CHEMICAL REVIEWS

REVIEW

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Chemistry of Diglycolamides: Promising Extractants for Actinide Partitioning

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1. INTRODUCTION

The high level waste (HLW) generated during spent nuclear fuel reprocessing contains unextracted U, Pu, a bulk of minor actinides such as Am, Np, Cm, and a host of fission product elements such as Tc, Pd, Zr, I, Cs, and Sr, and lanthanides, activation products (Ni, Sb, Zr), structural elements (Fe, Ni, Co, Zr), and process chemicals (salts of Fe, Al, and Na). At present, the most accepted conceptual approach for the management of HLW is to vitrify it in a glass matrix followed by interim storage for ∼100 years to allow the decay of heat dissipating nuclides such as ^{137}Cs and ^{90}Sr and its subsequent disposal in deep geological repositories.[1] Since the half-lives of a few minor actinides and some fission product elements range between a few hundred to millions of years, the surveillance of vitrified blocks for such a long period is a subject of debate from economic as well as environmental safety considerations. The latter is due to the possible risk of the migration of long-lived α emitting minor actinides from the repository to the aquatic environment. As depicted in Figure 1, if actinides are not removed from the spent fuel, it will require millions of years to reduce its radiotoxicity to the level of natural uranium ore. However, if uranium, plutonium, minor actinides, and other long-lived fission products are removed from the waste, its radiotoxicity could reach such a level in only a few hundreds of years. Therefore, the strategy of P&T (Partitioning of long-lived radionuclides followed by Transmutation) is being explored by several countries worldwide, which envisages the complete removal of minor actinides from radioactive waste and their subsequent incineration in the high flux reactors/accelerator driven subcritical systems.[1−4] After partitioning of the actinides along with the long-lived fission product elements, the residual waste is proposed to be disposed in subsurface repositories (after vitrification) at a much reduced risk and cost.

Radiochemists and separation scientists have been engaged in the development of new extractants for actinide partitioning for the past few decades. In this context, several organophosphorus as well as amide based extractants have been developed and evaluated for the recovery of minor actinides from HLW.[3−9] Among the organophosphorus compounds, octyl-(phenyl)-*N*,*N*-diisobutyl

Received: January 2, 2011
Published: November 04, 2011

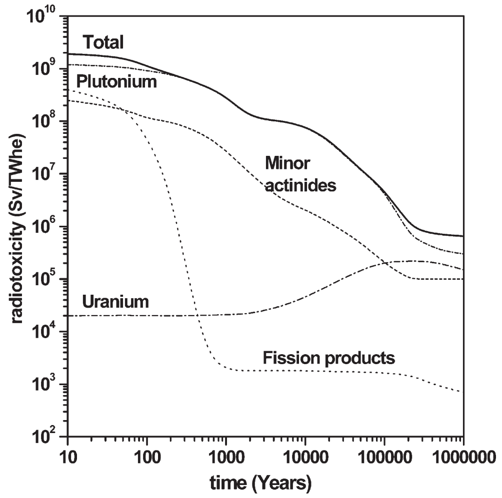
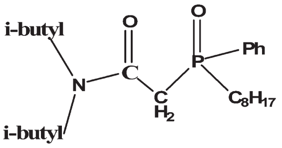
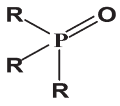


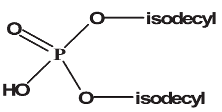
Figure 1. Partitioning of minor actinides and radiotoxicity of residual waste. Reproduced with permission from ref 8. Copyright 2008 Oldenbourg Verlag.



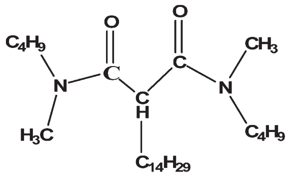
(a) CMPO



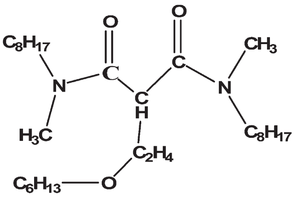
(b) TRPO



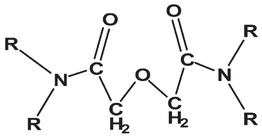
(c) DIDPA



(d) DMDBTDMA



(e) DMDOHEMA



(f) Diglycolamide (DGA)

Figure 2. Structural formulas of proposed extractants for actinide partitioning.

carbamoyl methyl phosphine oxide (CMPO, Figure 2a) and diphenyl carbamoyl methyl phosphine oxide have been investigated extensively.[5,6] Their bifunctional nature facilitated the extraction of trivalent actinides (Am and Cm) from HLW at 3−4 M HNO_3. However, stripping of actinide ions from the loaded organic phase was cumbersome and required multiple contacts with complexing media.[5] Other phosphorus based extractants, such as trialkyl phosphine oxide (TRPO, Figure 2b) and diisodecylphosphoric acid (DIDPA, Figure 2c) have limitations, as they extract trivalent actinides only at low acidity (≤1 M HNO_3). Though these extractants are useful for actinide partitioning from the waste stored at lower acidity (∼0.5 M HNO_3), they are not effective for HLW (which is usually stored at 3−4 M HNO_3).[5,6] Substituted malonamide extractants, on the other hand, have been found promising for the partitioning of minor actinides under HLW conditions.[3−10] The fact that these extractants are not as efficient as CMPO at lower acidity (≤1 M HNO_3) makes them versatile during back-extraction stages. In addition, malonamides are completely incinerable, which implies that the amount of secondary waste generated could be reduced significantly. Among several malonamide extractants, *N,N′*-dimethyl-*N,N′*-dibutyl tetradecyl malonamide (DMDBTDMA, Figure 2d) and *N,N′*-dimethyl-*N,N′*-dioctyl-2-(2-hexyloxyethyl)malonamide (DMDOHEMA, Figure 2e) have been extensively studied for actinide partitioning in the proposed DIAMEX processes.[3−10] However, the distribution ratio (*D*) values for trivalent actinides are low, which necessitates the use of high concentration of the malonamide ligands. Therefore, efforts to design more efficient extractants with similar green characteristics continued. In this context, diglycolamide (DGA: Figure 2f) extractants, investigated extensively for actinide partitioning during the past decade, displayed superior extraction properties as compared to malonamide extractants as well as CMPO based extractants.

Though actinide partitioning work with other extractants has been reviewed,[3−9] a comprehensive review on the complexation/separation chemistry of the diglycolamide extractants is not available. This article will provide the historical perspective and the highlights of the recent advances on the fascinating chemistry of diglycolamides, with special emphasis on their proposed applications in radioactive waste management. The present article also addresses some of the intriguing questions pertaining to the unusual extraction behavior of the diglycolamide extractants, such as the following: (i) What makes diglycolamides efficient extractants particularly for trivalent lanthanides/actinides? (ii) What is the role of diluent and phase modifier with diglycolamide extractants? (iii) In view of the submillimolar concentration of minor actinides in HLW, is there an alternative technique to solvent extraction which facilitates the reduction of VOCs and secondary waste? This article also presents the future directions which could have significance in strengthening the knowledge on diglycolamide extractants and their use in the development of actinide partitioning processes.

2. DIGLYCOLAMIDES: A NEW CLASS OF EXTRACTANTS FOR ACTINIDE PARTITIONING

During the past decade, a new class of diamide extractants, namely diglycolamides (containing ether linkages between two amide groups, Figure 2f), have received particular attention of separation groups engaged in the area of actinide partitioning.[11] The complexation chemistry of diglycolamide ligands with metal ions is intriguing, as these ligands display high affinity for trivalent metal ions as compared to hexavalent metal ions. Several attempts have been made to explain the unusual complexation behavior of diglycolamide based extractants with *f*-elements. The basic studies include aqueous complexation (with water-soluble DGA ligands), theoretical calculations, spectroscopy, and synthesis of solid complexes with diglycolamide extractants. The applied studies focus on the evaluation of diglycolamide extractants for actinide partitioning from nuclear waste solutions.

2.1. Historical Development of Diglycolamides for Actinide Partitioning

The genesis of the work on diglycolamides as extractants can be traced back to Stephan et al.,[12,13] when they studied the extraction of various metal ions with multidentate amido

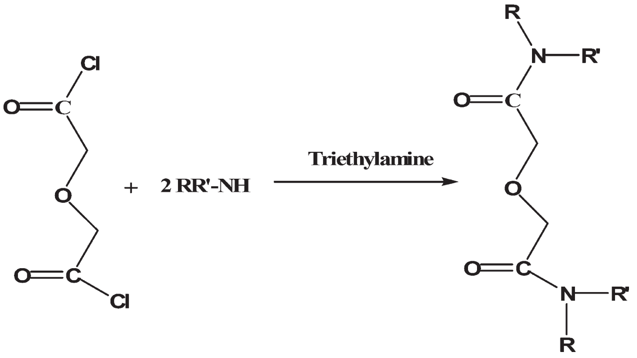
Table 1. Physicochemical Properties of Various Diglycolamide Extractants[11]

diglycolamide (DGA)	solubility in water (mmol/L)	solubility in *n*-dodecane	D_{Am} by 0.1 mol/L DGA (at 1 mol/L HNO_3)
TPDGA	57.0	very poor	
TBDGA	2.3	poor	
TADGA	0.27	soluble	100
THDGA	0.11	soluble	40
TODGA	0.042	freely soluble	30
TDDGA	0.042	freely soluble	18
TdDDGA	0.040	freely soluble	11

podands. The open-chain ether dicarboxylic acid diamides (diglycolamides) exhibited very high *D* values for rare earth ions, viz. La(III) and Yb(III) from picrate and nitrate media at pH 5. On the other hand, the *D* values for Ca(II) and Sr(II) were a few orders of magnitude lower than those of lanthanides under identical experimental conditions. In accordance with Pearson's HSAB (Hard & Soft Acid Base) concept,[14] it was postulated that the nitrogen atoms do not take part in complexation, and the interaction with metal ions was preferentially through the hard donor oxygen atoms. In the late nineties, Sasaki and Choppin carried out the extraction studies of actinides with diglycolamides.[15−19] They used *N*,*N*-dimethyl-*N*′,*N*′-dihexyl diglycolamide and its analogous compounds for the extraction of actinides and lanthanides from aqueous solutions of pH ranging from 1 to 4. Subsequently, Narita et al.[20] employed *N*,*N*-dimethyl-*N*′,*N*′-diphenyl diglycolamide for the extraction of lanthanides from acidic solutions. Structural studies by X-ray diffraction (XRD) and extended X-ray absorption fine structures (EXAFS) showed that the diglycolamide ligands form tridentate complexes with lanthanides.[21]

Continuing their efforts, Sasaki et al.[11] synthesized a series of diglycolamides with different alkyl chains (ranging from *n*-propyl to *n*-dodecyl) attached to the amidic nitrogen atoms. The solubility and extraction properties of Am(III) by the synthesized diglycolamides are summarized in Table 1. It was found that the DGA derivatives with lower alkyl chains (propyl and butyl) were soluble in water and, therefore, could be employed as masking agents (sequestering agents) for f-block metal ions.[22,23] In contrast, higher homologues of DGA were practically insoluble in water and were freely soluble in paraffinic solvents and, therefore, could be employed for the extraction of actinides. The *D* value for Am(III) with DGA extractants decreased with increased chain length due to the presence of bulky alkyl groups, which induce steric hindrance during the complexation of the metal ion. The distribution constant of the ligand also possesses a reverse dependence on the extraction constant. Consequently, the lipophilicity of the diglycolamides needs to be optimized. Among several derivatives of DGA extractants, *N*,*N*,*N*′,*N*′-tetraoctyl diglycolamide (TODGA) was found to be the most promising due to its high solubility in paraffinic solvent, poor solubility in aqueous medium, and significantly high *D* value for trivalent actinides such as Am(III). A series of DGA extractants with varying alkyl groups were also synthesized at other laboratories, and similar sets of data were obtained.[24] Recently, a branched alkyl derivative of diglycolamide, viz. tetra-2-ethylhexyl diglycolamide (TEHDGA), has been studied.[25−29] Though its extraction affinity toward Am(III) is lower than that of the linear chain DGA homologue (TODGA), it seems quite useful for actinide partitioning studies.[28,29]

Scheme 1. Synthesis Route for Diglycolamides



2.2. Synthesis and Characterization of Diglycolamides

Sasaki et al.[11] synthesized a series of diglycolamides with varying alkyl substituents on the amidic nitrogen. The synthesis was carried out by reacting diglycolic anhydride (in dichloromethane) with an equivalent amount of secondary amine. The mixture was then stirred overnight at room temperature. This step was followed by the addition of an equivalent amount of dicyclohexylcarbodiimide (DCC) and another equivalent amount of the secondary amine. The resultant mixture was stirred for 1 week to allow the completion of the reaction. The product (DGA) was separated by distillation of solvent and finally purified on a silica gel column. This method was followed by Modolo et al.[30] and by the authors' group[31] for the synthesis of TODGA at kilogram scale, with the product yield of 65−80%. In a slightly modified method, Mowafy et al.[24] synthesized DGA extractants in three stages starting with diglycolic acid instead of diglycolic anhydride. The product yield was, however, lower (∼50%) as compared to that of the previously described method (65−80%).[11] Japanese researchers mainly used commercially available TODGA (purity >99%) supplied by Kanto Chemical Company, Japan.

Recently, a single step synthesis route (Scheme 1) has been reported and is being followed by many laboratories for the synthesis of diglycolamides, even on commercial scale.[32−39] This route deals with the direct reaction of 1 mol of diglycolyl chloride with 2 mol of the desired dialkyl amine in the presence of triethylamine dissolved in either tetrahydrofuran (THF) or diethyl ether. The reaction appears to be faster and can be completed in about 2 h with better product yield (>90%). After completion of the reaction, the product is washed with HCl and Na_2CO_3 to remove basic and acidic impurities. This route of synthesis avoids the tedious purification step with a silica gel column, as the impurities could be completely removed by acid and alkali washings. In a typical ^{1}H-NMR spectrum of TODGA, the signal peaks are multiplets at 1.26 and 1.56, triplets at 0.92 and 3.18, and a singlet at 4.39 ppm. These peaks were assigned to the protons of $\text{-N-CH}_2\text{-}(\mathbf{CH_2})_5\text{-CH}_2\text{-CH}_3$, $\text{-N-CH}_2\text{-}\mathbf{CH_2}\text{-}(\text{CH}_2)_5\text{-CH}_3$, $\text{-N-CH}_2\text{-CH}_2\text{-}(\text{CH}_2)_5\text{-}\mathbf{CH_3}$, $\text{-N-}\mathbf{CH_2}\text{-CH}_2\text{-}(\text{CH}_2)_5\text{-CH}_3$, and $\text{-CO-}\mathbf{CH_2}\text{-O-}\mathbf{CH_2}\text{-CO-}$, respectively.[11]

Recently, various diglycolamide ligands with structural modifications in their skeleton were synthesized in good yields.[40] These modifications include (1) the increase in chain length from one carbon to two carbons between the central ether oxygen atom and the amide moieties, (2) the addition of substituents on the carbons between the central oxygen atom and the amide moieties on either one or on sides of the central oxygen, (3) the replacement of the central oxygen by a (substituted) nitrogen atom, and (4) synthesis of rigidified diglycolamides. These ligands were evaluated for their extraction properties toward Am(III) and Eu(III) at various nitric acid concentrations.

3. BASIC COMPLEXATION STUDIES WITH DIGLYCOLAMIDES

These studies were mainly aimed at understanding the unique complexation behavior of diglycolamides which lead to their exceptionally high affinity for trivalent actinides and lanthanides. These fundamental studies included the aqueous complexation studies, structural studies on solid metal−ligand complexes, as well as spectroscopic investigations on the metal−ligand complexes employing techniques such as time resolved laser-induced fluorescence spectroscopy (TRLFS) and EXAFS.

3.1. Aqueous Complexation Studies

The lipophilic properties of diglycolamide compounds can be tailored by attaching suitable alkyl groups (with different numbers of carbon atoms) on the amidic *N*-atoms. In this context, novel water-soluble diglycolamides, e.g. *N*,*N*,*N*′,*N*′-tetramethyl diglycolamide (TMDGA), *N*,*N*,*N*,*N*′-tetraethyl diglycolamide (TEDGA), *N*,*N*,*N*′,*N*′-tetrapropyl diglycolamide (TPDGA), and *N*,*N*-dipropyl diglycolamic acid (DPDGAc), etc., were synthesized and examined for their complexation with An(III) and An(IV).[22,23] These ligands formed stronger complexes with Pu(IV) and Am(III) than does ethylenediamine tetraacetic acid (EDTA: a well-known hexadentate complexing ligand).[23] These water-soluble diglycolamides were evaluated as alternatives to carboxylic acids/aminocarboxylic acids as masking/sequestering agents as well as strippants. The advantage of these water-soluble neutral diglycolamide ligands is that these compounds may find applications in acidic solutions and can be recovered from the aqueous solution by extraction with primary alcohols after their use.

The stepwise complexation of diglycolamide ligand (L) with M^{n+} can be written as follows:

$$M^{n+} + L \rightleftarrows M(L)^{n+} \tag{1}$$

$$M(L)^{n+} + L \rightleftarrows M(L)_2{}^{n+} \tag{2}$$

$$M(L)_2{}^{n+} + L \rightleftarrows M(L)_3{}^{n+} \tag{3}$$

TRFS studies for the complexation of Eu^{3+} with TODGA under varying ligand-to-metal (L/M) ratios in an ethanol−water (3:2 ratio) mixture suggested the formation of 1:1, 1:2, and 1:3 species, viz., $Eu(TODGA)^{3+}$, $Eu(TODGA)_2{}^{3+}$, and $Eu(TODGA)_3{}^{3+}$, respectively.[41] The relation between the intensity and emission wavelength of the complex is shown in Figure 3. The conditional stability constants log β_1, log β_2, and log β_3 were calculated as 6.1 ± 0.5, 10.8 ± 0.7, and 14.3 ± 0.6, respectively.[41] Janczewski et al.[42] synthesized a new series of C-pivot tripodal diglycolamide ligands and examined their complexation behavior with trivalent lanthanides and actinides. These ligands displayed very high affinity for Am(III) and Eu(III), which increased significantly upon alkylation or arylation of the *N*-position of the diglycolamide moieties. These ligands showed 1:1 metal to ligand stoichiometry and were remarkably (five times more) selective toward Eu(III) over Am(III).

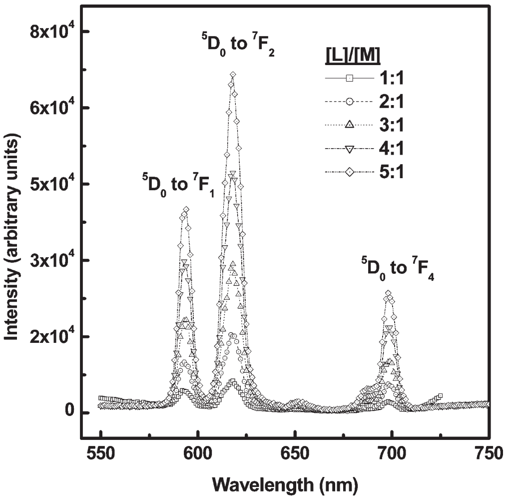


Figure 3. Eu(III)-TODGA fluorescence spectra; [Eu(III)] = 1 × 10^{-4} M; [HNO_3] = 1 × 10^{-3} M; ethanol/water (v/v) 3:2. Reproduced with permission from ref 41. Copyright 2009 Elsevier.

3.2. Theoretical Calculations

Molecular dynamics simulation studies were carried out to understand the complexation behavior of diglycolamide extractants with hexavalent uranium and trivalent europium in aqueous and in methanol phases.[43] The structural stabilities of DGA complexes of Eu^{3+} and $UO_2{}^{2+}$ in aqueous as well as in methanol phases were calculated in the presence of $NO_3{}^-$ as the counteranion. The calculations revealed that both the complexes were unstable in the aqueous phase. However, the Eu^{3+}−DGA complex was found to be stable in the methanol medium. The interaction energy for Eu^{3+} was larger than that of $UO_2{}^{2+}$, which cannot be explained on the basis of the ionic potential of these metal ions, suggesting the difference in the nature of bonding for the two ions of different size. The geometrical optimization by density functional theory (DFT) of M^{2+}−TODGA complexes ($M^{2+} = Ca^{2+}$, Sr^{2+}, and Ba^{2+}) showed that the metal ion had more affinity with carbonyl oxygen than with the ether oxygen, and the distance between the center of the oxygen donor and the edge of the cation corresponds to the van der Waals radius of the oxygen atom.[44] As a consequence, the stability of the 1:1 complex formed with M^{2+} ions decreased with increasing ionic radius from Ca^{2+} to Ba^{2+}. The results of DFT calculations were corroborated by solvent extraction studies with TODGA where the D_M values of alkaline earth metal ions at 3 M HNO_3 followed the order $Ca^{2+} > Sr^{2+} > Ba^{2+}$.[45,46]

3.3. Spectroscopic Studies

The extraction behavior of trivalent metal ions such as Am^{3+} and Eu^{3+} with TODGA is fascinating in view of the change in the stoichiometry of the extracted species with the nature of the diluent and the nature of the acid.[47,48] Solvent extraction studies from HNO_3 medium suggested that three to four TODGA molecules are complexed with the metal ion in a nonpolar diluent such as *n*-dodecane, while polar diluents such as 1-octanol, 1,2-dichloroethane, and nitrobenzene showed predominantly the presence of only two TODGA molecules in the extracted complexes. Similar variations in the stoichiometry of the metal−ligand complex were further corroborated by EXAFS studies.[21] The TRLFS study on the complexation of Eu^{3+} with TODGA in *n*-dodecane revealed that the complexed fraction of Eu^{3+} with

TODGA was devoid of water molecules in the inner coordination sphere of the metal ion.[41,49] The absence of a water molecule in the inner coordination sphere was confirmed under varying HNO_3 concentration in the aqueous phase and varying ligand concentration in the *n*-dodecane phase.[49] These observations indicated that the inner-sphere coordination sites of Eu^{3+} were completely devoid of water molecules and were occupied by TODGA and/or NO_3^- ions. In contrast, EXAFS studies of Er^{3+}−DGA complex in ethanol suggested that only two of the four DGA molecules were bonded in tridentate fashion with some water molecules in the inner coordination sphere. This clearly shows that the polarity of the diluent influences the nature of bonding of Ln(III)−DGA complex.

3.4. Synthesis and Characterization of Solid Complexes

The coordination number of trivalent lanthanides in aqueous solution varies usually from 9 to 8 across the lanthanide series,[50] and in the solid state the lanthanide aquo-complexes adopt a nearly rigorous tricapped trigonal prismatic (TTP) nine coordinate geometry (Figure 4).[50,51] In this context, tripodal chelates bearing three DGA units precisely arranged on a triphenoxymethane platform were synthesized to mimic the preferred TTP geometry favored by lanthanides coordinating through oxygen donor atoms.[32,33] The structural features of the tripodal chelates and Ln(III) complexes were elucidated by ICR-MS (ion cyclotron resonance mass spectrometry) and by X-ray analysis. The *t*ris-DGA ligand was designed to satisfy the coordination preference of trivalent lanthanides for the TTP geometry. The solubility of this ligand was easily modulated through substitutions at the three DGA arms. It was shown that the preorganization of the three DGA arms onto the triphenoxymethane platform causes significant enhancement in the extraction efficiency of lanthanides, suggesting favorable orientation of nine oxygen donor atoms for complexation with the trivalent f-metal ions.

Kannan et al.[34] synthesized La(III) and uranyl(VI) complexes of tridentate DGA ligands (L) $O(CH_2C(O)NR_2)_2$ [where R = *iso*-propyl or *iso*-butyl]. Single crystal X-ray crystallography suggested their composition as $La(L_3)^{3+}$ and $UO_2(NO_3)_2L$, respectively (Figure 5). The $[La(L)_3]^{3+}$ cation comprised a nine-coordinated La center wrapped by three tridentate DGA ligands in a D_3-symmetric triple-stranded helix in which the central ether oxygen atom of the DGA ligands adopts the capping positions of a twisted TTP geometry. It was found that the cationic species $[La(L)_3]^{3+}$ was associated with a homoleptic $[La(NO_3)_6]^{3-}$ counteranion regardless of metal/ligand stoichiometry. In contrast to the effectiveness displayed by diglycolamide ligands in extracting large spherical trivalent ions, which reflects a well matched nine-coordinate metal center encapsulated by three tridentate ligands as was seen in the solid-state structure of $[La(L)_3]^{3+}$, relatively poor affinity was observed with the linear uranyl(VI) ion. It was observed that uranyl(VI) cations coordinated only with one DGA molecule, giving a stoichiometry of $UO_2(NO_3)_2L$. The equatorial region of the uranyl(VI) complex, $UO_2(NO_3)_2L$, had one DGA molecule and two nitrate ligands, one of which was coordinated in an unusual quasi-bidentate mode and had an orientation parallel to the dioxo group. This apparent mismatch probably stems from the stereochemical incompatibility of the diglycolamide ligand (and its relatively large bite angle) with the equatorial coordination plane of the uranyl dioxo group. Interestingly, the structural characterization of the NpO_2^+−DGA complex showed that the two DGA ligands were indeed capable of occupying the slightly more expanded equatorial region belonging to the larger neptunyl(V) center.[35]

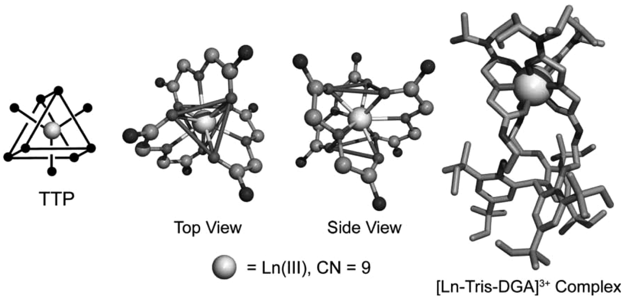


Figure 4. Model of an ideal tricapped trigonal prismatic (TTP) geometry around a nine coordinate metal ion (left). Top and side views of a slightly distorted TTP coordination environment of the Yb(III) center in the complex with tris-DGA ligand (right). Reproduced with permission from ref 33. Copyright 2006 Taylor & Francis.

4. SOLVENT EXTRACTION STUDIES WITH TODGA

4.1. Role of Nature of Acid and Aggregation Phenomenon

Due to the amphiphilic nature of TODGA, the concepts of coordination chemistry as well as surfactant chemistry are important to understand its special affinity for trivalent lanthanides and actinides. The presence of water and acid drives the formation of a polydisperse mixture of TODGA monomers and aggregates in nonpolar solvents such as *n*-dodecane, even in the absence of any metal ion, as shown in eq 4.

$$H^+_{(aq)} + A^-_{(aq)} + xL_{(org)} \overset{K_H}{\rightleftharpoons} HA\cdot xL_{(org)} \\ /(H_{hyd}\cdot Lx^+\cdot A^-)_{(org)} \quad (4)$$

Similarly, the extraction of metal ion by TODGA (L) can be represented by the following equilibrium reaction:

$$M^{n+}_{(aq)} + nA^-_{(aq)} + yL_{(org)} \overset{K_{ex}}{\rightleftharpoons} M(A)_n\cdot yL_{(org)} \\ /(M_{hyd}\cdot L_y{}^{n+}\cdot nA^-)_{(org)} \quad (5)$$

where *x* is the number of TODGA molecules extracted with an acid molecule. The extracted species may be of the type HA·*x*L for nitric acid and $(H_{hyd}\cdot Lx^+\cdot A^-)$ for perchloric and hydrochloric acid. The subscripts (aq) and (org) represent the aqueous and the organic phases, respectively, and A^- is the counteranion associated with the metal ion or acid. In equilibrium reactions 4 and 5, H_2O molecules have been omitted from the extracted acid/metal ion species in the organic phase. The value of *y* (number of ligand molecules complexed with the extracted species) was found to be 3 or 4 for Am(III) and lanthanides.[48] Pioneering work carried out by Jensen et al.[52] demonstrated that aggregation of TODGA leads to the formation of dimers as well as tetramers and they coexist; their respective proportion is influenced by the nature and concentration of acid as well as the polarity of diluents. SANS and tensiometric studies (Figure 6) revealed that tetramers are the dominating species when 0.1 M TODGA−*n*-octane is equilibrated with >1 M HNO_3. The inner core of these tetramers was found to be ∼7 Å. These aggregates seem to provide the preorganized cavity to encapsulate species involving trivalent lanthanides, which account for the

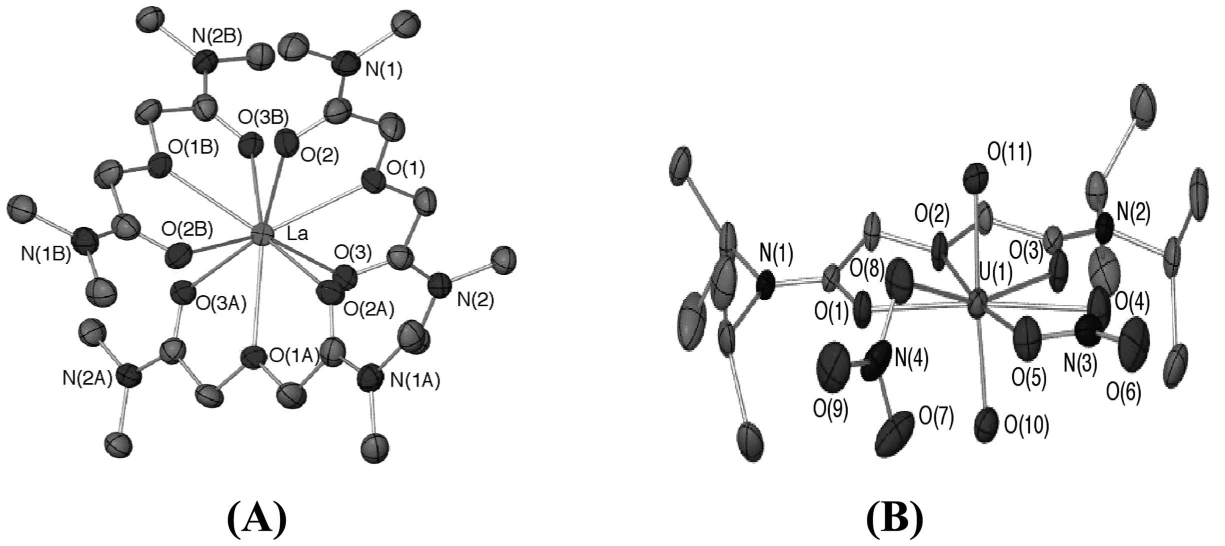


Figure 5. Crystal structures of $[LaL_3][La(NO_3)_6]$ (A) [L, *O*(CH_2C(*O*)$NR_2)_2$; R, *i*-Bu] and $UO_2(NO_3)_2L$ (B) [L, *O*(CH_2C(*O*)$NR_2)_2$; R, *i*-Pr] complexes. *Italic "O"* refers to the coordinating sites. Reproduced with permission from ref 34. Copyright 2008 American Chemical Society.

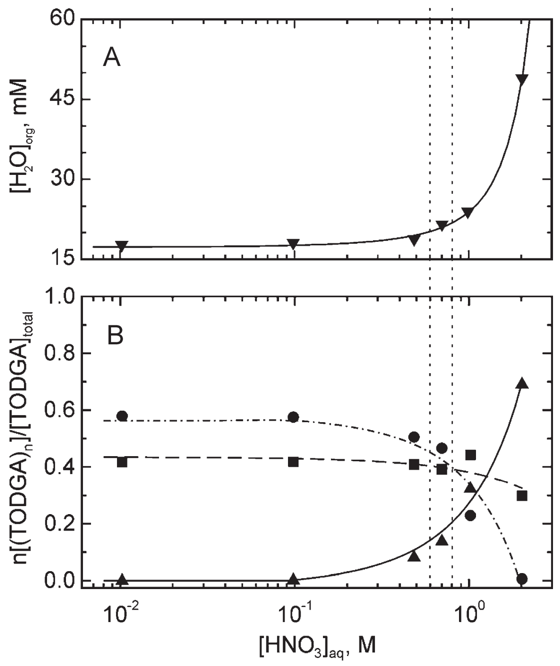


Figure 6. (A) Shows a rapid increase in the water content of the organic phase and (B) shows the changes in the speciation of TODGA derived from SANS and VPO measurements. The fraction of TODGA present as monomer (■), dimer (●), and tetramer (▲) is indicated at each acidity. Dotted vertical lines indicate $[HNO_3]_{aq}$ = 0.7 ± 0.1 M. Reproduced with permission from ref 52. Copyright 2007 American Chemical Society.

exceptionally high extraction constants of these ions. Yaita et al.[53] and Nave et al.[54] also reported the presence of TODGA aggregates dispersed in nonpolar diluents. The presence of a spherical metal ion such as Nd(III) appears to provide an additional energetic driving force for it is encapsulation.

It was interesting to note that, with increased aqueous phase acidity, the aggregates remained spherical, though their size increased with the extracted amount of water and acid. It was also observed that this is not a favored mechanism if the nitric acid is replaced by HCl, *n*-octane is replaced by polar diluents such as *n*-octanol, and Nd(III) is replaced by other oxidation state cations of actinides. Poor water/acid extraction in HCl medium and strong interaction of TODGA with molecules of *n*-octanol inhibit the formation of preorganized reverse micelles (tetramers) essential for the unique affinity of trivalent lanthanides and actinides. Even for 5f metal ions such as Pu^{4+} and UO_2^{2+} with high ionic potential, though intrinsically stronger metal ligand electrostatic (ion−dipole/ion−ion) bonds may be formed (as compared to trivalent actinides), the reverse micelle mechanism is not a favored mechanism. Instead, in all these cases, the mechanism is through a discrete, classical coordination complex. Dynamic light scattering studies[55,56] revealed that the critical size of the aggregates of TODGA in *n*-dodecane is 2 nm, which provides the preorganized configuration for the special affinity of trivalent lanthanides and actinides, as reflected in the unusually high D_{Am} value (>200). This size was attained in the HNO_3 system at 2 M, in the HCl system at 6 M, but in the $HClO_4$ system only at <0.5 M (Figure 7). These studies corroborate the studies of Jensen et al.[52] with respect to threshold acidity. But there is a difference in the critical aggregate size (~1 nm) reported by these authors on the basis of their SANS studies. It suggests again the key role played by protonated water species ($H_3O^+/H_5O_2^+$) in the dodecane phase. Apart from the acidity of the aqueous phase, it seems to be influenced strongly by the nature of the counteranion. Whereas dehydrated ClO_4^- is readily transferred to the dodecane phase, energetically, strongly hydrated Cl^- prefers the aqueous phase over the *n*-dodecane phase. The behavior of nitrate ion falls in between.

4.2. Effect of Nature of Diluent on Extraction of Americium

The effect of organic diluent on the extraction behavior of Am(III) by TODGA is shown in Table 2. The D_{Am} values were high for polar diluents such as 1-octanol and nitrobenzene. However, low D_{Am} values were observed for chlorinated and aromatic solvents, which was attributed to their interaction with the donor oxygen atoms of diglycolamide (as halogenated and aromatic solvents have high acceptor numbers), leading to a decrease in the effective ligand concentration.[11] Horwitz et al.[57]

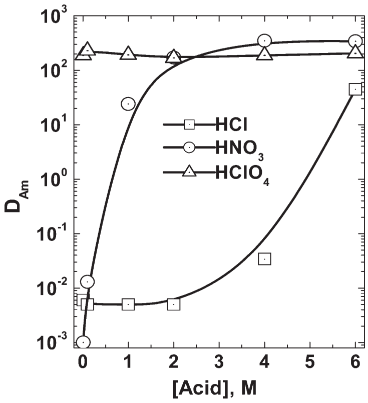


Figure 7. Variation of the D_{Am} with aqueous phase acidity. Extractant: 0.1 M TODGA in *n*-dodecane. Temperature: 25 °C. Reproduced with permission from ref 31. Copyright 2005 Dekker.

Table 2. Distribution Data and Number of TODGA Molecules in the Extracted Species of Am(III) Obtained in Different Diluents[a]

diluents	dielectric constant	D_{Am}	slope (*n*)
n-hexane	1.91	33	–
n-dodecane	2.01	30	3.78 ± 0.23
1-octanol	10.3	81	2.33 ± 0.03
nitrobenzene	34.8	220	1.76 ± 0.06
tetrachloromethane	2.24	0.09	–
chloroform	4.90	0.12	3.28 ± 0.18
1,2-dichloroethane	10.4	9.90	1.92 ± 0.07
benzene	2.28	0.39	3.70 ± 0.11
toluene	2.42	0.30	3.58 ± 0.09

[a] Extractant: 0.1 M TODGA. Aqueous phase: 1 M HNO_3. Temperature: 25 °C.[47,48]

made similar observations regarding the distribution behavior of Am(III) with several diluents, employing CMPO as the extractant, and they reported that the D_{Am} was higher in *n*-dodecane as compared to either toluene or CCl_4. Sasaki et al.[48] also reported an increase in distribution of lanthanides and actinides by TODGA with the polarity of the diluents. These observations support the outer sphere interaction of solvated cation with the solvated anion in the organic phase as shown by the following equilibrium reaction:[48]

$$M^{n+}_{(aq)} + nA^{-}_{(aq)} + yL_{(org)} \rightleftarrows [(MLy)^{n+}\cdot n(A^{-})]_{(org)} \qquad (6)$$

It has been shown that the stoichiometry of the extracted complex (value of *y* in the complex) changes with the polarity of the organic diluent (Table 2).[47,48] It appears that the polar diluents such as nitrobenzene, 1-octanol, and 1,2-dichloroethane do not allow the formation of TODGA aggregates as nonpolar diluents such as *n*-hexane and *n*-dodecane do. This behavior was attributed to the diluent–DGA interaction, which was subsequently validated by recording an IR spectrum where a ~30 cm^{-1} down shift in the >C=O stretching frequency was observed for TODGA/1-octanol solution.[47] Such a shift was not observed when *n*-dodecane was used as the diluent, suggesting a marked difference in the nature of the extracted species with change of diluent polarity. It is also apparent that the nature of the extracted species with trivalent Ln/An varies with the nature of the counteranion. TRFS studies on Eu(III)–TODGA–*n*-dodecane–HNO_3 revealed that the inner sphere of Eu^{3+} did not possess H_2O molecules, suggesting the presence of nitrate in the inner coordination sphere of the metal ion.[41] On the other hand, the counteranions Cl^- and ClO_4^- are likely to be present in the outer sphere, thereby favoring the presence of H_2O molecules in the inner coordination sphere of the metal ion. Because of the fact that *n*-octanol and nitrobenzene can solvate the anion, the D_{Am} values are favored in these polar diluents over those obtained in *n*-dodecane.[47,48] There is a need, however, to obtain direct spectroscopic evidence (using techniques such as EXAFS/TRLFS) to validate this hypothesis.

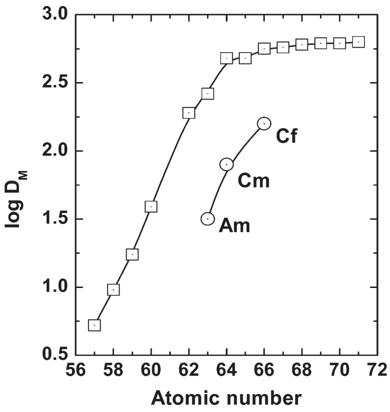


Figure 8. Distribution of lanthanides and actinides by 0.1 M TODGA dissolved in *n*-dodecane. Aqueous phase: 1 M HNO_3. Temperature: 25 °C.[11]

4.3. Extraction of Metal Ions by TODGA

Zhu et al.[58,59] carried out a systematic study on the extraction behavior of 75 elements from nitric acid medium employing TODGA dissolved in *n*-dodecane. As expected, the extractability of the elements was strongly dependent on their oxidation states and ionic sizes. Monovalent and pentavalent ions were not extractable. For divalent metal cations, Ca(II) (ionic radius: 100 pm) showed the highest *D* value and it decreased with an increase or decrease in the ionic radius of the metal ions. The actinyl ions with higher oxidation states (+5 and +6) exhibited lower *D* values, as they form sterically unfavored metal complexes.[11,24,58] As shown in Figure 8, the extraction of lanthanides increased with decreased ionic size from La to Gd, beyond which there was no change, suggesting cation size as one of the factors for the complexation/extraction.[11] A similar trend was also observed for trivalent actinides, viz. Am(III), Cm(III), and Cf(III). In the presence of hydrophobic counteranion, viz. tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($TFPB^-$), the *D* values for lanthanides were 5 to 6 orders of magnitude higher.[60] Very recently, the extraction of lanthanides[61] and alkaline earth metal ions[62] by TODGA has been reported in ionic liquids, and the results were compared with those obtained in *iso*-octane diluent. In the *iso*-octane system, it was found that the extraction of lanthanide ions occurred involving nitrate ions in the outer sphere. On the other hand, in ionic liquid the extraction proceeded via a cation-exchange mechanism where organic cation from the ionic liquid was replaced by $[Ln(TODGA)_n]^{3+}$ cationic complex.

The possibility of separation of trivalent actinides from lanthanides by TODGA was explored in the presence of

Table 3. Extraction of Nd and HNO_3 by TODGA[a]

[TODGA], mol/L	LOC of Nd, mol/L	D_{HNO_3}
0.1	0.007	0.034
0.2	0.012	0.077
0.3	0.031	0.110
0.5	0.060	0.173
0.8	0.100	0.281

[a] Diluent: *n*-dodecane. Aqueous phase: 3 M HNO_3. Temperature: 25 °C.[66−68]

diethylenetriamine pentaacetic acid (DTPA).[63] It was found that the separation factor (SF) of Ln(III)/An(III) varied with pH due to the formation of different chemical species involving $DTPA^{5-}$ in the aqueous phase. Sasaki et al.[48] reported the SF values (SF = D_{Eu}/D_{Am}) >10 by TODGA from HNO_3 medium. The SF values varied with the concentration of $NaNO_3$ and HNO_3 in the aqueous phase, which was attributed to the formation of different species of the extracted complex of Am(III) and Eu(III) with TODGA. The relative extraction efficiency of Y(III) and Sr(II) by TODGA was investigated, and the SF value (SF = D_Y/D_{Sr}) was found to be 6×10^4 in 6 M HCl.[64] On the basis of the high SF values, separation for ^{90}Y from ^{90}Sr (containing ^{90}Y in secular equilibrium) has been demonstrated.

4.4. Evaluation of Phase Modifiers

Industrial scale solvent extraction operations on bulk separation of the metal ions often encounter situations where third-phase formation takes place depending on the concentration and the organophilicity of the metal−ligand complex loaded in the diluent.[65] The maximum concentration of the metal ions that can be loaded in the organic phase without third-phase formation is referred to as the limiting organic concentration (LOC). Since the concentration of lanthanides present in HLW is in the millimolar range (much larger than those of minor actinides), many of the proposed extractants for actinide partitioning are prone to third-phase formation under prevailing HLW conditions, necessitating the use of suitable phase modifiers. TODGA too forms a third-phase when the concentration of lanthanide exceeds a certain limit. Typically, the LOC values of Nd at 3 M HNO_3 for 0.1 M TODGA/*n*-dodecane at 15, 25, and 35 °C are 5.8×10^{-3}, 6.6×10^{-3}, and 7.4×10^{-3} mol/L, respectively.[66−68] The LOC value increased with temperature due to increased solubility of the metal−ligand complex in the solvent.[65] As summarized in Table 3, the LOC value of Nd increased with TODGA concentration. However, the extraction of HNO_3 (D_{HNO_3}) also increased with TODGA concentration, which impedes the back-extraction of Nd from the loaded organic phase due to the acid build up in the strip solution. For example, Nd extracted by 0.1 M TODGA could be back-extracted completely in two contacts with distilled water. By contrast, more than five contacts were required for its quantitative (>99.9%) stripping when 0.5 M TODGA was used as the extractant.[68] Therefore, for HLW one has to judiciously optimize the ligand concentration to avoid the coextraction of unwanted metal ions as well as third phase formation. Keeping this in mind, 0.1 M TODGA/*n*-dodecane was found to be suitable.

Several groups have proposed the use of phase modifier which can suppress the third phase formation without coextraction of unwanted metal ions. Actinide partitioning studies at Julich, Germany, have been pursued using 0.2 M TODGA + 0.5 M TBP (as phase modifier) in TPH (hydrogenated tetrapropene) as the diluent.[30,69,70] Apparently, TPH, which is a branched aliphatic diluent, suppresses the tendency for third phase formation.[65] In the presence of 0.5 M TBP (along with 0.1 M TODGA), the Nd loading in the organic phase was close to the stoichiometric value of 1:3 (Nd-TODGA).[30] Sasaki et al.[66−68] proposed 0.5 M *N*,*N*-dihexyl octanamide (DHOA) as the phase modifier along with 0.1 M TODGA and reported enhanced LOC values for Nd from 0.008 mol/L to 0.033 mol/L at 3 M HNO_3. The LOC value of Nd by 0.1 M TODGA + 0.5 M DHOA corresponded to the stoichiometric value of the extracted complex ($Nd(NO_3)_3 \cdot 3TODGA$). The LOC value was not affected by the concentration of the phase modifier. It should be noted that DHOA does not extract trivalent lanthanides or other metal ions present in HLW (except An(IV) and (An(VI)) and acts only as a phase modifier by increasing the polarity of the diluent *n*-dodecane. Subsequently, a series of *N*,*N*-dialkyl monoamides with varying alkyl groups and chain lengths, viz. di-*n*-butyl decanamide (DBDA), di(2-ethylhexyl) acetamide (D2EHAA), di(2-ethylhexyl) propionamide (D2EHPRA), di(2-ethylhexyl) *iso*-butyramide (D2EHIBA), di-*n*-hexyl decanamide (DHDA), 1-decanol (a long chain alcohol), and TBP (organic phosphate), were evaluated as the phase modifiers for the TODGA/*n*-dodecane system.[31,71] The loading of Nd (g/L) with 0.1 M TODGA + 0.5 M phase modifiers as well as the D_{Nd} as a function of initial Nd concentration are given in Figure 9. Though the LOC value of Nd was marginally higher with TBP as phase modifier, better loading as well as D_{Nd} values were observed for DHOA at lower aqueous metal concentrations. The use of DHOA over TBP would be preferred in view of the fact that (i) the maximum concentration of lanthanides in HLW may not exceed 10 g/L (even with very high burn-up fuels), (ii) uptake of HNO_3 by TBP is larger which may interfere during back extraction of minor actinides, and (iii) TBP is a phosphorus based extractant which requires special chemical treatment during disposal of the spent extractant.

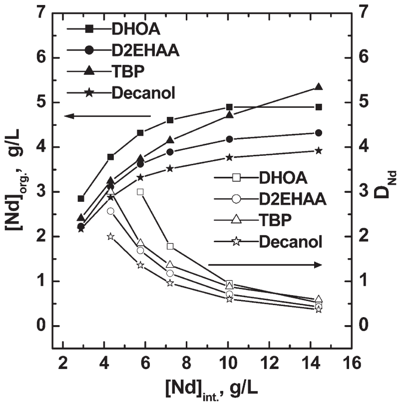


Figure 9. Nd loading and D_{Nd} as a function of aqueous Nd concentration. Extractant: 0.1 M TODGA + 0.5 M phase modifiers in *n*-dodecane. Aqueous phase acidity: 3 M HNO_3. Temperature: 25 °C.[31, 71]

The extraction behaviors of several metal ions (which are important from an actinide partitioning point of view) were evaluated by employing 0.1 M TODGA + 0.5 M DHOA/*n*-dodecane as the extractant (Figure 10).[31] The *D* values of actinide (An) ions followed the order An(III) ∼ An(IV) >> An(VI). The extraction of Fe(III) and Cs(I) was poor (D_M values $<10^{-2}$) in the entire range of acidity investigated. The extraction of hexavalent uranium was about 2 orders of magnitude lower than that of tri- and tetravalent actinides. Though

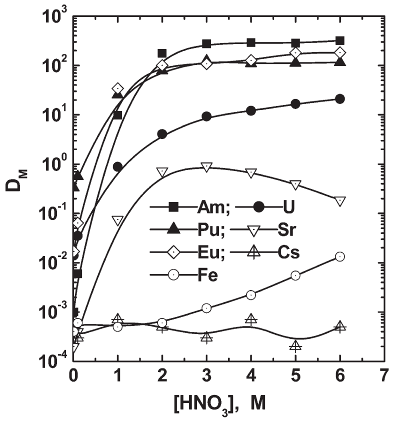


Figure 10. Variation of D_M with aqueous phase acidity. Extractant: 0.1 M TODGA + 0.5 M DHOA in *n*-dodecane. Temperature: 25 °C. Metal ions: Am(III), U(VI), Pu(IV), Sr(II), Eu(III), Cs(I), and Fe(III). Reproduced with permission from ref 31. Copyright 2005 Dekker.

Sr(II) was partially coextracted along with actinides, it could be selectively scrubbed with 6 M HNO_3.[45,46] Zr(IV) present as fission product/structural element (from clad) was also extracted by TODGA, which could be successfully directed to raffinate by addition of oxalic acid as masking agent.[30] Similarly, the extraction of Pd(II) was suppressed by the addition of HEDTA (*N*-(2-hydroxyethyl)ethylenediamine triacetic acid) in the aqueous phase, which is a selective complexant for Pd(II).

4.5. Stability of TODGA

Hydrolytic and radiolytic stability are of vital importance for any solvent proposed for hydrometallurgical separation in the back end of the nuclear fuel cycle. In this context, Sugo et al.[72] found no degradation product when 0.1 M TODGA/*n*-dodecane was kept in contact with 3 M HNO_3 for four weeks and analyzed by the gas chromatography mass spectrometry (GC-MS) technique. Similar hydrolytic stability has been observed by Modolo et al.[30] for 0.2 M TODGA + 0.5 M TBP in TPH when kept in contact with 3 M HNO_3 for 60 days. The radiolytic stability of pure TODGA (in the absence of solvent) was studied and the *G*-value (number of molecules decreased after absorption of 100 eV of energy) was found to be 8.5 ± 0.6.[72] It was found that the radiation stability of TODGA could be enhanced on the addition of benzene as well as DHOA. The main degradation products of TODGA were identified as dioctylamine, dioctyl acetamide, dioctyl glycolamide, and dioctyl formamide. Excellent radiolytic stability of TODGA solvent (0.1 M TODGA + 0.5 M DHOA in *n*-dodecane) was observed up to 500 kGy/dose when the solvent was irradiated in contact with simulated HLW.[71] Modolo et al.[30] and Mincher et al.[73] demonstrated excellent radiolytic stability of 0.2 M TODGA + 0.5 M TBP in TPH up to 600 kGy when the extractant was irradiated in contact with 3 M HNO_3. α-Radiolysis of TODGA in *n*-dodecane was investigated by the irradiation with a helium ion beam.[74] The radiolytic degradation of TODGA by a helium ion beam was found to be lower than that by γ rays. It was postulated that the charge transfer from the radical cations of *n*-dodecane to the TODGA molecules is greater with low LET (linear energy transfer) radiations such as γ rays. In contrast, under irradiation with high LET radiations, such as α particles, activated species are formed locally at a high density in the track where recombination is a predominant process. As a result, the degradation of TODGA by α particles is lower as compared to that with γ radiation. Diglycolamide derivatives containing aromatic functional groups exhibited higher radiation stability, possibly due to intramolecular energy transfer to the benzyl ring.[75] The maximum radiation dose during actinide partitioning from actual HLW depends on the design of the contactor and the flow rates of the aqueous and organic streams and may not exceed a few hundred kGy in each cycle. Under such conditions, the radiolytic damage to the TODGA solvent system is not likely to influence its performance in a few cycles of continuous use.

5. ACTINIDE PARTITIONING WITH DIGLYCOLAMIDES

Tri-*n*-butyl phosphate (TBP) used in the PUREX process (for reprocessing of the spent nuclear fuels) is not capable of separating trivalent actinides (mainly Am and Cm) from HLW essentially because of poorer complexation of Am(III) (with nitrate) at 3−4 M HNO_3 as compared to that of U(VI) and Pu(IV) ions.[76] Therefore, it was required to design and develop extractants for efficient separation of minor actinides from HLW emanating from the PUREX waste stream. Several processes have been proposed in recent years using bifunctional extractants such as CMPO, DMDBTDMA, and DMDOHEMA, which are capable of coextracting lanthanides and actinides from HLW (Table 4). However, if minor actinides are to be recycled in a transmutation fuel cycle, the separation of actinides from lanthanides is essential.[77] The main reason is that lanthanides do not form solid solutions with minor actinides in the metal alloy target and, as a result, segregate into separate phase. Since transplutonium actinides tend to concentrate in these phases, this leads to an unacceptable nonuniform heat distribution in the fuel matrix during their burning in a nuclear reactor. High neutron absorption cross sections of some rare earth nuclides may also cause neutron poisoning. After the actinide partitioning step, therefore, the subsequent group separation of An(III)/Ln(III) is proposed to be carried out in the SANEX process using soft donor ligands (Table 4). Recent reviews summarize the developments on different processes for group separation of lanthanides from actinides.[78−81] Wilden et al.[82] proposed a 1-cycle SANEX process for the direct selective extraction of trivalent actinides from a simulated PUREX raffinate using a mixture of CyMe4BTBP and TODGA. The solvent showed a high selectivity for trivalent actinides with a high lanthanide separation factor. However, the coextraction of some fission product elements (Cu, Ni, Zr, Mo, Pd, Ag, and Cd) from a simulated PUREX raffinate was observed. Whereas the extraction of Zr and Mo was prevented using oxalic acid, the extraction of Pd was suppressed by the addition of L-cysteine (sulfur-bearing amino acid) into the aqueous phase.

Recently discovered DGA extractants, viz. TODGA and TEHDGA, have shown superior extraction properties for actinide partitioning than the earlier proposed amide based extractants.[11,28] A comparative performance of DGA extractants with CMPO, TRPO, and DMDBTDMA for the extraction of Am (D_{Am}) from HNO_3 is shown in Figure 11. The striking feature of DGA extractants is that they exhibit very high distribution values for Am(III) under HLW acidity conditions (D_{Am}: >100) as compared to TRPO (D_{Am}: ∼0.5), CMPO (D_{Am}: ∼20), and DMDBTDMA (D_{Am}: ∼10). The major reason for the poor stripping behavior of CMPO is its sharp increase of D_{Am} with acidity in the range pH 2 to 1 M HNO_3. DMDBTDMA is an excellent candidate in this respect due to its gradual increase in

Table 4. Advanced Aqueous Partitioning Methods[3−9, 78−81]

process	purpose	remarks
TRUEX	Tansuranic elements (TRU) extraction from HLW.	Extraction of TRU with CMPO together with TBP as the phase modifier.
TRPO	Actinide partitioning from HLW of low acidity.	Extraction of actinides and lanthanides from waste of low acidity ($\leq$1 M HNO_3).
DIDPA	Actinide partitioning from HLW of low acidity.	Extraction of actinides and lanthanides from waste of low acidity ($\leq$0.5 M HNO_3).
DIAMEX	Actinide partitioning from HLW.	Solvent based on amides as alternative to phosphorus based extractants; expected to generate minimum organic waste, as the extractant is combustible.
TODGA	Actinide partitioning from HLW.	Similar to DIAMEX; solvent based on amides as alternative to phosphorus based extractants.
ARTIST	To recover and stock all actinides, uranium, and transuranics separately.	ARTIST process consists of (a) phosphorus-free branched alkyl monoamides (BAMA) for the separation of U, Pu, (b) TODGA for actinide and lanthanide recovery, and (c) N-donor ligand for actinide/lanthanide separation.
SANEX-S	Selective actinide extraction for group separation of actinides from lanthanides by sulfur donor ligands.	Use of acidic S-bearing extractants, for example synergistic mixture of Cyanex-301 (bis(2,4,4-trimethylpentyl) dithiophosphinic acid) with 2,2-bipyridyl.
SANEX-N	Group separation of actinides from lanthanides by nitrogen donor ligands.	Process for separating actinides from lanthanides from HLW by using neutral N-bearing extractants, viz. bis-triazinyl-pyridines (BTPs).

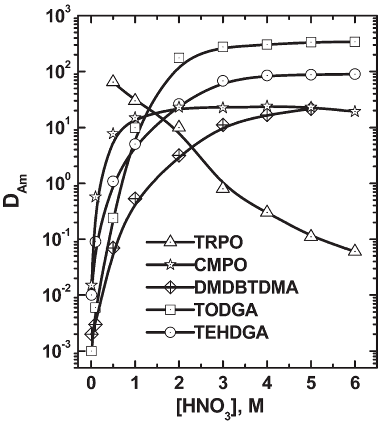


Figure 11. Variation of D_{Am} with HNO_3 concentration. Extractants: 30% TRPO, 0.2 M CMPO + 1.2 M TBP, 1 M DMDBTDMA, 0.1 M TODGA + 0.5 M DHOA, and 0.2 M TEHDGA + 30% *iso*-decanol. Diluent: *n*-dodecane, Temperature: 25 °C.[28, 31]

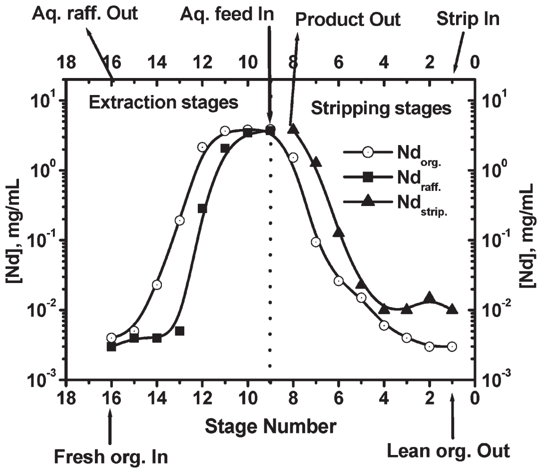


Figure 12. Nd concentration profile at different stages of mixer−settler units. Aqueous phase: 3.8 g/L Nd at 3.5 M HNO_3. Extractant: 0.1 M TODGA + 0.5 M DHOA in normal paraffinic hydrocarbons (NPH). Strippant: 0.2 M HNO_3. Extraction stages O/A = 1. Stripping stages O/A = 1. Temperature: 25 °C.[71]

D_{Am} value with HNO_3 concentration up to 5 M HNO_3. On the other hand, high extraction of Am(III) at 3−4 M acidity and gradual decrease in the D_{Am} values at lower acidity (between 2 M HNO_3 to pH 2) make DGA ligands very promising extractants for the partitioning of actinides from HLW solution. Among different derivatives of DGA, TODGA has been evaluated extensively for actinide partitioning and tested even with genuine nuclear waste solution. A brief summary of actinide partitioning work, mainly with TODGA, therefore, has been summarized in the following section.

5.1. Countercurrent Extraction Studies with TODGA

In the past few years, several reports have appeared on actinide partitioning employing diglycolamide extractants.[69−71,83,84] Countercurrent extraction studies were carried out with 0.1 M TODGA + 0.5 M DHOA in *n*-dodecane using a 16 stages mixer−settler battery.[71] The feed solution was 3.8 g/L Nd at 3 M HNO_3, and the strip solution was 0.2 M HNO_3. Figure 12 shows the profile of the Nd concentration in the organic phase as well as in the aqueous phase at steady state for different stages of mixer−settler units. Efficient (>99.9%) extraction and stripping of Nd was achieved in five stages each. The acid analysis suggested the presence of 0.37 M HNO_3 in the loaded organic phase. Recycling of the organic phase was also demonstrated without any significant change in its performance. Mixer−settler cold runs with simulated PHWR−HLW, which contained 0.6 g/L total lanthanides, suggested that all the lanthanides were efficiently (>99.9%) extracted and stripped, each in four stages.[71] Elements such as Fe, Ni, Mn, and Sr were practically not extracted from SHLW. Similar runs with irradiated solvent (100 kGy) under PHWR−SHLW conditions showed no change in the solvent performance.

Development of the TODGA based process for actinide partitioning was pursued at Julich, Germany, using 0.2 M TODGA + 0.5 M TBP/TPH as the extractant for countercurrent extraction studies with centrifugal contactors.[69] The feed solution used was a synthetic PUREX raffinate spiked with ^{241}Am, ^{244}Cm, ^{252}Cf, ^{152}Eu, and ^{134}Cs. The results showed that An(III) and Ln(III) were quantitatively extracted (>99.9%) with a very high decontamination factor (>10^3−10^4) with respect to fission product and structural elements. The experimental results obtained were in agreement with those predicted by the theoretical stage calculations. The coextraction of zirconium and palladium was prevented by adding oxalic acid and HEDTA, respectively, in

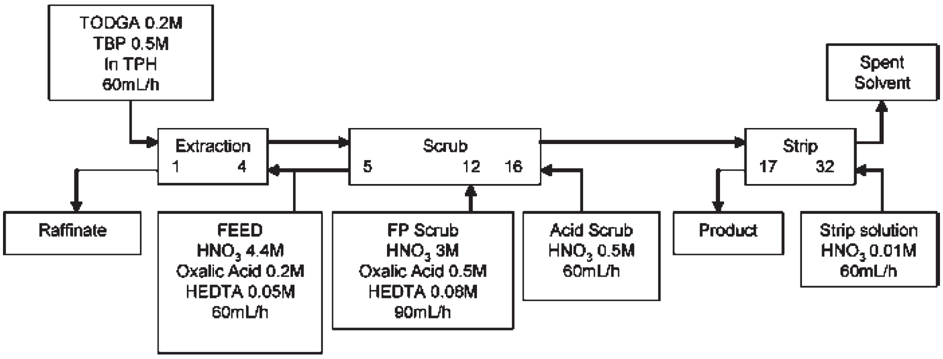


Figure 13. Flow sheet for the TODGA/TBP solvent tested at ITU, Karlsruhe. Reproduced with permission from ref 70. Copyright 2009 Dekker.

Table 5. Comparison of Results between Two DIAMEX and TODGA Processes Performed at ITU, Germany[a]

solvent	0.5 M DMDBTDMA	0.65 M DMDOHEMA	0.2 M TODGA + 1.2 M TBP
feed	irradiated UO_2, $[HNO_3] = 3.5$ M, [oxalic acid] = 0.1 M	irradiated MOX, $[HNO_3] = 4$ M, [oxalic acid] = 0.1 M, [HEDTA] = 0.01 M	irradiated UO_2, $[HNO_3] = 4.4$ M, [oxalic acid] = 0.2 M, [HEDTA] = 0.05 M
product	>99.9% An	>99.96% An	>99.99% An
	>99.9% Ln	>99.8% Ln	>99.9% Ln
	94% Pd	<0.04% Pd	<0.01% Pd
	16% Ru	3% Ru	~ 1% Ru
	51% Tc	62% Tc	
raffinate	<0.01% An	<0.04% An	<0.01% An
	<0.01% Ln	<0.2% Ln	<0.1% Ln
	99.9% Zr	99.7% Zr	99.9% Zr
	99.9% Mo	99.8% Mo	99.9% Mo
	84% Ru	96% Ru	~82% Ru
	<0.01% Pd	>99.9% Pd	>99.99% Pd

[a] Results are expressed as recoveries in the outgoing fractions. Reproduced with permission from ref 70. Copyright 2009 Dekker.

the feed solution. However, 12 stages for stripping were applied to achieve quantitative recovery of the extracted metal ions. The main features of the studies performed at Julich are the following: (i) Ln(III) and An(III) were not found in the raffinate; (ii) only 0.25% U(VI) was found in the raffinate; (iii) 12 stages of stripping resulted in quantitative back-extraction of Ln(III) and An(III); (iv) after stripping, the spent solvent was free from any metal ions, except Ru (~7.5%); and (v) the An(III)/Ln(III) product contained 0.03% Sr, 0.12% Zr, and 1.5% Ru.

In another campaign, the feasibility of the TODGA process was evaluated using genuine PUREX raffinate at ITU, Karlsruhe.[70] The PUREX raffinate was obtained after reprocessing a commercial UO_2 fuel of ~60 GWd/Te burn up. The flow sheet used at ITU-Karlsruhe (Figure 13) showed efficient extraction of lanthanide(III) and actinide(III) (>99.99%) with decontamination factor value $>10^4$ over fission products and structural elements. Out of fission products, only Y and a small fraction of Ru (~3%) contamination was found in the product. Table 5 compares the hot tests carried out using DMDBTDMA, DMDOHEMA, and TODGA solvents at ITU, Karlsruhe, Germany. It is evident that TODGA appears to be a better extractant with respect to (a) decontamination with fission product elements such as Ru and Tc, and (b) efficient recovery of actinides and lanthanides even with the use of lower concentration of the extractant. However, use of TBP as phase modifier and higher concentration of TODGA (0.2 M) enhanced the extraction of acid in the organic phase, which adversely affected the stripping of metal ions.

In continuation of their efforts to identify better solvent composition, Karlsruhe Institute of Technology has recently proposed 0.2 M TODGA + 5% 1-octanol as the extractant for actinide partitioning.[83] Use of octanol as the phase modifier can overcome the drawbacks of using TBP; viz. (i) coextraction of nitric acid can be reduced significantly (~50% lower than that of TBP), and (ii) large volume of secondary waste disposal. It is interesting that at BARC, India, an improved composition of TODGA solvent, viz. 0.05 M TODGA + 5% (v/v) *iso*-decanol/*n*-dodecane has been evaluated for actinide partitioning from SHLW of PHWR origin, where the concentration of total extractable lanthanides and actinides is expected to be <2 g/L.[84] The use of lower TODGA concentration helps in reducing the extraction of fission products such as Sr, Tc, and Mo, leading to better decontamination from the fission products. The loading of Nd in the organic phase by 0.05 M TODGA + 5% *iso*-decanol/*n*-dodecane was found to be 2.28 g/L (0.016 mol/L) at 3 M HNO_3, which was sufficient for HLW corresponding to ~7000 MWd/Te. The extraction data of various metal ions (which are important from the actinide partitioning point of view) with 0.05 M TODGA + 5% *iso*-decanol are summarized in Table 6. The *D* values of Am(III) and Eu(III) were large enough ($D_M > 100$) for their efficient extraction from HLW.

The flow sheet followed for the countercurrent extraction studies with the improved TODGA solvent is shown in Figure 14. The results of mixer—settler runs obtained by radiometric analysis are summarized in Table 7. All the lanthanides and Am(III) were selectively extracted in six stages with a decontamination factor over fission products >1000. Similar to previous runs, the extraction of Zr and Pd was prevented by addition of oxalic acid and HEDTA in the feed solution. The extracted actinides and lanthanides were stripped (>99.9%) with 0.2 M HNO_3 in four stages. Raffinate of the system was found to be free from any α activity. Subsequently, the countercurrent extraction studies were also carried out with solvent irradiated to 500 kGy dose under identical conditions to that of unirradiated solvent.[84] In the case of irradiated solvent, quantitative extraction of Am and Eu required 10 stages as compared to unirradiated solvent, where complete extraction was possible in 6 stages. No traces of fission products were found along with lanthanide and actinide fractions in the organic phase. However, Mo was extracted to an extent of ~80% and could not be removed from the organic phase in the scrubbing cycle. The loaded lanthanides and actinides could be successfully stripped in four stages with 0.2 M HNO_3. Surprisingly, Mo could not be stripped even in 12 stages of stripping and the lean organic phase contained a significant amount (~60%) of molybdenum. It seems that amine formed during the radiolysis of TODGA[72] complexes with the molybdate anions, thus preventing its back-extraction from the organic phase.

Table 6. Distribution Ratio of Different Metal Ions under Extraction and Stripping Conditions[a]

	distribution ratio of metal ions		
metal ions	0.01 M HNO_3	3 M HNO_3	PHWR—SHLW
Cs(I)	<0.001	<0.001	<0.001
Sr(II)	<0.001	0.05 ± 0.01	0.02 ± 0.01
Pd(II)	<0.001	0.24 ± 0.08	0.20 ± 0.05
Fe(III)	<0.001	<0.001	<0.001
Eu(III)	<0.001	230 ± 30	125 ± 25
Am(III)	<0.001	235 ± 35	110 ± 20
Pu(IV)	–	250 ± 35	138 ± 25
U(VI)	<0.001	0.50 ± 0.05	0.4 ± 0.05
Mo(VI)	3.8 ± 0.6	0.14 ± 0.01	0.13 ± 0.01
Tc(VII)	45.8 ± 2.5	0.46 ± 0.05	0.38 ± 0.07

[a] Organic phase: 0.05 M TODGA + 5% *iso*-decanol in *n*-dodecane. Temperature: 25 °C.[84]

5.2. ARTIST Process at JAEA

Since the development of diglycolamides, the major focus of the Japan Atomic Energy Agency (JAEA) has been the development of the ARTIST (Amide-based Radio-resources Treatment with Interim Storage of Transuranics) process using amide based extractants.[85] The main objectives of the ARTIST process are to recover and stock all actinides (uranium and transuranics separately) and to dispose only fission products. The process consists of mainly two steps: (i) exclusive isolation of uranium using branched alkyl monoamides (BAMA) and (ii) total recovery of TRU using TODGA. The concept of the ARTIST process is shown in Figure 15. In the first stage, selective extraction of uranium (which is the major component of spent fuel) is proposed using branched amides such as bis(2-ethylhexyl) butyramide (D2EHBA), which selectively extracts U(VI) over Pu(IV) and other elements. This is followed by recovery of Pu using straight chain monoamides such as *N*,*N*-dioctyl hexanamide (DOHA). Subsequently, minor actinides and lanthanides are extracted using TODGA as the extractant, leaving the other fission products in the raffinate. In the TRU separation stage, lanthanides and actinides are recovered together due to their similar chemical properties. Therefore, another stage has been introduced in the ARTIST process for the separation of transuranics from lanthanides to obtain target material for the transmutation of the former in an ADS (accelerator driven system) or in a FBR (fast breeder reactor).

6. ACTINIDE PARTITIONING STUDIES WITH OTHER DIGLYCOLAMIDES

In the late 1990s, Sasaki and Choppin carried out the extraction studies of actinides with *N*,*N*-dimethyl-*N*′,*N*′-dihexyl diglycolamide and its analogous compounds for the extraction of actinides and lanthanides from aqueous solutions of pH ranging from 1 to 4.[15−19] Subsequently, studies were extended for the extraction of lanthanides from acidic solutions employing *N*,*N*-dimethyl-*N*′,*N*′-diphenyl diglycolamide.[20] Very recently, another DGA derivative, viz. *N*,*N*-dioctyl-*N*′,*N*′-di-(2-ethylhexyl) diglycolamide was synthesized and studied for its extraction behavior toward actinides and fission products.[86] Extraction properties of actinides and lanthanides by this extractant have resemblance with TODGA. However, systematic actinide partitioning studies with other diglycolamide extractants are limited, except TEHDGA (few studies have been reported from India recently).[25−29] Similar to TODGA, TEHDGA also showed third phase formation under high metal loading conditions in the organic phase and, therefore, 30% *iso*-decanol was proposed as the phase

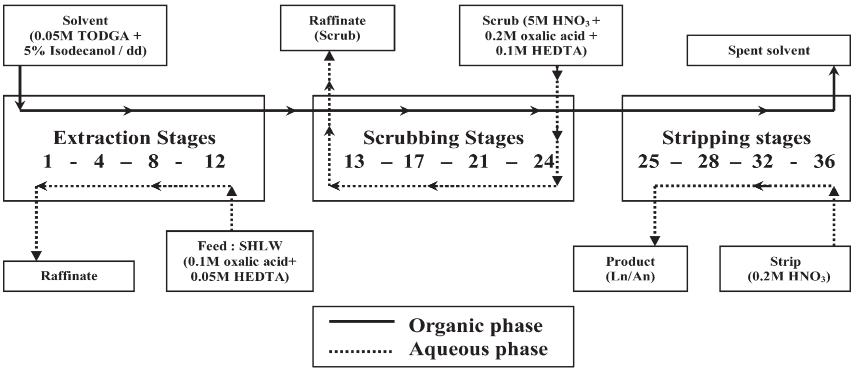


Figure 14. Flow sheet followed for the countercurrent extraction with improved TODGA solvent.[84]

Table 7. Results of Mixer−Settler Runs Obtained by Radiometric Analysis[a]

		recoveries (% of feed)			
element	feed (counts/5 min)	product	raffinate	% material balance	DF w.r.t.^{241}Am
^{241}Am	7511 ± 350	>99.9	<0.01	102.9	–
^{152}Eu	7450 ± 325	>99.9	<0.01	101.3	0.98 ± 0.09
^{85,89}Sr	6226 ± 250	<0.01	>99.9	97.4	2990 ± 235
^{59}Fe	6025 ± 275	<0.01	>99.9	99.7	1997 ± 135
^{137}Cs	3940 ± 285	<0.01	>99.9	103.1	3918 ± 380
^{106}Ru	1415 ± 85	<0.01	>99.9	96.1	1407 ± 150
^{99} Mo	6530 ± 450	<0.01	>99.9	94.8	3250 ± 375
^{109}Pd	2385 ± 215	<0.01	>99.9	103.1	1185 ± 225
^{95}Zr	1780 ± 125	<0.01	>99.9	95.8	1150 ± 125

[a] Extractant: 0.05 M TODGA + 5% *iso*-decanol in *n*-dodecane. Feed: PHWR−SHLW containing 0.1 M oxalic acid and 0.05 M HEDTA. Scrub: 0.2 M oxalic acid + 0.1 M HEDTA at 5 M HNO_3. Strippant: 0.2 M HNO_3.[84]

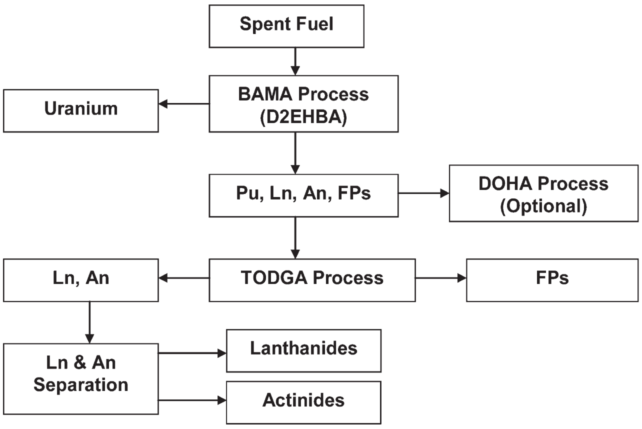


Figure 15. Concept of the ARTIST process proposed at JAEA, Japan[85]

Table 8. Distribution Ratio of Different Metal Ions under Extraction and Stripping Conditions[a]

	distribution ratio of metal ions		
metal ions	0.01 M HNO_3	3 M HNO_3	PHWR-SHLW
Am	<0.002	29.3 ± 2.55	13.9 ± 1.85
Pu	–	55.7 ± 3.51	35.6 ± 2.58
U	<0.002	1.43 ± 0.26	1.08 ± 0.52
Eu	<0.002	95.4 ± 5.8	45.8 ± 3.30
Sr	<0.002	0.16 ± 0.02	0.07 ± 0.02
Cs	<0.001	<0.001	<0.001
Tc	27.4 ± 2.0	0.38 ± 0.05	0.34 ± 0.04
Pd	<0.002	0.05 ± 0.02	0.02 ± 0.01
Fe	<0.001	<0.001	<0.001
Mo	7.0 ± 1.5	0.42 ± 0.05	0.31 ± 0.05

[a] Organic phase: 0.1 M TEHDGA + 5% *iso*-decanol in *n*-dodecane. Temperature: 25°C. Reproduced with permission from ref 28. Copyright 2010 Dekker.

modifier along with 0.2 M TEHDGA.[25] However, systematic studies on the effect of phase modifier suggested DHOA as a better phase modifier, though acid extraction was larger than with *iso*-decanol.[27] Recent investigations on the evaluation of several phase modifiers with 0.1 M TEHDGA/*n*-dodecane revealed the LOC values of Nd at 3 M HNO_3 as 0.036 ± 0.03 mol/L in the presence of 0.5 mol/L phase modifiers, viz. *iso*-decanol, 1-decanol, and DHOA. However, with 0.5 mol/L TBP, the LOC of Nd was lower (0.023 mol/L).[28]

The distribution behavior of various elements by 0.1 M TEHDGA + 5% *iso*-decanol in batch studies is given in Table 8. Though 0.2 M TEHDGA + 30% *iso*-decanol in *n*-dodecane has been originally proposed for actinide partitioning studies,[25] use of a lower concentration of extractant and phase modifier (0.1 M TEHDGA + 5% *iso*-decanol) was adequate for the extractable metal ions from PHWR-HLW and also improved stripping efficiency. The trivalent actinides and lanthanides were efficiently extracted from PHWR-SHLW, as the total concentration of extractable metal ions was <1 g/L. It should be noted that the *D* values of trivalent actinides by TEHDGA were distinctly lower than those with TODGA (Table 6), in spite of using TEHDGA at twice the concentration. Uranium was moderately extracted due to steric hindrance caused by axial oxygen atoms of uranyl ions during complexation with the ligand. The D_{Sr} value was 0.16 at 3 M HNO_3, which decreased to 0.07 in the presence of other extractable metal ions present in SHLW. A similar effect was also observed for Pd. Metal ions such as Fe and Cs were not extracted. Though Tc and Mo were moderately extracted (∼25%) under SHLW conditions, they could be scrubbed along with Sr(II) with ∼5 M HNO_3.

Manohar et al.[25] carried out mixer-settler runs using 0.2 M TEHDGA + 30% *iso*-decanol for extraction of lanthanides and actinides from simulated HLW using $V_o/V_a = 0.5$. Table 9 shows that the product carried 15.3% Mo, 4.2% Ru, and 3.2% Sr. Subsequently, countercurrent mixer settler studies for actinide partitioning were carried out using 0.1 M TEHDGA + 5% *iso*-decanol as the extractant in the authors' laboratory.[29] The flow sheet followed was similar to that shown in Figure 14. The feed solution was PHWR-SHLW spiked with ^{241}Am, ^{244}Cm, ^{152}Eu, ^{137}Cs, ^{85,89}Sr, ^{59}Fe, ^{106}Ru, ^{109}Pd, ^{95}Zr, and ^{99}Mo tracers. The results of mixer-settler runs suggested that >99.9% of the trivalent actinides and lanthanides were extracted in four stages with decontamination factor values >10^3 for most fission products. The coextraction of Zr and Pd was prevented by the addition of oxalic acid and HEDTA into the feed solution. However, ∼20% Ru and 10% Mo was extracted into the organic phase, which was successfully scrubbed using a mixture of 0.2 M oxalic acid and 0.1 M HEDTA in 5 M HNO_3. Finally, the extracted actinides and lanthanides were quantitatively stripped

Table 9. Results of Mixer−Settler Experiment Carried out with SHLW using TEHDGA[a]

element	feed (ppm)	raffinate (ppm)	product (ppm)	% recovery	material balance (%)
La	304	9	596	98.0	101
Ce	186	0.3	305	82.0	82.1
Ru	24	23	2	4.2	100
Mo	154	123	47	15.3	95.1
Sr	67	65	5	3.7	100.7

[a] Extractant: 0.2 M TEHDGA + 30% *iso*-decanol in *n*-dodecane. Strippant: 0.01 M HNO_3.[25]

with 0.2 M HNO_3. Raffinate of the extraction cycle was found to be free from any α activity.

Radiolytic stability of 0.2 M TEHDGA dissolved in *n*-dodecane and different proportions of *iso*-decanol has been studied.[87] Interestingly, the radiolysis of neat TEHDGA was found to be lower as compared to that of 0.2 M TEHGDA dissolved in *n*-dodecane. The *G*-value for neat TEHDGA was found to be 8.65 ± 1.0. The degradation products of TEHDGA were identified as bis(2-ethylhexyl)amine, *N*,*N*-bis(2-ethylhexyl) formamide, *N*,*N*-bis(2-ethylhexyl) acetamide, *N*,*N*-bis(2-ethylhexyl) glycolamide, and *N*,*N*′-bis(2-ethylhexyl)-*N*,*N*′-dipropyl diglycolamide. The D_{Am} by TEHDGA in the presence of different phase modifiers, viz. DHOA, TBP, 1-decanol, and *iso*-decanol, decreased with increased radiation dose studied up to 1000 kGy.[88,89] However, degradation products do not affect the stripping of the metal ions with 0.2 M HNO_3. Physical parameters such as density, viscosity, and interfacial tension are not affected by the irradiation of the solvent significantly.

7. DIGLYCOLAMIDES AS EXTRACTANTS IN ALTERNATIVE SEPARATION TECHNIQUES

In view of their continuous nature, solvent extraction based processes have been extensively employed in industrial scale operations. However, the major problem associated with this technique is the generation of large volumes of secondary waste and handling of large volumes of volatile organic compounds. In this context, techniques such as liquid membrane (LM),[90,91] magnetically assisted chemical separation,[92] and extraction chromatography (EXC)[93,94] have been explored for the treatment of wastes containing low (submillimolar) concentrations of recoverable constituents. A brief summary of the use of diglycolamide extractants in the separation techniques such as LM and EXC for the recovery of lanthanides and actinides is given in the following section.

7.1. Liquid Membrane Studies

The liquid membranes containing an extractant offer a promising approach for the separation of metal ions from dilute aqueous solutions.[90,91] The important features of liquid membranes are (i) the possibility of simultaneous extraction and stripping of the metal ions, (ii) diffusion controlled transport, and (iii) low secondary waste. Two types of liquid membranes, viz. flat sheet supported liquid membranes (FSSLMs) and hollow fiber supported liquid membranes (HFSLMs), have mainly been evaluated for the recovery of actinides and lanthanides from nuclear waste solution using TODGA and TEHDGA as the extractants. In addition to this, few studies with polymer inclusion membrane (PIM) using TODGA have been reported.

Table 10. Correlation of Permeability Coefficient (*P*) of Am(III) with Feed Acidity in Flat Sheet SLM[a]

feed acidity, [HNO_3], M	$P \times 10^3$ (cm/s)	% transport of Am(III) in 4 h	strip phase acidity after 4 h, M
0.75	1.2 ± 0.1	90.2	0.02
1	2.1 ± 0.3	99.8	0.02
2	3.8 ± 0.7	101.2	0.05
3	3.7 ± 0.4	100.2	0.07
4.5	3.1 ± 0.2	100.0	0.10
6	2.2 ± 0.1	96.9	0.13

[a] Membrane: 0.45μm PTFE. Extractant: 0.1 M TODGA in *n*-dodecane. Receiver: distilled water. Temperature: 25 °C.[95]

7.1.1. Flat Sheet Supported Liquid Membrane (FSSLM) Studies.

Extensive investigations were carried out on the transport of actinides and fission products by FSSLM using TODGA as the extractant.[95−97] The permeability coefficient (*P*) of Am(III), which is a measure of transport rate, revealed a gradual increase in the transport of Am(III) up to 2 M HNO_3 and then declined afterward (Table 10).[95] There was a gradual increase in the strip phase acidity from 0.04 M (at feed acidity of 1 M HNO_3) to 0.19 M (at feed acidity of 6 M HNO_3). Enhanced acid transport at >2 M HNO_3 suppressed the effective transport of Am(III). However, the permeability coefficient (*P*) of Am(III) increased linearly with TODGA concentration from 3×10^{-5} cm/s at 0.02 M TODGA to 4×10^{-4} cm/s at 0.15 M TODGA,[95] which was typical of the diffusion controlled membrane permeation processes.[98]

The transport of actinides, lanthanides, and some of the fission products by TODGA-SLM at 3 M HNO_3 is shown in Figure 16. The transport of trivalent actinides and lanthanides was faster than that of the hexavalent actinides. As discussed earlier, the Ln^{3+}/An^{3+}−TODGA complex is stronger as compared to the UO_2^{2+}−TODGA complex (as reflected in their corresponding distribution data), thereby showing their larger permeation than that of uranium. The transport studies on fission products and structural elements (on tracer level) revealed that >99.9% Zr(IV), ∼8% Ru(III), ∼85% of Sr(II), and ∼56% of Pd(II) were also cotransported in 5 h.[97] However, the transport of Zr(IV) was suppressed by addition of 0.4 M oxalic acid in the feed solution. It was observed that the transport of Am(III) was not affected by the presence of either 20 g/L uranium or 6 g/L of Fe. The transport rate of Am(III) decreased in the presence of extractable lanthanides, and >15 h was required for quantitative transport of Am(III) under SHLW conditions, which contained ∼0.6 g/L lanthanides. The flat sheet SLM results suggest that TODGA can be used for plutonium recovery from the high level waste along with Am(III) recovery during the "actinide partitioning" stage with a suitable adjustment of its oxidation state to either the +3 or +4 state.[99−101] Supported liquid membrane studies with TEHDGA revealed that Am(III) was quantitatively transported in 3 h from 3 M HNO_3.[102] On the other hand, only about 80% transport of U(VI) was possible in 5 h.[103] This behavior was attributed to the low affinity of uranyl ions with diglycolamides. The supported liquid membrane based separation method with TEHDGA as the carrier extractant has been used for the separation of carrier free Y-90 from Sr-90.[104] The separation efficiency was found to be dependent on the diluent

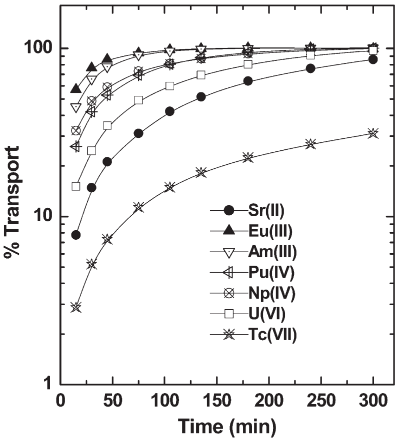


Figure 16. Transport of metal ions from nitric acid by flat sheet SLM. Membrane: 0.45 μm PTFE. Extractant: 0.1 M TODGA in *n*-dodecane. Feed: 3 M HNO_3. Receiver: Distilled water. Temperature: 25 °C.[96]

composition, and an *n*-dodecane + 30% *iso*-decanol mixture or chloroform as the diluent yielded satisfactory separations. Very recently, a novel tripodal diglycolamide (T-DGA) has been reported for the extraction and membrane separation of actinides and fission products.[105] The results demonstrate that T-DGA is a far superior extractant for minor actinides as compared to TODGA and TEHDGA. The FSSLM studies with T-DGA showed that the transport efficiency of actinides followed the order Am(III) > Pu(IV) ≫ Np(IV) > U(VI).

7.1.2. Hollow Fiber Supported Liquid Membrane (HFSLM) Studies. Although flat sheet SLM techniques have shown conceptually the possibility of separation and concentration of a variety of metal ions, they suffer from poor transport rates due to the small surface area for the permeation of metal ions. In this context, the reconfiguration of SLM by using tubular hollow fibers can improve the metal ions transport rates significantly.[106,107] The major advantage of hollow fiber SLM over flat sheet SLM is the very large active surface area available for metal ion transport. The HFSLM has been applied successfully in various fields, viz. clinical, pharmaceutical, and environmental separation studies.[90,91,106] The HFSLM module is operated in two modes: (a) the recycling mode, i.e. the feed solution is circulated continuously through one side of the HFSLM module, whereas the strippant is circulated continuously through other side, and (b) the once-through mode, i.e. the feed and the strip solutions pass only once through the module. Danesi[107] has proposed a model to explain the transport of metal ions in HFSLM.

Ansari et al.[108−111] have extensively studied the transport of metal ions from nitric acid as well as from PHWR-SHLW by HFSLM. The performance of various extractants proposed for actinide partitioning, viz. CMPO and DMDBTDMA, was compared with those of TODGA and TEHDGA. As shown in Figure 17, >99.9% transport of Am(III) was achieved in 30 min with TODGA and TEHDGA as carriers in HFSLM systems from a 500 mL feed solution containing 0.6 g/L Nd at 3 M HNO_3 spiked with ^{241}Am tracer. This behavior was distinctly better than those of other extractants where it was not possible to achieve quantitative transport (CMPO, ∼50%; DMDBTDMA, ∼85%).[109] Better performance of the DGA ligands was (apart from the higher D_{Am} values at 3 M HNO_3 (Figure 11)) due to lower transport of acid on the strip side (Figure 18). As observed in solvent extraction studies, the transport of acid was much larger for the

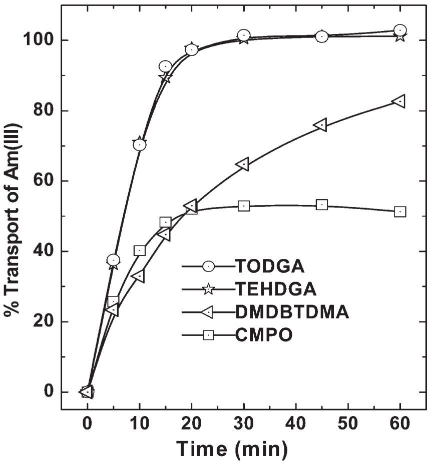


Figure 17. Transport of Am(III) by HFSLM. Extractant: 0.1 M TODGA + 0.5 M DHOA, 0.2 M TEHDGA + 30% *iso*-decanol, 1 M DMDBTDMA and 0.2 M CMPO + 1.2 M TBP. Diluent: normal paraffinic hydrocarbons (NPH). Feed: 0.6 g/L Nd at 3 M HNO_3 spiked with ^{241}Am tracer (500 mL). Strip: distilled water (500 mL). Flow rate: 200 mL/min.[109]

TRUEX solvent (0.2 M CMPO + 1.2 M TBP) due to the presence of a large concentration of TBP, where the strip phase acidity reached 1 mol/L in 30 min of operation.

The applicability of TODGA−HFSLM for actinide partitioning was demonstrated using 20 L SHLW as feed and distilled water as the receiver phase.[111] The transport of Nd(III) from 20 L of feed solution containing 0.6 g/L Nd at 3 M HNO_3 showed >99.9% transport of Nd in 18 h of operation (Figure 19). The product Nd could be concentrated two and four times by maintaining the feed to strip phase volume ratios of 2:1 and 4:1, respectively. However, with increased feed to strip phase volume ratio, the concentration of acid in the receiver phase increased significantly, which was neutralized periodically by adding NaOH to allow >99.9% transport of Nd within ∼20 h. The final compositions of product streams were as follows: 1.2 g/L Nd + 0.2 M $NaNO_3$ at 0.9 M HNO_3 and 2.4 g/L Nd + 0.5 M $NaNO_3$ at 1.2 M HNO_3 for two and four times concentrated product, respectively. This composition was suitable for the subsequent lanthanide actinide separation using extractants such as Cyanex-301.[112] The actinide partitioning studies with 20 L PHWR-SHLW suggested quantitative recovery of all the lanthanides in ∼18 h.[111] Negligible transport of metal ions such as Al, Fe, Ba, Mn, Ni, Na, K, and Cs was observed (<0.01%), while Sr, Mo, and Cr were partially transported (in the range of 5−10%).

The long-term stability of the HFSLM is important for its industrial application. Pearson[113] identified the probable causes of membrane instability as: (a) loss of extractant by solubility in adjacent aqueous solution, (b) progressive wettability of the support pores induced by lowering of the organic−water interfacial tension which results from the surface active nature of the extractant molecules, and (c) the differential pressures existing between the inside and outside of the HFSLM caused by pumping of the solutions. Danesi[114] observed that the loss of extractant from the pores is significant when extractant molecules are very strong surfactants such as alkyl/aryl sulfonic acids and long chain quaternary ammonium salts. On the other hand, no significant loss was observed when weaker surface active extractants such as CMPO, TOPO, and long chain amines were used.

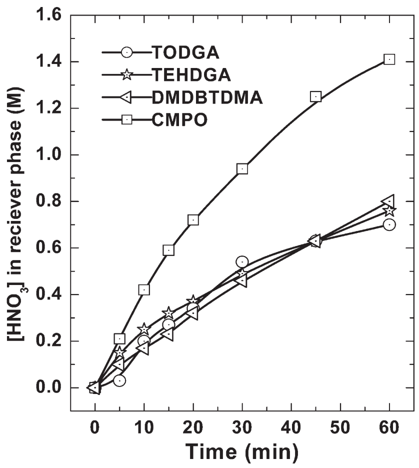


Figure 18. Transport of HNO_3 by HFSLM. Extractant: 0.1 M TODGA + 0.5 M DHOA, 0.2 M TEHDGA + 30% *iso*-decanol, 1 M DMDBTDMA and 0.2 M CMPO + 1.2 M TBP. Diluent: normal paraffinic hydrocarbons (NPH). Feed: 0.6 g/L Nd at 3 M HNO_3 (500 mL). Strip: distilled water (500 mL). Flow rate: 200 mL/min.[109]

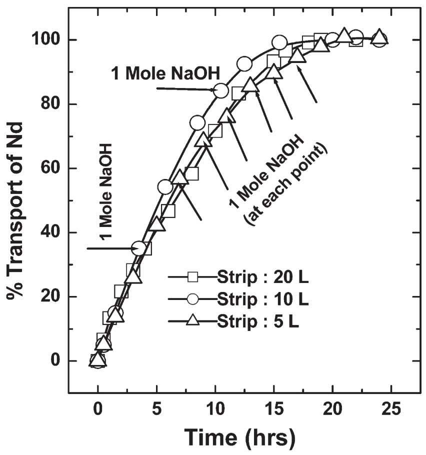


Figure 19. Transport of Nd by HFSLM. Extractant: 0.1 M TODGA + 0.5 M DHOA in *n*-dodecane. Feed: 0.6 g/L at 3 M HNO_3 (20 L). Strip: distilled water (5−20 L). Flow rate: 200 mL/min. Reproduced with permission from ref 111. Copyright 2011 Oldenbourg Verlag.

They found that the HFSLM system was quite stable for 60 days of continuous operation with the polypropylene hollow fiber SLM containing tridodecylamine in *n*-dodecane as the extractant, when outside and inside hydraulic pressures were balanced. Because TODGA is a weak surface active extractant, one may expect a similar stability of HFSLM, though its stability has been demonstrated only for 5 days of continuous operation.[110]

7.1.3. Polymer Inclusion Membrane Studies.

Though SLM has been shown to be an effective separation technique, lack of physical stability is a limitation of this method which hinders its long-term application. The instability is caused by the loss of solvent (which is impregnated in the micropores of membrane) to the surrounding aqueous solutions due to the formation of emulsion droplets or due to differential pressure across the membrane. Sugiura et al.[115,116] prepared a plasticized cellulose triacetate (CTA) membrane containing carrier, known as a polymer inclusion membrane (PIM). Here, the liquid plasticizer acts as an organic solvent. Schow et al.[117] reported that the stability of the plasticized CTA membrane (PIM) was better than that of SLM.

Kusumocahyo et al.[118] developed a PIM consisting of CTA as the polymeric matrix, NPOE (2-nitrophenyl octyl ether) as the solvent and TODGA as the extractant, and they demonstrated the facilitated transport of Ce(III). They observed that the TODGA-PIMs were very effective for the removal of cerium ions from the acidic aqueous feed solution with a relatively high flux. The transport rate of cerium was strongly influenced by the experimental conditions such as the solvent/polymer ratio, the temperature, the membrane thickness, the extractant concentration, and the initial Ce(III) concentration. Their experimental results showed that the rate-limiting step of the transport was the diffusion of the metal−ligand complex within the membrane. They also carried out mathematical modeling to explain the transport of Ce(III) through the TODGA-PIM.[119] The transport studies with TODGA-PIM suggested the transport of lanthanides followed the order of their ionic potential, viz. Lu(III) > Eu(III) > La(III).[120] Similar transport behavior was also observed for actinides, viz. Cm(III) > Am(III). The experimental results indicated that the transport of metal ions by TODGA-PIM was controlled by the diffusion of the metal−ligand complex in the membrane phase.

Recently, a new method for the preparation of PIM, called the post-treatment method, has been developed to prepare a hollow fiber PIM.[121] Using this method, a TODGA based CTA hollow fiber PIM was prepared. A CTA hollow fiber membrane was allowed to swell in a mixture of NPOE and TODGA in the presence of chloroform. After evaporating chloroform, a hollow fiber PIM containing NPOE and TODGA was obtained. The cerium ions were found to be effectively transported from the feed solution (0.05 M HNO_3 + 2.95 M $NaNO_3$) to the strip solution (distilled water) through the hollow fiber PIM.

7.2. Extraction Chromatography Studies

Extraction chromatography (EXC) is often described as a technique that combines the selectivity of solvent extraction with the ease of operation of chromatography.[93,94,122,123] Horwitz et al.[122] found a similar correlation for the extraction of lanthanides by HD2EHP with the two techniques. There is, however, a difference between solvent extraction and EXC with respect to the activities of the extractant and the extracted complex due to the presence of solid support. The performances of TODGA and TEHDGA EXC-resins (prepared by impregnating these extractants on inert solid support) for the recovery of minor actinides from HLW were found to be comparable.[123] The affinity of TODGA-EXC resin for the sorption of Am(III) was also compared with those prepared by the impregnation of other extractants for actinide partitioning, viz. CMPO, TRPO, and DMDBTDMA.[124] Similar to solvent extraction studies (Figure 11), the distribution coefficient (K_d, mL/g) of Am(III) by TODGA-EXC resin increased sharply up to 1 M HNO_3 and remained steady up to 6 M HNO_3. This behavior was similar to that of CMPO but was in contrast to that of DMDBTDMA resin, where sorption of Am(III) increased only gradually with nitric acid concentration and reached moderate values at 3 M HNO_3. On the other hand, TRPO resin exhibited reasonably good K_d values only at lower acidity (K_d = 140 at 0.5 M HNO_3). The K_d values of Am(III) by different EXC-resins, studied at 3 M HNO_3, followed the order 7200 (TODGA) > 2000 (CMPO) > 35 (DMDBTDMA) > 3 (TRPO). The sorption profiles of several metal ions such as Am(III), Eu(III), Pu(IV), U(VI), Fe(III), Sr(II), and Cs(I) by TODGA EXC-resin are shown in Figure 20. The order of K_d values for actinide ions was similar to their D_M values observed in solvent extraction studies, i.e. An(III) ~ An(IV) > An(VI). The K_d values for Cs(I) and Fe(III) were less than 0.5 mL/g in the entire range of acidity investigated, suggesting insignificant sorption of these metal ions. EXC resin prepared by impregnating TODGA on magnetic particles (as the inert support) indicated similar results as shown in Figure 20 for the uptake of several metal ions from nitric acid as well as from SHLW.[125] The advantages of such EXC-resins include the fact that these resins can be added directly to the bulk of the solution and can be separated by magnetic field after sorption of the metal ions, leaving behind the lean aqueous stream.

To evaluate the process applicability of this technique, the effect of some of the selected metal ions, viz. U(VI) and Nd(III), on the sorption of Am(III) by TODGA-EXC resin was studied.[124] The sorption of Am(III) on TODGA-EXC resin was not affected even in the presence of 20 g/L of uranium. However, the K_d value decreased sharply in the presence of Nd(III), suggesting a strong competition between Nd(III) and Am(III) for the sorption on TODGA EXC-resin. In the column studies, 10 mg of europium could be loaded without any breakthrough of Am(III) from 0.5 g of resin. On the other hand, when a solution containing 20 g/L U spiked with ^{241}Am tracer (at 3 M HNO_3) was passed through this column, no breakthrough for ^{241}Am was observed even after passing 100 mL of the feed solution. This result suggests that U(VI) does not compete with Am(III) for sorption on TODGA-EXC resin. The mutual separation of lanthanides by a TODGA-EXC resin column was also attempted.[126] Though the mutual separation of all the lanthanides was not possible, nevertheless, lower lanthanides such as La could be separated from the higher ones such as Lu at 0.1 M HNO_3.

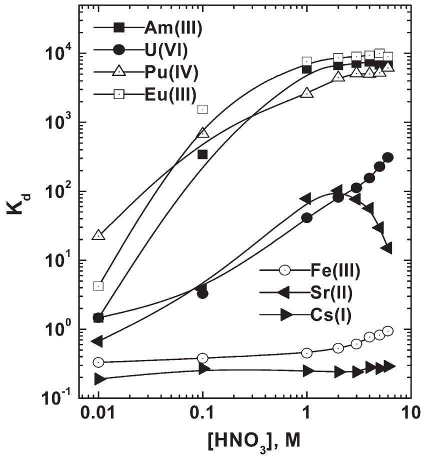


Figure 20. Sorption of metal ions as a function of HNO_3 concentration by TODGA/chromosorb-W resin. Temperature: 25 °C.[124]

The performance of TODGA-EXC resin was compared with that of DMDOHEMA EXC-resin for the uptake of Am(III) from simulated LLW solution.[127] The inert support used was Amberchrom CG-71C (polymethyl acrylate) with particle size 120 μm. The studies revealed 3−4 orders of magnitude higher uptake (K_d values in mL/g) of trivalent actinides by the TODGA resin as compared to the DMDOHEMA resin. On the other hand, the uptake of Mo, Pd, and Zr was relatively higher for the DMDOHEMA resin as compared to the TODGA resin. Nevertheless, Zr and Mo were successfully masked with oxalic acid and Pd with HEDTA without affecting the uptake of lanthanide/actinide. EXC resin by impregnating 30% TODGA + 10% TBP on Amberchrom CG-71C suggested that all the actinides and lanthanides could be separated from the other constituents of SHLW in column operation.[128] Hoshi et al.[129] used TODGA impregnated resin for the development of a flow sheet of the ERIX (electrolytic reduction and ion exchange process) process for reprocessing of FBR-MOX fuel dissolved in 3 M HNO_3. The flow sheet for the ERIX process is given in Figure 21. The process consists of three stages, viz. pretreatment, main process, and, finally, minor actinide separation process with a combination of a TODGA/BTP column for the recovery of actinides and lanthanides separately. Zhang et al.[130−133] proposed TODGA impregnated resin in the MAREC (minor actinide recovery from HLW by extraction chromatography) process. They have extensively

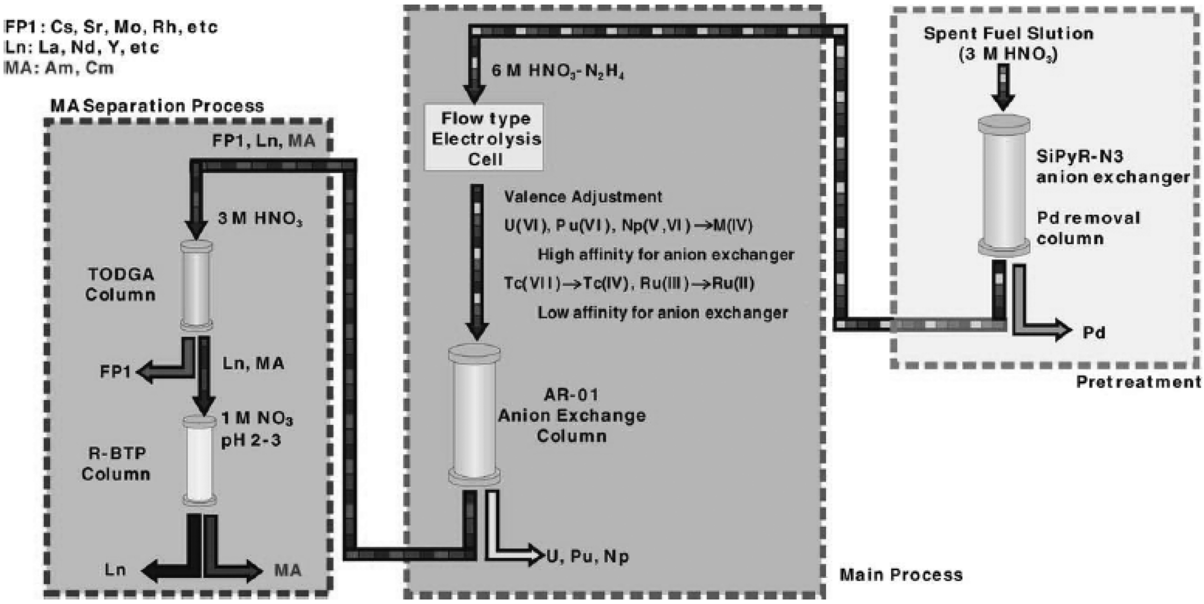


Figure 21. Advanced reprocessing process (ERIX process). Reproduced with permission from ref 129. Copyright 2004 Elsevier.

studied the radiolytic and hydrolytic stability of the resin under HLW conditions.

Horwitz et al.[36] demonstrated the synergistic enhancement of the uptake of trivalent actinides/lanthanides by TODGA resin in the presence of carrier trivalent metal ions from HCl medium (viz. Fe, Ga, In, and Tl, which tend to form anionic species in HCl medium). They found that synergistic species contained a trivalent actinide or a lanthanide complexed by three TODGA molecules with three anionic metal chloride complex ions balancing the charge. They succeeded in the separation of Am and Pu in tracer quantity from the bulk of the soil sample. After leaching the Am/Pu by 3 M HCl, the leached solution was passed through the TODGA column, where all the impurities were washed out except Am and Pu. A significant amount of Fe was also held on the column, which was washed out with 3 M HNO_3. Finally, Am/Pu were recovered with a mixture of 0.03 M oxalic acid and 0.25 M HCl (20 mL). Greater than 95% recovery was possible for Am/Pu with a concentration factor of 25 from 450 mL of leached solution. Horwitz et al.[37,38] have also patented the procedure for the separation of nuclear medicine grade Ac-225 from the Th-229 target using a TODGA coated resin column. Dutta et al.[134] reported an efficient EXC based separation method using TODGA loaded Chromosorb-W as the resin for the separation of carrier free ^{90}Y from ^{90}Sr. This separation method used EDTA as the eluent and was found to be superior to that reported for similar separations by Horwitz et al.[122] The TEHDGA EXC resin has been shown to offer a new possibility for rapid, robust, and effective separation of Ac-225 from Ra-225 for application in targeted cancer therapy.[135] The resin shows a strong retention of Ac(III) from 6 to 7 M HNO_3 and efficient stripping of Ac(III) in dilute nitric acid. Consequently, the use of TEHDGA was implemented into the routine procedure used at ITU, Karlsruhe, for the production of Ac-225/Bi-213 radionuclide generators. Very recently, Pourmand et al.[136] determined the distribution coefficient of 60 elements by TODGA EXC resin obtained from Eichrom Technologies, Inc., USA. They also reported the elution behavior of 32 elements with the TODGA-resin column. TODGA EXC resin was found to be highly versatile with immense potential for matrix−analyte separation for high-precision elemental and isotope analysis of terrestrial and extraterrestrial materials.

8. CONCLUSIONS AND PERSPECTIVES

The separation of trivalent actinides and lanthanides from HLW solutions remains a challenging problem. However, recently developed tridentate diglycolamide based ligands have shown promising extraction efficiency over CMPO based as well as bidentate malonamide extractants. Among diglycolamides, *N*,*N*,*N*′,*N*′-tetraoctyl diglycolamide (TODGA) has been extensively evaluated and has shown excellent properties required by an extractant for the partitioning of actinides from HLW solution. *N*,*N*,*N*′,*N*′-tetra-2-ethylhexyl diglycolamide (TEHDGA) has shown similar behavior to that of TODGA, except that one needs to use a larger concentration of this extractant. The complexation behavior of trivalent actinides and lanthanides has shown the presence of three or four TODGA molecules. However, coordination of three or four tridentate TODGA molecules with Am(III) (or Ln(III)) in their inner coordination sphere does not seem plausible in view of the 8−9 coordination number of these metal ions. EXAFS studies for the Er(III)−DGA complex in ethanol suggested that only two DGA molecules are bonded with the metal ions in the inner coordination sphere. Since, the extraction processes that take place from the nuclear waste solutions are very complex, the precise structure of the extracted species is still a matter of investigation. Nevertheless, EXAFS studies on the extracted complexes in *n*-dodecane may give insight into the structure of the extracted species. Some of the important conclusions have been summarized as follows:

- Substituted diglycolamides are amphiphilic molecules with a polar interior and a nonpolar exterior. However, it has been observed that one needs additional polar compounds to mitigate the third phase problem encountered when their solutions in nonpolar diluents are equilibrated with acids/extractable metal ions beyond a threshold concentration (LOC values). It will be of interest to synthesize and evaluate new DGA molecules incorporating the features of phase modifiers.
- The preorganized cavity offered by the tetramer aggregates seems to be vital to explain the high affinity of trivalent lanthanides and actinides toward DGA extractants in nonpolar diluents. Matching the size of the cavity and the size of spherical metal bearing species appears to be pivotal for ion−dipole interactions which can be addressed by theoretical studies. There are very few modeling studies carried out so far to compute the cavity size offered by reverse micelles of different aggregation number.
- Whether the interaction of the donor oxygen atoms of DGA aggregates is with hydrated trivalent metal ion or with inner sphere complex species of the metal ion with counteranion needs to be unraveled. Work reported so far suggests that outer sphere complexation is favored in HCl medium and inner sphere complexation is favored in nitric acid medium. Little data in $HClO_4$ medium also seems to favor outer sphere complexation. These observations are based principally on distribution, SANS, and TRFS data. Systematic EXAFS studies may help in solving the puzzle. One available report on EXAFS is in ethanol medium, which is not a proper choice.
- The mechanism of extraction of trivalent lanthanides and actinides with amphiphilic DGA molecules in polar diluents such as *n*-octanol is solvation of hydrated cations and anions rather than acid driven reverse micelle formation. DGA molecules replace partially the H_2O molecules from the inner coordination sphere of metal ion to impart organophilicity to the extracted species. In spite of the lower (1:2) stoichiometry favored in octanol (vis-à-vis the 1:4 stoichiometry in *n*-dodecane), the D_{Eu} and D_{Am} values are larger for the polar diluent than those for the nonpolar diluent at lower acidity at a given ionic strength. It is worth investigating if the preferential extraction of Am(III) over U(VI) persists even in polar diluent.
- 0.05 M TODGA + 5% (v/v) *iso*-decanol/*n*-dodecane or 0.1 M TEHDGA + 5% (v/v) *iso*-decanol/*n*-dodecane appears to be the optimum concentration for actinide partitioning from the HLW of PHWR origin, where the total extractable metal ion may not exceed 1 g/L, which corresponds to about 6×10^{-3} M (considering the major proportion of extractable metal ions are lanthanide fission products). However with an increase of fuel burn up, the extractable metal ion concentration may increase several-fold, necessitating the enhancement of ligand as well as the phase modifier concentration. One needs to keep in view, however, the acid uptake, which may impede the stripping of the trivalent actinides.

- Radiation degradation studies have been performed until now up to 500 KGy using a ^{60}Co source, which need to be extended further to α particles as well as to the in situ dose to be experienced by the solvent under dynamic conditions. There are reports suggesting enhancement of degradation in the presence of nitric acid, particularly under dynamic (stirring) conditions. This needs to be investigated further for actinide partitioning studies.
- A gradual increase in D_{Am} value for the DGA−dodecane system with HNO_3 concentration helps with efficient stripping of Am(III) from the loaded organic phase with dilute acid solution (<0.5 M HNO_3). Wherever possible, flow rates (V_o/V_a ratios) should be adjusted to give quantitative stripping of Am(III), and the composition of strippant should be optimized, where the product fraction can be directly employed for Ln(III)/An(III) separation with little feed adjustment.
- The hollow fiber supported liquid membrane technique appears promising for partitioning work, as it is fast and allows concentration of the product as well as reduction in the volume of VOCs and secondary waste. However, there is a need to develop radiation resistant hollow fibers which can be used over prolonged periods without affecting the performance of the membrane.

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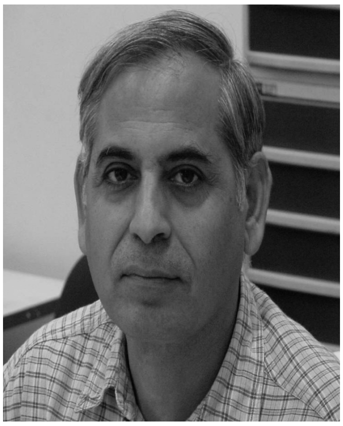

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ACKNOWLEDGMENT

One of the authors (V.K.M.) would like to acknowledge the support by a World Class University (WCU) programme through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (R31-2008-10029).

ABBREVIATIONS

ADS	accelerated driven system
An	actinide
CMPO	octyl-(phenyl)-*N*,*N*-diisobutyl carbamoyl methyl phosphine oxide
CTA	cellulose triacetate
DGA	diglycolamide
DHOA	*N*,*N*-dihexyl octanamide
DIAMEX	diamide extraction
DIDPA	di-isodecyl phosphoric acid
DMDBTDMA	*N*,*N*′-dimethyl-*N*,*N*′-dibutyl tetradecyl malonamide
DMDOHEMA	*N*,*N*′-dimethyl-*N*,*N*′-dioctyl-2-(2-hexyloxyethyl) malonamide
DTPA	diethylenetriamine pentaacetic acid
EDTA	ethylenediamine tetraacetic acid
ERIX	electrolytic reduction and ion exchange
EXAFS	extended X-ray absorption fine structure
EXC	extraction chromatography
FBR	fast breeder reactor
FSSLM	flat sheet supported liquid membrane
Gwd/Te	gigawatt day per tonne
HD2EHP	bis-2-ethylhexyl phosphoric acid
HEDTA	*N*-(2-hydroxyethyl)ethylenediamine triacetic acid
HFSLM	hollow fiber supported liquid membrane
HLW	high level waste
ICR-MS	ion cyclotron resonance mass spectrometry
LET	linear energy transfer
LLW	low level liquid waste
Ln	lanthanide
LOC	limited organic concentration
MAREC	minor actinide recovery by extraction chromatography
MAs	minor actinides
Mwd/Te	megawatt day per tonne
NPOE	2-nitrophenyl octyl ether
PHWR	pressurized heavy water reactor
PIM	polymer inclusion membrane
PUREX	plutonium uranium extraction
SANS	small angle neutron scattering
SAXS	small angle X-ray scattering
SF	separation factor
SHLW	simulated high level waste
TBP	tri-*n*-butyl phosphate
TEHDGA	*N*,*N*,*N*′,*N*′-tetra-2-ethylhexyl diglycolamide
TODGA	*N*,*N*,*N*′,*N*′-tetraoctyl diglycolamide
TPH	hydrogenated tetrapropene
TRLS	time resolved luminescence spectroscopy
TRLFS	time resolved laser-induced fluorescence spectroscopy
TRPO	trialkyl phosphate
TRU	transuranium
TRUEX	transuranium extraction

REFERENCES

(1) Baisden, P. A.; Choppin, G. R. Nuclear waste management and the nuclear fuel cycle. In *Radiochemistry and Nuclear Chemistry*; Nagyl, S., Ed.; Encyclopedia of Life Support Systems (EOLSS); EOLSS Publishers: Oxford, U.K., 2007.

(2) Baestle, L. H. *IAEA Bull.* **1992**, *34*, 32.

(3) Bourga, S.; Hill, C.; Caravaca, C.; Rhodes, C.; Ekberg, C.; Taylor, R.; Geist, A.; Modolo, G.; Cassayre, L.; Malmbeck, R.; Harrison, M.; Angelis, G.; Espartero, A.; Bouvet, S.; Ouvrier, N. *Nucl. Eng. Des.* **2011**, *241*, 3427.

(4) Madic, C.; Testard, F.; Hudson, M. J.; Liljenzin, J.; Christansen, B.; Ferrando, M.; Facchini, A.; Geist, A.; Modolo, G.; Espartero, G.; Mendoza, J. *PARTNEW—New Solvent Extraction Processes for Minor Actinides—Final Report*; 2004; *CEA-Report 6066*.

(5) Nash, K. L.; Madic, C.; Mathur, J. N.; Lacquement, J. Actinide Separation and Technology. In *The Chemistry of the Actinide and Transactinide Elements*, 3rd ed.; Morss, L. R., Edelstein, N. M., Fuger, J., Katz, J. J., Eds.; Springer: The Netherlands, 2006; Vol. 4, pp 2622.

(6) Ansari, S. A.; Pathak, P. N.; Mohapatra, P. K.; Manchanda, V. K. *Sep. Purif. Rev.* **2011**, *40*, 43.

(7) Manchanda, V. K.; Pathak, P. N. *Sep. Purif. Technol.* **2004**, *35*, 85.

(8) Madic, C.; Ouvrier, N. *Radiochim. Acta* **2008**, *96*, 183.

(9) Musikas, C. *Inorg. Chim. Acta* **1987**, *140*, 197.

(10) Purroy, D. S.; Baron, P.; Christiansen, B.; Glatz, J. P.; Madic, C.; Malmbeck, R.; Modolo, G. *Sep. Purif. Technol.* **2005**, *45*, 157.

(11) Sasaki, Y.; Sugo, Y.; Suzuki, S.; Tachimori, S. *Solv. Extr. Ion Exch.* **2001**, *19*, 91.

(12) Stephan, H.; Gloe, K.; Beger, J.; Muhl, P. *Solvent Extr. Ion Exch.* **1991**, *9*, 435.

(13) Stephan, H.; Gloe, K.; Beger, J.; Muhl, P. *Solvent Extr. Ion Exch.* **1991**, *9*, 459.

(14) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533. **1987**, *64*, 561.

(15) Sasaki, Y.; Choppin, G. R. *Anal. Sci.* **1996**, *12*, 225.

(16) Sasaki, Y.; Choppin, G. R. *J. Radioanal. Nucl. Chem.* **1997**, *207*, 383.

(17) Sasaki, Y.; Adachi, T.; Choppin, G. R. *J. Alloys Compd.* **1998**, *271*−*273*, 799.

(18) Sasaki, Y.; Choppin, G. R. *Radiochim. Acta* **1998**, *80*, 85.

(19) Sasaki, Y.; Choppin, G. R. *J. Radioanal. Nucl. Chem.* **2000**, *246*, 267.

(20) Narita, H.; Yaita, T.; Tamura, K.; Tachimori, S. *Radiochim. Acta* **1998**, *81*, 223.

(21) Narita, H.; Yaita, T.; Tachimori, S. Extraction Behavior for Trivalent Lanthanides with Amides and EXAFS Study of Their Complexes. *Proceedings of the International Solvent Extraction Conference, ISEC'99*; 2001; p 693.

(22) Sasaki, Y.; Suzuki, H.; Sugo, Y.; Kimura, T.; Choppin, G. R. *Chem. Lett.* **2006**, *35*, 256.

(23) Sasaki, Y.; Sugo, Y.; Kitatsuji, Y.; Kirishima, A.; Kimura, T.; Choppin, G. R. *Anal. Sci.* **2007**, *23*, 727.

(24) Mowafy, E. A.; Ali, H. H. *Solvent Extr. Ion Exch.* **2007**, *25*, 205.

(25) Manohar, S.; Sharma, J. N.; Shah, B. V.; Wattal, P. K. *Nucl. Sci. Eng.* **2007**, *156*, 96.

(26) Gujar, R. B.; Ansari, S. A.; Murali, M. S.; Mohapatra, P. K.; Manchanda, V. K. *J. Radioanal. Nucl. Chem.* **2010**, *284*, 377.

(27) Deepika, P.; Sabharwal, K. N.; Srinivasan, T. G.; Rao, P. R. V. *Solvent Extr. Ion Exch.* **2010**, *28*, 184.

(28) Gujar, R. B.; Ansari, S. A.; Mohapatra, P. K.; Manchanda, V. K. *Solvent Extr. Ion Exch.* **2010**, *28*, 350.

(29) Gujar, R. B.; Ansari, S. A.; Prabhu, D. R.; Raut, D. R.; Pathak, P. N.; Sengupta, A.; Thulasidas, S. K.; Mohapatra, P. K.; Manchanda, V. K. *Solvent Extr. Ion Exch.* **2010**, *28*, 764.

(30) Modolo, G.; Asp, H.; Schreinemachers, C.; Vijgen, V. *Solvent Extr. Ion Exch.* **2007**, *25*, 703.

(31) Ansari, S. A.; Pathak, P. N.; Husain, M.; Prasad, A. K.; Parmar, V. S.; Manchanda, V. K. *Solvent Extr. Ion Exch.* **2005**, *23*, 463.

(32) Matloka, K.; Gelis, A.; Regalbuto, M.; Vandegrift, G. F.; Scott, M. J. *J. Chem. Soc., Dalton Trans.* **2005**, *23*, 3719.

(33) Matloka, K.; Gelis, A.; Regalbuto, M.; Vandegrift, G. F.; Scott, M. J. *Sep. Sci. Technol.* **2006**, *41*, 2129.

(34) Kannan, S.; Moody, M. A.; Barnes, C. L.; Duval, P. B. *Inorg. Chem.* **2008**, *47*, 4691.

(35) Tian, G.; Xu, J.; Rao, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 6200.

(36) Horwitz, E. P.; McAliste, D. R.; Thakkar, A. K. *Solvent Extr. Ion. Exch.* **2008**, *26*, 12.

(37) Horwitz, E. P.; Barrans, R. E.; Bond, A. H. U.S. Patent 7157022 (January 2, 2007).

(38) Bond, A. H.; Horwitz, E. P.; McAlister, D. R. U.S. Patent 7087206 (August 8, 2006).

(39) Guoxin, S.; Min, L.; Yu, C.; Meilong, Y.; Shaohong, Y. *Solvent Extr. Ion Exch.* **2010**, *28*, 482.

(40) Iqbal, M.; Huskens, J.; Verboom, W.; Sypula, M.; Modolo, G. *Supramol. Chem.* **2010**, *22*, 827.

(41) Pathak, P. N.; Ansari, S. A.; Godbole, S. V.; Dhobale, A. R.; Manchanda, V. K. *Spectrochim. Acta, Part A* **2009**, *73*, 348.

(42) Janczewski, D.; Reinhoudt, D. N.; Verboom, W.; Hill, C.; Allignol, C.; Duchesne, M. T. *New J. Chem.* **2008**, *32*, 490.

(43) Hirata, M.; Guilbaud, P.; Dobler, M.; Tachimori, S. *Phys. Chem. Chem. Phys.* **2003**, *5*, 691.

(44) Sasaki, Y.; Masaki, T.; Saeki, M. *Chem. Lett.* **2007**, *36*, 488.

(45) Tachimori, S.; Suzuki, S.; Sasaki, Y.; Apichaibukol, A. *Solvent Extr. Ion Exch.* **2003**, *21*, 707.

(46) Suzuki, H.; Sasaki, Y.; Sugo, Y.; Apichaibukol, A.; Kimura, T. *Radiochim. Acta* **2004**, *92*, 463.

(47) Ansari, S. A.; Pathak, P. N.; Husain, M.; Prasad, A. K.; Parmar, V. S.; Manchanda, V. K. *Radiochim. Acta* **2006**, *94*, 307.

(48) Sasaki, Y.; Rapold, P.; Arisaka, M.; Hirata, M.; Kimura, T.; Hill, C.; Cote, G. *Solvent Extr. Ion Exch.* **2007**, *25*, 187.

(49) Arisak, M.; Kimura, T. *Solvent Extr. Ion Exch.* **2011**, *29*, 72.

(50) Cossy, C.; Helm, L.; Merbach, A. E. *Inorg. Chem.* **1988**, *27*, 1973. **1989**, *28*, 2699.

(51) Floris, F. M.; Tani, A. *J. Chem. Phys.* **2001**, *115*, 4750.

(52) Jensen, M. P.; Yaita, T.; Chiarizia, R. *Langmuir* **2007**, *23*, 4765.

(53) Yaita, T.; Herlinger, A. W.; Thiyagarajan, P.; Jensen, M. P. *Solvent Extr. Ion Exch.* **2004**, *22*, 533.

(54) Nave, S.; Modolo, G.; Madic, C.; Testard, F. *Solvent Extr. Ion Exch.* **2004**, *22*, 527.

(55) Pathak, P. N.; Ansari, S. A.; Kumar, S.; Tomar, B. S.; Manchanda, V. K. *J. Colloid Interface Sci.* **2010**, *342*, 114.

(56) Ganguli, R.; Sharma, J. N.; Choudhury, N. *J. Colloid Interface Sci.* **2011**, *355*, 458.

(57) Horwitz, E. P.; Martin, K. A.; Diamond, H. *Solvent Extr. Ion Exch.* **1988**, *6*, 859.

(58) Zhu, Z.; Sasaki, Y.; Suzuki, H.; Suzuki, S.; Kimura, T. *Anal. Chim. Acta* **2004**, *527*, 163.

(59) Sasaki, Y.; Zhu, Z.; Sugo, Y.; Kimura, T. *J. Nucl. Sci. Technol.* **2007**, *44*, 405.

(60) Suzuki, H.; Naganawa, H.; Tachimori, S. *Phys. Chem. Chem. Phys.* **2003**, *5*, 726.

(61) Shimojo, K.; Kurahashi, K.; Naganawa, H. *J. Chem. Soc., Dalton Trans.* **2008**, 5083.

(62) Turanov, A. N.; Karandashev, V. K.; Baulin, V. E. *Solvent Extr. Ion Exch.* **2010**, *28*, 367.

(63) Apichaibukol, A.; Sasaki, Y.; Morita, Y. *Solvent Extr. Ion Exch.* **2004**, *22*, 997.

(64) Dutta, S.; Mohapatra, P. K.; Manchanda, V. K. *Appl. Radiat. Isot.* **2011**, *69*, 158.

(65) Rao, P. R. V.; Kolarik, Z. *Solvent Extr. Ion Exch.* **1996**, *14*, 955.

(66) Tachimori, S.; Sasaki, Y.; Suzuki, S. *Solvent Extr. Ion Exch.* **2002**, *20*, 687.

(67) Sasaki, Y.; Sugo, Y.; Suzuki, S.; Kimura, T. *Anal. Chim. Acta* **2005**, *543*, 31.

(68) Sasaki, Y.; Zhu, Z.; Sugo, Y.; Suzuki, H.; Kimura, T. *Anal. Sci.* **2005**, *21*, 1171.

(69) Modolo, G.; Asp, H.; Vijgen, H.; Malmbeck, R.; Magnusson, D.; Sorel, C. *Solvent Extr. Ion Exch.* **2008**, *26*, 62.

(70) Magnusson, D.; Christiansen, B.; Glatz, J.; Malmbeck, R.; Modolo, G.; Purroy, D.; Sorel, C. *Solvent Extr. Ion Exch.* **2009**, *27*, 26.

(71) Ansari, S. A.; Prabhu, D. R.; Gujar, R. B.; Kanekar, A. S.; Rajeswari, B.; Kulkarni, M. J.; Murali, M. S.; Babu, Y.; Natarajan, V.; Rajeswari, S.; Suresh, A.; Manivannan, A.; Antony, M. P.; Srinivasan, T. G.; Manchanda, V. K. *Sep. Purif. Technol.* **2009**, *66*, 118.

(72) Sugo, Y.; Sasaki, Y.; Tachimori, S. *Radiochim. Acta* **2002**, *90*, 161.

(73) Mincher, B. J.; Modolo, G.; Mezyk, S. P. *Solvent Extr. Ion Exch.* **2009**, *27*, 579.

(74) Sugo, Y.; Izumi, Y.; Yoshida, Y.; Nishijima, S.; Saski, Y.; Kimura, T.; Sekine, T.; Kudo, H. *Radiat. Phys. Chem.* **2007**, *76*, 794.

(75) Sugo, Y.; Sasaki, Y.; Kimura, T.; Sekine, T. Attempts to Improve Radiolytic Stability of Amidic Extractants. *Global 2007*; Boise, ID, 2007.

(76) *Science and Technology of Tributyl Phosphate*; Schulz, W. W., Burger, L. L., Navratil, J. D., Bender, K. P., Eds.; CRC Press Inc.: Boca Raton, FL, USA, 1990; Vol. III.

(77) Christiansen, B.; Apostolidis, C.; Carlos, R.; Malmbeck, R.; Pagliosa, G.; Romer, K.; Purroy, D. S. *Radiochim. Acta* **2004**, *92*, 475.

(78) Kolarik, Z. *Chem. Rev.* **2008**, *108*, 4208.

(79) Dam, H. H.; Reinhoudt, D. N.; Verboom, W. *Chem. Soc. Rev.* **2007**, *36*, 367.

(80) Ekberg, C.; Fermvik, A.; Retegan, T.; Skarnemark, G.; Foreman, M. R. S.; Hudson, M. J.; Englund, S.; Nilsson, M. *Radiochim. Acta* **2008**, *96*, 225.

(81) Jensen, M. P.; Bond, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 9870.

(82) Wilden, A.; Schreinemachers, C.; Sypula, M.; Modolo, G. *Solvent Extr. Ion Exch.* **2011**, *29*, 190.

(83) Geist, A.; Modolo, G. TODGA process development: an improved solvent formulation. In *Proceeding of International Conference GLOBAL 2009*, Paris, September 6–11, 2009; Paper No. 9193, page nos. 1022–1026.

(84) Gujar, R. B.; Ansari, S. A.; Prabhu, D. R.; Pathak, P. N.; Sengupta, A.; Thulasidas, S. K.; Mohapatra, P. K.; Manchanda, V. K. *Solvent Extr. Ion Exch.* **2011**accepted.

(85) Tachimori, S.; Sasaki, Y.; Morita, Y.; Suzuki, S. Recent progress of partitioning process in JAERI: development of amide-based ARTIST process. In *Proceedings of the 7th Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation*, Jeju (Korea), October 14–16, 2002.

(86) Ravi, J.; Suneesh, A. S.; Prathibha, T.; Venkatesan, K. A.; Antony, M. P.; Srinivasan, T. G.; Rao, P. R. V. *Solvent Extr. Ion Exch.* **2011**, *29*, 86.

(87) Sharma, J. N.; Ruhela, R.; Singh, K. K.; Kumar, M.; Janardhanan, C.; Achutan, P. V.; Manohar, S.; Wattal, P. K.; Suri, A. K. *Radiochim. Acta* **2010**, *98*, 485.

(88) Gujar, R. B.; Ansari, S. A.; Bhattacharyya, A.; Mohapatra, P. K.; Kanekar, A. S.; Pathak, P. N.; Manchanda, V. K. *J. Radioanal. Nucl. Chem.* **2010**, *288*, 621.

(89) Deepika, P.; Sabharwal, K. N.; Srinivasan, T. G.; Vasudeva Rao, P. V. *Solvent Extr. Ion Exch.* **2011**, *29*, 230.

(90) Boyadzhiev, L.; Lazarova, Z. In *Membrane Separations Technology: Principles and Applications*; Noble, R. D., Stern, S. A., Eds.; Elsevier Science B.V.: 1995; p 283.

(91) Noble, R. D., Way, J. D., Eds. *Liquid Membrane: Theory and Applications*; ACS Symposium Series: Washington, DC, 1987; Vol. 347.

(92) Kamaniski, M. D.; Nunez, L. *Sep. Sci. Technol.* **2000**, *35*, 2003.

(93) Cortina, J. L.; Warshawsky, A. In *Ion exchange and solvent extraction*; Marinsky, J. A., Marcus, Y., Eds.; Marcel Dekker: New York, 1975; Vol. 13, p 195.

(94) Akaza, I. In *Extraction Chromatography*; Braun, T., Ghersini, G., Eds.; Elsevier: New York, 1975; p 17.

(95) Ansari, S. A.; Mohapatra, P. K.; Prabhu, D. R.; Manchanda, V. K. *J. Membr. Sci.* **2006**, *282*, 133.

(96) Ansari, S. A.; Mohapatra, P. K.; Prabhu, D. R.; Manchanda, V. K. *J. Membr. Sci.* **2007**, *298*, 169.

(97) Ansari, S. A.; Mohapatra, P. K.; Prabhu, D. R.; Manchanda, V. K. *Desalination* **2008**, *232*, 254.

(98) Danesi, P. R.; Horwitz, E. P.; Rickert, P. G. *J. Phys. Chem.* **1983**, *87*, 4708.

(99) Panja, S.; Mohapatra, P. K.; Tripathi, S. C.; Manchanda, V. K. *J. Membr. Sci.* **2009**, *337*, 274.

(100) Panja, S.; Mohapatra, P. K.; Tripathi, S. C.; Manchanda, V. K. *Sep. Sci. Technol.* **2010**, *45*, 1112.

(101) Panja, S.; Mohapatra, P. K.; Kandwal, P.; Tripathi, S. C.; Manchanda, V. K. *Desalination* **2010**, *262*, 57.

(102) Panja, S.; Ruhela, R.; Misra, S. K.; Sharma, J. N.; Tripathi, S. C.; Dakshinamoorthy, A. *J. Membr. Sci.* **2008**, *325*, 158.

(103) Panja, S.; Mohapatra, P. K.; Tripathi, S. C.; Manchanda, V. K. *J. Hazard. Mater.* **2011**, *188*, 281.

(104) Dutta, S.; Mohapatra, P. K.; Manchanda, V. K. *Appl. Radiat. Isotop.* **2011**in press.

(105) Mohapatra, P. K.; Iqbal, M.; Raut, D. R.; Verboom, W.; Huskens, J.; Manchanda, V. K. *J. Membr. Sci.* **2011**, *375*, 141.

(106) Kocherginsky, N. M.; Yang, Q.; Seelam, L. *Sep. Purif. Technol.* **2007**, *53*, 171.

(107) Danesi, P. R. *Solvent Extr. Ion Exch.* **1984**, *2*, 115.

(108) Ansari, S. A.; Mohapatra, P. K.; Raut, D. R.; Adya, V. C.; Tulsidas, S. K.; Manchanda, V. K. *Sep. Purif. Technol.* **2008**, *63*, 239.

(109) Ansari, S. A.; Mohapatra, P. K.; Raut, D. R.; Kumar, M.; Rajeswari, B.; Manchanda, V. K. *J. Membr. Sci.* **2009**, *337*, 304.

(110) Ansari, S. A.; Mohapatra, P. K.; Manchanda, V. K. *Ind. Eng. Chem. Res.* **2009**, *48*, 8606.

(111) Ansari, S. A.; Gujar, R. B.; Sengupta, A.; Thulasidas, S. K.; Mohapatra, P. K.; Manchanda, V. K. *Radiochim. Acta* **2011**in press.

(112) Bhattacharyya, A.; Mohapatra, P. K.; Ansari, S. A.; Raut, D. R.; Manchanda, V. K. *J. Membr. Sci.* **2008**, *312*, 1.

(113) Pearson, D. In *Ion Exchange Membranes*; Flett, D. S., Ed.; Society of Chemical Industry: London, 1983; pp 55–73.

(114) Danesi, P. R. *Sep. Sci. Technol.* **1985**, *19*, 857.

(115) Sugiura, M.; Kikkawa, M.; Urita, S. *Sep. Sci. Technol.* **1987**, *22*, 2263.

(116) Sugiura, M.; Kikkawa, M.; Urita, S. *J. Membr. Sci.* **1989**, *42*, 47.

(117) Schow, A. J.; Peterson, R. T.; Lamb, J. D. *J. Membr. Sci.* **1996**, *111*, 291.

(118) Kusumocahyo, S. P.; Kanamori, T.; Sumaru, K.; Aomatsu, S.; Matsuyama, H.; Teramoto, M.; Shinbo, T. *J. Membr. Sci.* **2004**, *244*, 251.

(119) Kusumocahyo, S. P.; Sumaru, K.; Iwatsubo, T.; Shinbo, T.; Kanamori, T.; Matsuyama, H.; Teramoto, M. *J. Membr. Sci.* **2006**, *280*, 73.

(120) Ansari, S. A.; Mohapatra, P. K.; Manchanda, V. K. *Desalination* **2010**, *262*, 196.

(121) Kusumocahyo, S. P.; Kanamori, T.; Iwatsubo, T.; Sumaru, K.; Shinbo, T.; Matsuyama, H.; Teramoto, M. *J. Appl. Polym. Sci.* **2006**, *102*, 4372.

(122) Horwitz, E. P.; McAlister, D. R.; Bond, A. H.; Barrans, R. E. *Solvent Extr. Ion Exch.* **2005**, *23*, 319.

(123) Horwitz, E. P.; McAlister, D. R.; Dietz, M. L. *Sep. Sci. Technol.* **2006**, *41*, 2163.

(124) Ansari, S. A.; Pathak, P. N.; Husain, M.; Prasad, A. K.; Parmar, V. S.; Manchanda, V. K. *Talanta* **2006**, *68*, 1273.

(125) Shaibu, B. S.; Reddy, M. L. P.; Murali, M. S.; Manchanda, V. K. *Radiochim. Acta* **2007**, *95*, 159.

(126) Husain, M.; Ansari, S. A.; Mohapatra, P. K.; Gupta, R. K.; Parmar, V. S.; Manchanda, V. K. *Desalination* **2008**, *229*, 294.

(127) Hecke, K. V.; Modolo, G. *J. Radioanl. Nucl. Chem.* **2004**, *261*, 269.

(128) Modolo, G.; Asp, H.; Schreinemachers, C.; Vijgen, H. *Radiochim. Acta* **2007**, *95*, 391.

(129) Hoshi, H.; Wei, Y.; Kumagai, M.; Asakura, T.; Morita, Y. *J. Alloys Compd.* **2004**, *374*, 451.

(130) Zhang, A.; Wei, Y.; Hoshi, H.; Kumagai, M.; Kamiya, M.; Komaya, T. *Radiat. Phys. Chem.* **2005**, *72*, 669.

(131) Zhang, A.; Kuraoka, E.; Kumagai, M. *Sep. Purif. Technol.* **2006**, *50*, 35.

(132) Zhang, A.; Wei, Y.; Hoshi, H.; Kumagai, M. *Solvent Extr. Ion Exch.* **2005**, *23*, 231.

(133) Zhang, A.; Kuraoka, E.; Hoshi, H.; Kumagai, M. *J. Chromatgr., A* **2004**, *1061*, 175.

(134) Dutta, S.; Mohapatra, P. K.; Raut, D. R.; Manchanda, V. K. *J. Chromatogr., A* **2011**, *1218*, 6483.

(135) Zielinska, B.; Apostolidis, C.; Bruchertseifer, F.; Morgenstern, A. *Solvent Extr. Ion Exch.* **2007**, *25*, 339.

(136) Pourmand, A.; Dauphas, N. *Talanta* **2010**, *81*, 74.