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Liquid–liquid extraction and pertraction behavior of Am(III) and Sr(II) with diglycolamide carrier extractants

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ABSTRACT

Solvent extraction and supported liquid membrane transport properties of Am(III) and Sr(II) from nitric acid medium using several substituted diglycolamides (DGAs) were investigated in detail. The DGAs studied were N,N,N′N′-tetraamyl diglycolamide (TPDGA), N,N,N′N′-tetrahexyl diglycolamide (THDGA), N,N,N′N′-tetraoctyl diglycolamide (TODGA), N,N,N′N′-tetra(2-ethyl hexyl)diglycolamide (T2EHDGA) and N,N,N′N′-tetradecyl diglycolamide (TDDGA). Effects of feed acidity, phase modifier composition, nature of species were investigated for the solvent extraction of the radionuclides using the DGAs. The trend of Am(III) extraction was TPDGA ≫ THDGA ≫ TODGA > TDDGA ≫ T2EHDGA. The slope analysis method for Am(III) extraction has indicated extracted species containing 4 and 3 molecules of the extractant for TODGA and T2EHDGA, respectively and about two molecules of extractant were found to be associated with the other DGAs. When simulated high level waste was used as the feed, the distribution ratio values decreased significantly.

Supported liquid membrane transport of the radionuclides was evaluated to understand the effects of feed acidity, membrane pore size and phase modifier concentration for the DGAs. While the trends for Am(III) transport rate were TPDGA ~ THDGA ~ TDDGA > TODGA > T2EHDGA and usually 2–5 h were needed for quantitative transport (>99%), Sr(II) transport was found to be significant in this time scale. The trend for activation energies of transport of Am(III) was found to be TDDGA > THDGA > TPDGA (with 30% *iso*-decanol) > T2EHDGA > TODGA.

1. Introduction

Many reagents have been synthesized and evaluated for their solvent extraction of actinide ions, especially the minor actinides such as Am and Cm [1,2]. This process, famously known as ‘actinide partitioning’ is part of the evolving strategy of Partitioning & Transmutation (P&T). These reagents include several phosphorous based reagents such as: octyl-(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide (CMPO), diisodecylphosphoric acid (DIDPA) and trialkyl phosphine oxide (TRPO) [3–5] as well as malonamides such as N,N′,-dimethyl-N,N′-dibutyl tetradecyl malonamide (DMDBTDMA) and N,N′-dimethyl-N,N′-dioctylhexylethoxymalonamide (DMDOHEMA) and diglycolamides such as N,N,N′,N′-tetraoctyldiglycolamide (TODGA) [6–9]. Though partitioning behavior of actinides is the prime objective of these separations, extraction behavior of certain long lived fission products and those of ^{90}Sr ($t_{1/2}$: 28.5 y) and ^{137}Cs ($t_{1/2}$: 30.1 y) is also required to be investigated to understand the decontamination behavior [10,11]. Invariably, ^{137}Cs extraction is negligible with these extractants. However, ^{90}Sr extraction has been found to be significant with TODGA and there have been studies to find methods of separation of Am from Sr [12]. The phosphorous based reagents are not completely incinerable and produce secondary waste during incineration while the malonamides though considered CHON reagents, have certain disadvantages like difficulty in back extraction of actinides and interference from solvent degradation products. The diglycolamides on the other hand, appear to be the most promising and hence, have been extensively studied for actinide partitioning trial runs using simulated as well as actual high level wastes [13–15].

Abbreviations: CHON, carbon hydrogen oxygen nitrogen; CMPO, carbamoylmethylphosphine oxide; DIDPA, di-*iso*-decyl phosphine oxide; DMDBTDMA, N,N′-dimethyl-N,N′-dibutyl tetradecyl malonamide; DMDOHEMA, N,N′-dimethyl-N,N′-dioctylhexylethoxymalonamide; HLW, high level waste; PTFE, polytetrafluoroethylene; SLM, supported liquid membrane; T2EHDGA, N,N,N′,N′-tetra(2-ethylhexyl)diglycolamide; TDDGA, N,N,N′,N′-tetradecyl diglycolamide; TPDGA, N,N,N′,N′-tetrapentyl-diglycolamide; THDGA, N,N,N′,N′-tetrahexyl diglycolamide; TODGA, N,N,N′,N′-tetraoctyl diglycolamide; TRPO, tri-n-alkylphosphineoxide; VOCs, volatile organic compounds.

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Though solvent extraction processes have been found promising, liquid membrane based separations in general, and supported liquid membranes in particular have been found to be promising alternatives from environmental considerations [16–19]. This is due to the fact that the SLM based separation methods utilize much lower VOC (volatile organic compound) inventory as compared to the solvent extraction methods. Moreover, the SLM based methods have the advantages of simultaneous extraction and stripping and alleviate problems associated with the solvent extraction processes such as third phase formation, phase disengagement limitations, and phase entrainment [17]. Diglycolamide based extractants such as N,N,N′N′-tetraoctyl diglycolamide (TODGA) and tetra(2-ethyl hexyl) diglycolamide (T2EHDGA) have been extensively studied for their potential for lanthanide and actinide transport using SLM methods [20–25]. However, there is no report on the effect of substituent in the diglycolamides using SLM methods by systematically varying the alkyl chain length. Sasaki et al. [9,26,27] have reported solvent extraction behavior of lanthanides and actinides using a series of diglycolamides with alkyl chain length ranging from *n*-propyl to *n*-dodecyl.

In this work, we have carried out detailed solvent extraction studies of Am(III) and Sr(II) from nitric acid medium using the above mentioned substituted diglycolamides. Effect of nitric acid concentration on the extractability of the metal ions mentioned above and effect of phase modifier on the metal ion extractability were studied in detail. The extractability of Am(III) and Sr(II) were also studied from simulated high level waste (SHLW) at different acidities. The nature of the extracted species was determined for Am(III) with all the DGA extractants. The transport behavior of Am(III) and Sr(II) was also investigated at varying acidities with TODGA, T2EHDGA, THDGA (N,N,N′N′-tetrahexyl diglycolamide), TDDGA (N,N,N′N′-tetradecyl diglycolamide) and TPDGA (N,N,N′N′-tetrapentyl diglycolamide). Effect of membrane pore size on the transport of Am(III) and Sr(II) has also been investigated in detail using each reagent. Effect of phase modifier, i.e., 30% *iso*-decanol on the transport of the metal ions has also been investigated.

2. Experimental

2.1. Materials

Diglycol amides (>97% pure) were synthesized following a reported method and their purity was checked by HPLC, NMR, IR and elemental analysis as described elsewhere [28]. ^{241}Am tracer was purified by a procedure previously described [29]. ^{85,89}Sr (used as a surrogate for ^{90}Sr) was obtained from BRIT, Mumbai and was used as such. PTFE membranes used in the present study were procured from Sartorius, Germany. The membrane porosity was analyzed as reported in an earlier publication [30]. Thickness of the PTFE flat sheets was measured by a Mututoyo digital micrometer and was found to be 70 μm for membranes with 0.2 μm pore size while the thickness for the 0.45 μm, 1.2 μm and 5.0 μm membranes were measured to be 90 μm. Simulated high level waste was prepared as per the compositions given in Table 1 using AR grade reagents. Acidity of the SHLW solutions was analyzed by titrating against standard alkali using phenolphthalein indicator in the presence of saturated potassium oxalate (Merck). Potassium oxalate is used as a masking agent as most of the metal ions can otherwise get hydrolyzed with the addition of the alkali and can lead to erroneous results. All reagents used were of AR grade and were used as procured. Radiometric assay of Am and Sr was done by gamma counting using a NaI(Tl) scintillation detector (Para Electronics, India).

Table 1
Composition of a typical simulated high level waste (SHLW) solution of pressurized heavy water reactor.

Constituent	Concentration (mg/L)	Constituent	Concentration (mg/L)
Se[b]	12.3	Rb[a]	74.5
Sr[a]	186.3	Y[d]	99.0
Zr[a]	771.3	Mo[b]	731.3
Ru[d]	463.8	Co[a,f]	127.5
Pd[d]	267.5	Ag[a]	18.6
Cd[a]	16.3	Sn[b]	15.6
Sb[b]	4.7	Te[b]	102.8
Cs[a]	543.8	Ba[a]	308.8
La[d,e]	263.8	Ce[a]	532.5
Nd[c]	862.5	Eu[c]	22.6
Sm[c]	163.8	Fe[b]	500
Na[a]	3000	Cr[a]	100.0
Ni[a]	100	Mn[a,g]	181.3
U[a]	20,000	Tb[c]	5.0
Pr[c]	243.8	Dy[c]	2.0
Gd[c]	165.0		

[a] Nitrate salt.
[b] Metal powder.
[c] Oxide.
[d] Chloride salt.
[e] Taken in place of Pm.
[f] Taken in place of Rh.
[g] Taken in place of Tc.

2.2. Methods

2.2.1. Solvent extraction studies

Solutions of the desired concentration of diglycolamides (DGA) prepared in *n*-dodecane were agitated with an equal volume of the aqueous phase spiked with the requisite quantity of tracer (about 1.0×10^{-8} Ci ^{241}Am or $^{85+89}$Sr) in a rotary thermostated water bath for an hour at 25.0 ± 0.1 °C. The molar concentration of the metal ions are in the range of 1.0×10^{-7} M (Am) and 1.0×10^{-4} M (Sr) and do not add significantly to the metal ion concentration (particularly, Sr) in the SHLW. Usually, the organic solutions were pre-equilibrated with the aqueous feed (usually 3 M HNO_3) prior to the actual experiments containing the radiotracers. The two phases were then centrifuged and assayed by taking suitable aliquots (usually 100 μL) from both the phases followed by counting using a liquid scintillation counter. The distribution ratio (D) is defined as the ratio of concentration of metal ion in the organic phase to that in the aqueous phase.

2.2.2. Transport studies

SLM studies were carried out in 30 mL glass transport cells where the feed (SHLW as given in Table 1) and the strip solutions (0.1 M HNO_3) were stirred at an optimum speed of 200 rpm as reported in an earlier publication [30]. The micro porous PTFE membranes (usually of 0.2 μm pore size, about 70 μm thickness, unless mentioned otherwise) were soaked in the carrier solution (usually 0.1 M DGA in *n*-dodecane) for at least 10 min prior to use which was reported to be the adequate soaking time [21]. Subsequently, the submerged membrane was removed from the solution and wiped carefully with a tissue paper to remove the excess carrier solution on both the sides. Aliquots were removed from the feed as well as the receiver compartments (usually 100 μL) at regular intervals and assay of radiotracer was done as mentioned above. The transport studies were carried out at ambient temperatures (24 ± 1 °C). The material balance in these studies was found to be within ±5%.

2.3. Transport equations

The transport of the metal ion from the feed compartment to the receiver compartment in the supported liquid membranes mainly