium. Equilibrium thorium and nitric acid concentrations in the aqueous EXIT samples were 192±2 g/l and 3.8±0.1 M, respectively. Fig. 11(a) and (b) shows the stage wise concentration profile of U, Th and nitric acid in organic and aqueous phases.

2.2.2.2. Stripping cycle. Loaded organic phases obtained after extraction cycles using 0.5 M D2EHIBA and 5% TBP solutions in *n*-dodecane as extractants were treated as the feed solutions during stripping cycle. Distilled water was used as strippant. O/A was restricted to 2 during stripping cycle. Six stage mixer settler runs were carried out for the stripping of U

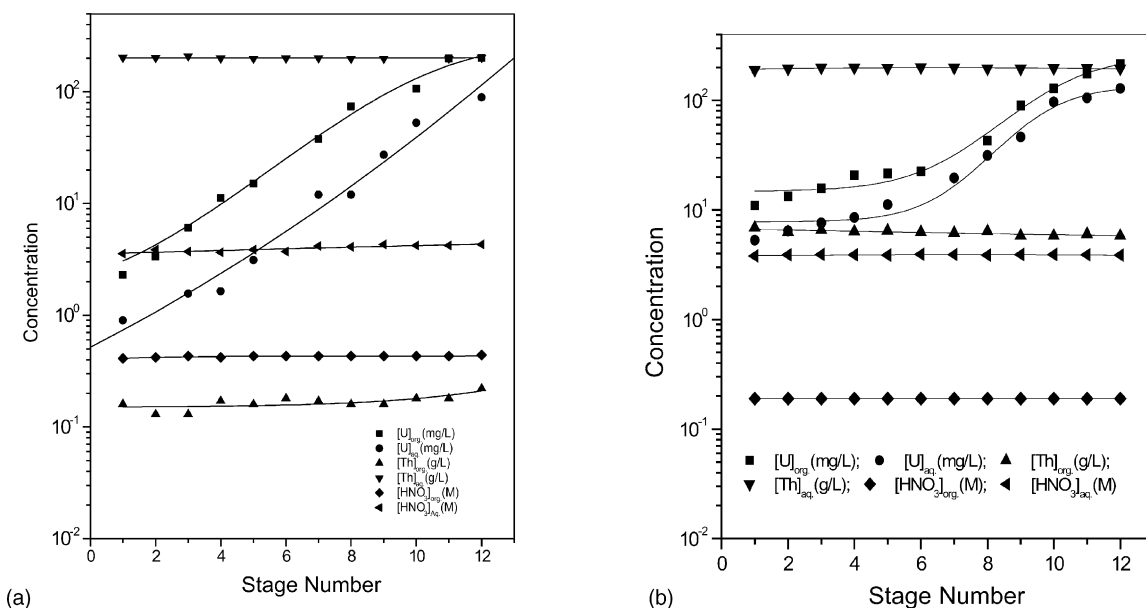| Org. IN →													Org. OUT →
	1	2	3	4	5	6	7	8	9	10	11	12	
← Aq. OUT													← Aq. IN

Fig. 11. Stage analysis during extraction cycle using (a) 0.5 M D2EHIBA; (b) 5% TBP in *n*-dodecane solutions as the extractants. Initial feed composition: [Th] = 207 g/l; [U] = 202 mg/l; [HNO$_3$] = ~4 M; [HF] = ~0.01 M; and [Al(NO$_3$)$_3$] = ~0.1 M, O/A:1.
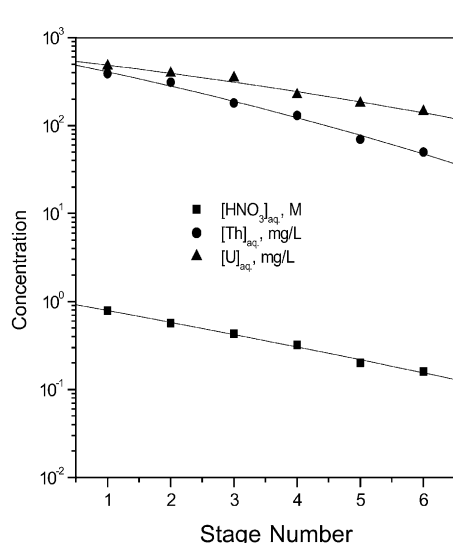
and Th from loaded organic phases. The organic phase flow rate was maintained as ~4 ml/min and that of the aqueous phase was ~2 ml/min. In case of 0.5 M D2EHIBA, the acidity of the stripped organic phase was found to be 0.03 M but no traces of uranium and thorium could be detected (<1 mg/l). Final concentration of uranium, thorium and nitric acid in the aqueous phase collected after stripping was 410 mg/l, 380 mg/l and 0.75 M, respectively. On the other hand, in case of 5% TBP, organic phase acidity after stripping was found to be 0.005 M. Spectrophotometric analysis of the stripped organic phase for uranium and thorium showed their concentrations to be 5 and 16 mg/l, respectively, suggesting incomplete stripping. Final concentration of uranium, thorium and nitric acid in the aqueous phase collected after stripping was 438 mg/l, 11 g/l and 0.39 M, respectively. Invariably in TBP system, extra scrubbing cycle is incorporated to free organic phase of Th. Fig. 12(a) and (b) shows the stage

analysis data of the aqueous phase during stripping cycle employing loaded 0.5 M D2EHIBA and 5% TBP solutions in *n*-dodecane as the organic feed solutions.

Table 3 lists the important observations of mixer settler runs carried out using 0.5 M D2EHIBA and 5% TBP in *n*-dodecane on THOREX feed solution. Loss of uranium to the raffinate is significantly lower in case of 0.5 M D2EHIBA (1%) than that in 5% TBP (5%). It is clear that significant decontamination of U over Th is achieved in case of 0.5 M D2EHIBA as compared to that of 5% TBP [DF: 1.2 × 10^3 (0.5 M D2EHIBA) and ~40 (5% TBP)]. Purification of uranium from thorium in the stripped solution was carried out by cation exchanger Dowex 50 × 4. Quantitative recovery of uranium could be achieved during purification stage.

Results obtained during this work clearly demonstrate the potential of D2EHIBA in meeting the challenges encountered during the reprocessing of

Org. IN →							Org. OUT →	
	1	**2**	**3**	**4**	**5**	**6**		
← Aq. OUT							← Aq. IN	
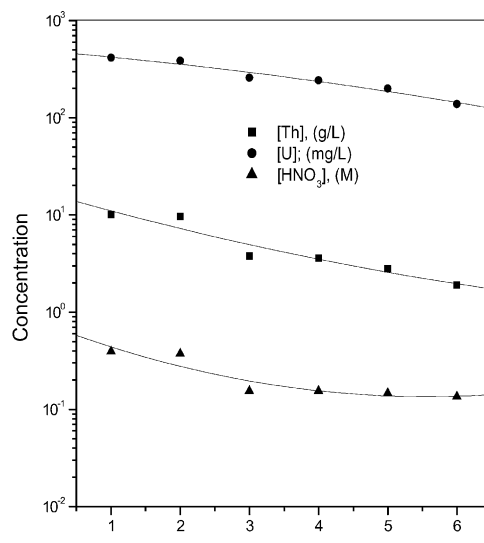
Fig. 12. Stage analysis during stripping cycle using loaded organic phases of (a) 0.5 M D2EHIBA and (b) 5% TBP solutions in *n*-dodecane as the extractants (obtained after extraction cycle): strippant, distilled water, O/A:2.

Table 3
Comparison of performance of 0.5 M D2EHIBA with 5% TBP during mixer settler runs: diluent, *n*-dodecane

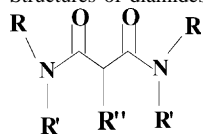| Parameter	0.5 M D2EHIBA	5% TBP
Uranium loss (%)	1	5
Thorium uptake (g/l)	0.18	5.9
Acid uptake (M)	0.4	0.17
Strippant	Distilled water	Distilled water
After stripping		
$[U]_{org}$ (mg/l)	Not detected (<1)	5
$[Th]_{org}$ (mg/l)	Not detected (<1)	16
$[HNO_3]$ (M)	0.03	0.005
DF[a]	1.2×10^3	~40

[a] After extraction cycle.

irradiated thorium. It offers very selective extraction of uranium over thorium and a large number of fission products. Recently, experiments were performed in our laboratory to precipitate Th as thorium oxalate direct from the organic phase. Aqueous supernatant was subsequently treated with ammonia to precipitate U quantitatively as ammonium diuranate (ADU). (Pu, Th)O_2 is likely to be used as the driver fuel for the proposed advanced heavy water reactor (AHWR) in India. In the context of recovery of Pu from AHWR fuel scrap, branched amides are also under investigation in our laboratory after oxidation of Pu to Pu(VI) [76,77].

2.3. Pentaalkyl malonamides: promising extractants in actinide-partitioning

A number of pentaalkyl malonamides, viz. *N,N,N′,N′*-tetrabutyl undecyl malonamide (TBUDMA), *N,N,N′,N′*-tetrabutyl dodecyl malonamide (TBD-DMA), *N,N,N′,N′*-tetrabutyl tetradecyl malonamide (TBTDMA) and *N,N′,N,N′*-dimethyl dibutyl tetradecyl malonamide (DMDBTDMA) were synthesised (discussed later) in our laboratory (Table 4). Efficacy of these extractants was evaluated for Am(III) from nitric acid medium [54]. Fig. 13 shows that DMDBT-DMA is the most promising malonamide at 3–4 M

Table 4
Structures of diamides used in the present studies

Diamide	R	R′	R″
TBUDMA	C_4H_9	C_4H_9	$C_{11}H_{23}$
TBDDMA	C_4H_9	C_4H_9	$C_{12}H_{25}$
TBTDMA	C_4H_9	C_4H_9	$C_{14}H_{29}$
DMDBTDMA	CH_3	C_4H_9	$C_{14}H_{29}$

HNO_3 (acidity at which HLW is usually stored) and therefore more elaborate work was undertaken to study the distribution behaviour of actinides and fission products using DMDBTDMA.

2.3.1. Synthesis of penta alkyl malonamides

First step in the synthesis of diamides involves the condensation of secondary amines, viz. dibutyl amine and methyl butyl amine with malonyl chloride (2:1 mole ratio) in presence of triethyl amine in dichloro methane medium. Second step is the alkylation of
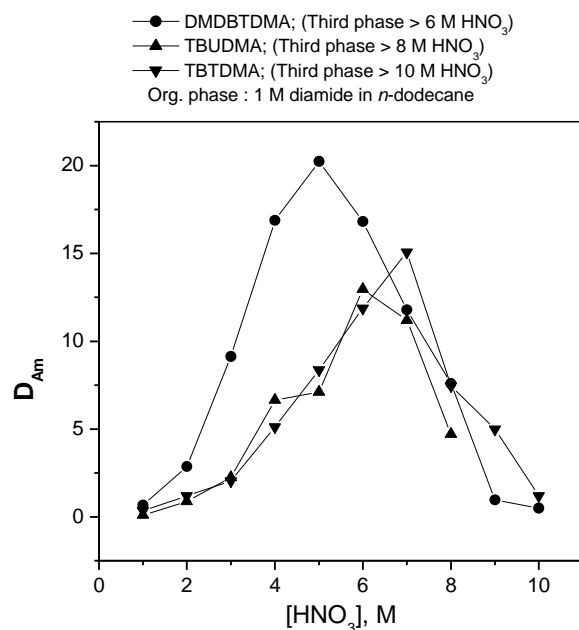

Fig. 13. Distribution ratio of Am(III) as a function of $[HNO_3]_{initial}$ for various diamides: diluent, *n*-dodecane; temperature, 25 °C.

tetra alkyl malonamides, viz. *N,N,N′,N′*-tetrabutyl malonamides and *N,N′*-dimethyl–*N,N′*-dibutyl malonamide. Sodium hydride (washed with dry pentane) was dissolved in dry dimethyl sulphoxide (DMSO) at 60–70 °C. The corresponding tetra alkyl malonamide was then added slowly and the solution was stirred for 3 h. The alkyl halide in dry benzene was added drop wise followed by petroleum ether and chilled water. The organic phase was separated and the final product was obtained by vacuum distillation. Purity of the product was checked by non-aqueous potentiometric titration [75]. Purified diamide products were characterised by elemental analysis, IR and PMR spectra [54].

2.3.2. Extraction of actinides and fission products from nitric acid medium

DMDBTDMA extracts actinide ions including trivalent ions like Am(III) and Eu(III) preferentially over Cs(I) and Sr(II) in the acidity range 3–5 M (Fig. 14). D_{Pu} and D_U values increased with acid concentration up to 2 M and were steady thereafter since the enhancement expected due to the law of mass action for increased nitrate concentration is compensated by the decreased free ligand concentration (caused by the HNO_3: diamide adduct formation). D_{Pu} values were higher than D_U values at all acid concentrations which is attributed to the high ionic potential of Pu(IV) over U(VI). Major fission products like Sr(II) and Cs(I) were poorly extracted at all acid concentrations ($D_{Sr} < 10^{-2}$ and $D_{Cs} < 10^{-3}$). Tc(VII) showed peculiar distribution behaviour with increase of acidity. While for all other metal cations, D values increased with acidity, interestingly D_{Tc} decreased with increasing acid concentration, which is attributed to the presence of Tc as TcO_4^- anion in acidic solutions. Reverse trend of D values with acidity is due to increasing concentration of NO_3^- ion which competes with TcO_4^-. Reasonably large D_{Tc} value at 3 M HNO_3 suggests that ^{99}Tc can be co-extracted along with minor actinides from acidic medium. Zr(IV) and Fe(III) are extracted moderately.

2.3.3. Extraction of actinides and fission products from simulated waste

Fig. 15 summarises the extraction behaviour of actinides, fission products and Fe from simulated
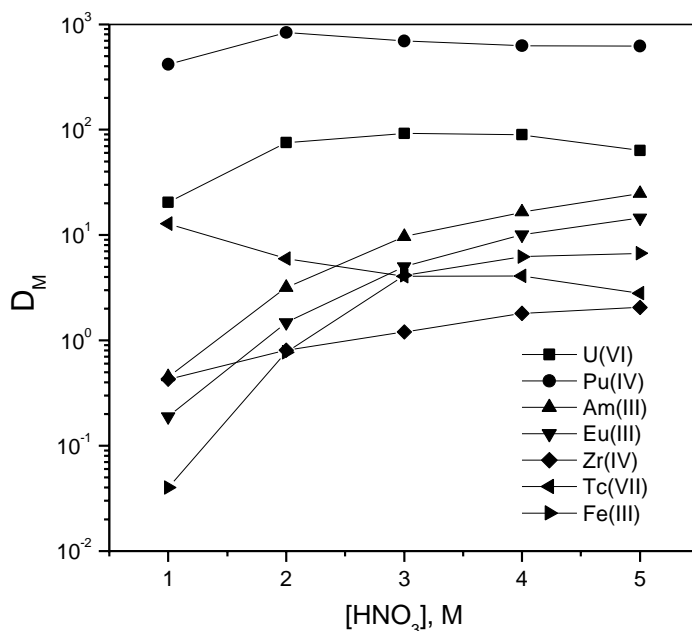
Fig. 14. Variation of D_M with nitric acid concentration: organic phase, 1 M DMDBTDMA in n-dodecane; aqueous phase, pure tracers in varying nitric acid concentration; temperature, 25 °C.
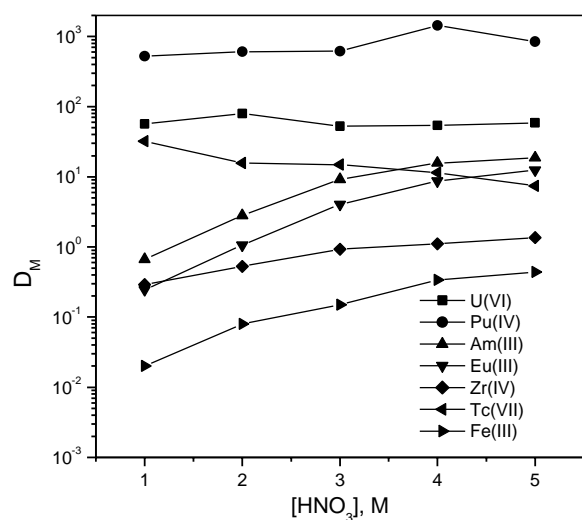

Fig. 15. Variation of D_M with nitric acid concentration in presence of simulated waste: organic phase, 1 M DMDBTDMA in n-dodecane; aqueous phase, PHWR simulated waste containing respective tracers at various acidities; temperature, 25 °C.

PHWR–HLW waste as a function of nitric acid concentration [56]. D_{Tc} increased for simulated waste as compared to the pure tracer throughout the acidity range. On the other hand, D_{Fe} decreased throughout the acidity range in case of simulated waste. For all other metal ions, viz. U(VI), Pu(IV), Am(III), Eu(III) and Zr(IV), D_M values are either in the same range or decrease marginally as compared to the corresponding pure tracer values. Relatively low values of D_{Fe} and D_{Zr} and high values of D_{Tc} suggest the possibility of separating Fe and Zr from long-lived actinides and fission products at least partially. There are reports indicating the possibility of improved separation of these metal ions in the presence of oxalic acid. D_{Am} (at 3 M HNO$_3$) of $\sim$9 is sufficient for the quantitative Am(III) separation from HLW in three to four contacts ($V_O / V_A = 1$). D_{Sr} and D_{Cs} values varied in the range 10^{-2} to 10^{-3} suggesting efficient separation of these fission products from actinides. The extractant dependence experiments for Pu(IV), U(VI) and Am(III) suggested the stoichiometry of the extracted species as Pu(NO$_3$)$_4$·3L, UO$_2$(NO$_3$)$_2$·2L and Am(NO$_3$)$_3$·3L (where L = DMDBTDMA), respectively. On the other hand, Tc extracted as HTcO$_4$·2L (in the absence

Table 5
Comparison of DIAMEX and TRUEX solvents: diluent, *n*-dodecane

Point of comparison	DIAMEX (1 M DMDBTDMA)	TRUEX (0.2 M CMPO + 1.2 M TBP)
Synthesis and purification	Two stage (simple)	Three stage (cumbersome)
Phase modifier	Optional (D2EHAA)[a]	Mandatory ($\geq$1.2 M TBP)
Additional cycle for prior U separation	Optional	Mandatory
[HNO$_3$] for $D_{Am} > 3$	$\geq$3 M	$\geq$0.5 M
[HNO$_3$] for $D_{Am} < 0.01$	~0.1 M	<0.01 M
No. of contact for quantitative stripping	2	7
Extraction capability for various metal ions		
Excellent ($D > 100$)	Pu(IV), Np(IV)	Pu(IV), U(VI), Np(VI)
Good ($100 > D > 10$)	U(VI)	Am(III), Eu(III)
Moderate ($10 > D > 0.5$)	Am(III), Eu(III), Tc(VII), Zr(IV), Fe(III)	Zr(IV), Fe(III), Tc(VII)
Poor ($D \leq 0.01$)	Cs(I), Sr(II)	Cs(I), Sr(II)

[a] D2EHAA: di(2-ethylhexyl) acetamide).

of U) and as UO$_2$(NO$_3$)(TcO$_4$)·2L (in the presence of U) whereas Fe extracted as Fe(NO$_3$)$_3$·2L.

2.3.4. Stripping studies

Based on the extensive work carried out with several stripping agents, following scheme was proposed for individual stripping of Am, Pu and U from the extract of simulated waste. Two contacts of 0.05 M HNO$_3$ which stripped >99.9% Am and <25% U; three contacts of 0.3 M NH$_2$OH·HCl/0.5 M HNO$_3$ to strip >95% Pu and finally three contacts of 0.1 M oxalic acid to recover residual U and Pu. No reagent employed in the present study could strip quantitatively all the three actinides together. Nevertheless, three contacts of 0.05 M HF/0.05 M HNO$_3$ effected stripping of >99.9% Am, ~91% U and >99.9% Pu.

2.3.5. Comparison of DIAMEX process with TRUEX process

Table 5 summarises the salient features of the two processes commonly employed for the partitioning of actinides from HLW. From synthesis consideration, it is rather convenient to prepare DMDBTDMA as it involves two steps. First step is simply the sub ambient condensation reaction between a secondary amine and an acyl chloride. Second step requires somewhat extra care in view of the use of NaH for the alkylation of middle carbon atom of tetra alkyl malonamides. Overall yield is ~70%. On the other hand, synthesis of CMPO is carried out in three steps. First step is the esterification of phenyl phosphinic acid using triethyl phosphate resulting in the formation of ethyl phenyl

phosphinate. Second step involves reaction between Grignard reagent (*n*-octyl magnesium bromide) with ethyl phenyl phosphinate. The product so obtained was treated with *N*,*N*-diisobutyl-2-chloroacetamide to give CMPO. Overall yield of the product is ~40%. It is possible to dissolve 1.5 M of DMDBTDMA in *n*-dodecane, which does not form any third phase up to 10 M HNO$_3$. Usually 0.5 M or 1.0 M of DMDBTDMA in NPH has been employed as solvent in the DIAMEX process. On the other hand, 1.2 or 1.4 M TBP as phase modifier is employed while using 0.2 M CMPO as solvent in the TRUEX process. This is done to avoid third phase formation when the solvent is equilibrated with HLW solution. In spite of using phase modifier, it was observed that the third phase appeared when the TRUEX solvent is contacted with an aqueous solution containing 10 g/l of Nd or 11 g/l of U at 3 M HNO$_3$. PHWR–HLW solution involves U concentration up to 18 g/l. It was found therefore essential to have an additional cycle of 30% TBP to diminish the U concentration in the range of mg/l. In the DIAMEX process, third phase did not form either with 10 g/l of Nd or with a mixture of 2 g/l of Nd and 18 g/l of U but it does occur in case of simulated waste ($V_O/V_A = 1$). Third phase can be eliminated by employing $V_O/V_A = 1.5$.

Fig. 16 shows the extraction behaviour of Am(III) for these two solvents in *n*-dodecane. Whereas D_{Am} gradually increases with nitric acid concentration for DMDBTDMA, the value for TRUEX solvent increases sharply initially and reaches a maxima at 2 M HNO$_3$. As a consequence, the TRUEX solvent could treat solutions varying widely in acidity
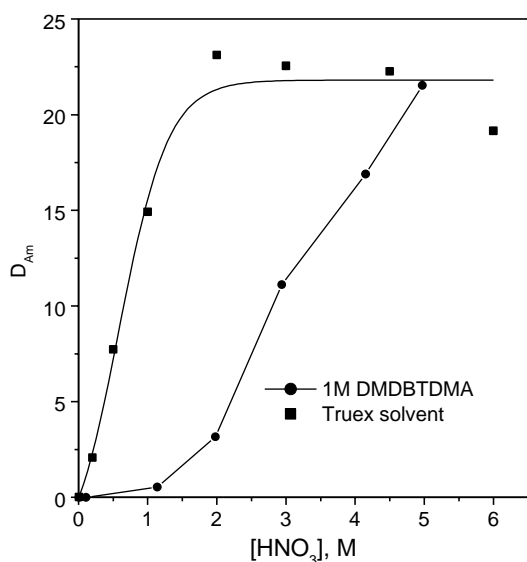
Fig. 16. Distribution data of Am(III) as a function of nitric acid concentration: organic phase, 1 M DMDBTDMA and 0.2 M CMPO + 1.2 M TBP solutions in *n*-dodecane; temperature, 25 °C.

(0.75–6 M HNO$_3$). On the other hand, DIAMEX solvent showed significant variation in D_{Am} in the acidity range 0.1–5 M. Therefore for efficient extraction of Am(III), ~3 M HNO$_3$ concentration was required in the DIAMEX process. On the other hand, a multistage stripping process involving diamide is expected to be efficient and help in reducing the number of contacts needed to strip Am quantitatively from the extract containing actinides. Various metal ions investigated for their distribution behaviour were classified in four groups, viz. excellent ($D > 100$), good ($100 > D > 10$), moderate ($10 > D > 0.5$) and poor ($D \leq 0.01$) employing the two solvents. Table 5 shows that whereas TRUEX solvent extracts both tetravalent and hexavalent actinides excellently, DIAMEX solvent extracts only tetravalent ions with D values of the same order. Distribution ratio value of U(VI) is however larger for DIAMEX process as compared to those of Am(III), Eu(III) and Tc(VII). DIAMEX solvent has larger D_{Tc} (4.07) as compared to D_{Tc} (0.42) observed for TRUEX solvent. Comparable extraction of Zr(IV) and Fe(III) and poor extraction of Cs(I) and Sr(II) is obtained with both solvents. The most important criterion to be used in ranking different methods is the overall DF obtained

during actinide-partitioning of HLW. According to the hot cell tests carried out at JRC-ITO at Karlsruhe, the DIAMEX process represents the best compromise where DFs of ~1000 have been reported for the minor actinides from 3.5 M acid concentrated HLW.

Partitioning of Zr and Tc along with minor actinides is desirable considering the long half-lives of isotopes like ^{93}Zr (1.5×10^6 years) and ^{99}Tc (2.1×10^5 years) and potential radiological toxicity of these radionuclides. On the other hand, it is desirable to leave structural elements like Fe and Ni and short-lived fission products including lanthanides, Cs and Sr in the aqueous raffinate as they contribute unnecessarily towards the volume of waste to be vitrified and deposited in deep repositories. It is possible to achieve good DF values of minor actinides from Fe by choosing suitable contact time or by adding desired concentration of oxalic acid. DIAMEX flow sheet was found to be similar, but somewhat simpler than TRUEX process flow sheet. Whereas extensive hydrolytic and radiolytic degradation of process solvent reduced the stripping efficiency of the TRUEX solvent, no significant problem was encountered in case of the DIAMEX solvent. Therefore, no involved periodic solvent cleanup step would be required, as with the TRUEX solvent. In contrast to the TRUEX solvent, the DIAMEX solvent was completely incinerable leading to lesser secondary waste volumes. However, very high viscosity of diamide may necessitate high pressure for achieving the desired flow rate of the organic stream and larger settling time for phase separation.

2.3.6. Alternate approach

Since uranium is the major actinide present in HLW, it influences both actinide-partitioning as well as vitrification process. Work has been initiated in our laboratory to develop a scheme for the preferential separation of uranium over Np, Pu and Am using di(2-ethylhexyl) pivalamide (D2EHPVA) and very encouraging results have been obtained in recent past (Fig. 17). DIAMEX/TRUEX solvent can be subsequently employed conveniently to reduce the alpha activity (transuranics concentration) of the HLW to the desired level. In view of the millimolar concentration of residual actinides, the potential of extraction chromatography/membrane separation for the separation of transuranics from short lived/inactive components
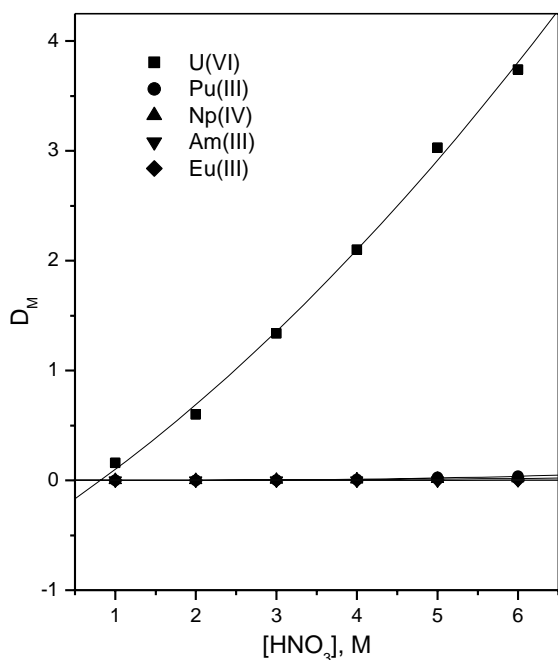
Fig. 17. Distribution data of metal ions as a function of nitric acid concentration in presence of SHLW: reducing agent, 0.3 M hydroxyl amine nitrate (HAN) + 0.8 M hydrazine nitrate (HN); organic phase, 1 M D2EHPVA in *n*-dodecane; temperature, 25 °C.

of high-level waste is also being explored [55,78–80].

Acknowledgements

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