



Facilitated transport of uranium(VI) across supported liquid membranes containing T2EHDGA as the carrier extractant

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ABSTRACT

Facilitated transport of uranyl ion from nitric acid feed solutions was investigated across PTFE supported liquid membranes using N,N,N',N'-tetra-2-ethylhexyl-3-pentane-diamide (T2EHDGA) in *n*-dodecane as the carrier extractant containing 30% *iso*-decanol as the phase modifier. Solvent extraction studies indicated extraction of species of the type, $\text{UO}_2(\text{NO}_3)_2 \cdot \text{T2EHDGA}$. The distribution coefficients increased in the presence of NaNO_3 as compared to equivalent concentration of HNO_3 which was exactly the opposite of what was reported for Am(III)-TODGA extraction system. Supported liquid membrane studies indicated about 11 h were required for quantitative transport of U(VI) from a feed of 3 M HNO_3 using 0.2 M T2EHDGA in *n*-dodecane containing 30% *iso*-decanol as the carrier extractant. Effect of various parameters such as feed acidity, T2EHDGA concentration, and nature of the strippant on the transport rate was investigated. The transport was found to be diffusion controlled in the membrane phase and the permeability coefficient was calculated to be $(3.20 \pm 0.13) \times 10^{-4}$ cm/s for the feed composition of 3 M HNO_3 , receiver phase composition of 0.01 M HNO_3 and membrane carrier phase of 0.2 M T2EHDGA in *n*-dodecane containing 30% *iso*-decanol. The present results may be useful for the separation of U from lean solutions or radioactive wastes considered hazardous due to the presence of alpha-particle emitting radionuclides.

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1. Introduction

Recovery of actinides at the back end of the fuel cycle involves various processes using solvent extraction (SX) based separation methods. The PUREX (plutonium uranium reduction extraction) process is designed for the recovery of U and Pu from the spent fuel and uses TBP (tri-*n*-butyl phosphate) as the extractant in *n*-dodecane or equivalent diluent. The raffinate from the PUREX cycle, termed as the high active waste (HAW), is concentrated to about four times and the acidity is adjusted to 3–4 M HNO_3 and is then called the high level waste (HLW) which also contains small amounts of U and Pu from the losses in the PUREX cycle. The HLW also contains the minor actinides such as Am, Np and Cm, some of which have very long half-lives ($>10^3$ y). Though the general practice of HLW management involves vitrification followed by burial in

deep geological repositories, the long half-lives and high radiotoxicities associated with the minor actinides require surveillance of the waste blocks up to millions of years. Therefore, it is pertinent to separate the minor actinides by a partitioning technique called as 'actinide partitioning' followed by their transmutation in high flux reactors or accelerator driven systems (ADS) [1]. This emerging strategy is called 'partitioning and transmutation' and requires robust methodology for the effective separation of the minor actinides [2].

Out of the 'actinide partitioning' methods, those using diglycolamides as the extractant are found to be quite promising. N,N,N',N'-Tetraoctyl-3-pentane-diamide (TODGA) is extensively used in solvent extraction [3–5], extraction chromatography [6] and liquid membrane [7,8] techniques and has been found to be an efficient extractant, showing rather unique feature of extracting bivalent, trivalent, tetravalent and hexavalent metal ions with equal ease [9]. On the other hand, the branched analog, N,N,N',N'-tetra-2-ethylhexyl-3-pentane-diamide (T2EHDGA) shows higher selectivity though with lower extraction efficiency [10]. Manohar et al. [11], have reported on the solvent extraction of trivalent actinides and lanthanides using T2EHDGA. In the 'actinide partitioning' strategy, two different procedures are recommended for the removal of bulk U, which can sometimes be as high as 10 g/L in the HLW. In the first method, U is removed prior to the 'actinide

Abbreviations: CMPO, carbamoylmethylphosphine oxide; HLW, high level waste; PTFE, polytetrafluoroethylene; PUREX, plutonium uranium reduction extraction; SLM, supported liquid membrane; T2EHDGA, N,N,N',N'-tetra-2-ethylhexyl-3-pentane-diamide; TODGA, N,N,N',N'-tetraoctyl-3-pentane-diamide; WPPA, wet process phosphorous acid.

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Nomenclature

Symbols

A	geometrical surface area
$C_{f,t}$	concentration of metal ion in aqueous feed at time t
$C_{f,0}$	initial metal ion concentration (at $t=0$)
$C_{r,t}$	concentration of metal ion in aqueous receiver at time t
D_o	diffusion coefficient in the membrane phase
D_U	distribution coefficient of uranium
J	overall flux in the transport process
K_H	acid uptake constant of TODGA
Q	effective surface area
$\%T$	percent U transported
T	temperature
V	time average aqueous feed volume
$V_{f,0}$	feed volume at zero time
$V_{f,t}$	feed volume at a given time, t

Greek letters

ε	porosity of the membrane
η	viscosity of the solvent

partitioning' step, while in the second method, there is no prior removal of U. When CMPO (carbamoyl methyl phosphine oxide) is used as the extractant for 'actinide partitioning', prior removal of U is a pre-requisite as third phase formation (the organic phase is split into two phases, a heavy metal complex rich phase and a light diluent rich phase [12]) is encountered otherwise [13]. Prior U removal is not a pre-requisite when T2EHDGA is used as the extractant with 30% *iso*-decanol as a modifier, as no third phase is formed up to 12 g/L of U [10].

Though SX is the work horse of the nuclear industry, both in the front as well as back end of the nuclear fuel cycle, of late, liquid membrane based separation methods are being suggested as viable 'green' alternatives [14–16]. Some liquid membrane methods have been applied in the process scale too, for example, the recovery of U from wet process phosphoric acid (WPPA) solutions [17]. The advantages of liquid membrane technique include: (i) low ligand inventory; (ii) simultaneous extraction and stripping; (iii) limited possibility of third phase formation (due to low metal concentration build up in the membrane phase) and phase entrainment, two of the major drawbacks of SX processes; (iv) and low operation cost as compared to traditional SX methods. [17,18].

Supported liquid membrane studies have revealed that the transport rate of Am(III) using TODGA as the carrier were comparable to that with T2EHDGA [19,20]. Though U transport rate is lower as compared to Am(III) with TODGA, it was of interest to study the transport behaviour for understanding the possible interference during the recovery of minor actinides from HLW with TODGA as the carrier extractant. In view of the interesting observations made during the transport studies involving U(VI) with TODGA as the carrier extractant [21], it was thought of interest to investigate the transport behaviour of U(VI) with T2EHDGA as the carrier extractant.

The present study aims at understanding the transport behaviour of U(VI) from HNO₃ feed solutions and investigates the effect of various parameters that influence the transport behaviour, e.g. feed acidity, carrier extractant concentration, and concentration of phase modifier, using TEHDGA as carrier in the flat sheet supported liquid membrane (FSSLM) mode.

2. Experimental

2.1. Materials

N,N,N',N'-Tetra-2-ethylhexyl-3-pentane-diamide (T2EHDGA) was synthesized as reported earlier [10,11]. The product was characterized by GC-MS and elemental analyzer and the purity and yield were checked by high performance liquid chromatography. Polytetrafluoroethylene (PTFE) membranes used in the present study were procured from Sartorius, Germany. ²³³U tracer was purified from the associated radiotracer impurities by ion-exchange methods reported earlier [21]. Stock solutions of the radiotracers were made in dilute nitric acid after checking the purity by alpha spectrometry. All the other reagents were of AR grade and were used without further purification. Assaying of ²³³U was done by alpha-liquid scintillation counting.

2.1.1. Characterization of PTFE membrane filters

The membrane thickness was measured by a Mitutoyo Digital micrometer while porosities of the membranes were measured by an Electroscan 2020 environmental scanning electron microscope (ESEM) as reported earlier [22]. The active area for transport was measured and found to be 7.06 cm². The porosity of the membranes with pore size of 0.45 micron (used in the present study) was 64% implicating an effective area of the membrane flat sheets of 4.52 cm².

2.2. Methods

2.2.1. Solvent extraction studies

Solutions of desired concentration of T2EHDGA prepared in *n*-dodecane (with or without 30% *iso*-decanol as the phase modifier) were agitated, with an equal volume of the aqueous phase (containing the requisite quantity of ²³³U tracer), in a rotary thermostated water bath for an hour at 25.0 ± 0.1 °C. The two phases were then centrifuged and assayed by taking suitable aliquots. The distribution ratio (D) is defined as the ratio of concentration of U in the organic phase to that in the aqueous phase. All distribution studies were carried out in duplicate and the data were reproducible within ±5%.

2.2.2. Transport studies

The SLM studies were carried out using 16 mL glass transport cells with feed/strip solutions stirred at 200 rpm which was found to be optimum as per an earlier report [22]. The micro porous membrane filter (0.45 micron pore size) was soaked in the carrier solution (usually 0.2 M T2EHDGA in *n*-dodecane, containing 30% *iso*-decanol as the phase modifier) for 10 min prior to use [20]. Subsequently, the membrane was removed from the solution and wiped carefully with a tissue paper to remove the excess fluid. Usually, the feed compartment contained 3.0 M HNO₃ while the receiver phase solution was 0.1 M nitric acid. Aliquots were removed from the feed as well as the receiver compartments in regular intervals and an assay of ²³³U was done like mentioned above. The transport studies were carried out at ambient temperatures (24 ± 1 °C). The error in the material balance in these studies was found to be within ±5%.

2.3. Transport equations

Transport process in the supported liquid membranes involves three main steps, viz. extraction at the feed-membrane interface, diffusion inside the membrane phase and stripping at the membrane-receiver interface. The transport experiments are carried out under the condition that the uranium distribution coefficient (symbolized as D_U) is much larger (for instance about 7.6

for 3 M HNO₃) at the feed–membrane interface as compared to the membrane–receiver interface (for instance about 0.04 for 0.01 M HNO₃). Under steady state condition, by ignoring the concentration of the metal ion in the receiver phase, one can calculate the flux (J) from the following equation [23]:

$$J = PC_f \quad (1)$$

where P is the permeability coefficient at the feed–membrane interface and C_f is the concentration of the metal ion at the feed side of the membrane. The flux can alternatively be expressed as:

$$J = - \left(\frac{1}{Q} \right) \cdot \frac{dV_f C_f}{dt} \quad (2)$$

where V_f is the feed volume and Q is the active area of the membrane. Combining Eqs. (1) and (2), and integrating one obtains,

$$\ln \left(\frac{C_{f,0}}{C_{f,t}} \right) = \frac{QPt}{V_f} \quad (3)$$

where $C_{f,0}$ and $C_{f,t}$ represent the concentrations of feed at starting time and after time ' t ', respectively. Q is expressed as the product of the geometrical surface area (A) and the porosity (ϵ). The permeability coefficient (P) values were calculated using Eq. (3). The cumulative percent transported (% T) at a given time is determined by the following equation,

$$\% T = 100 \cdot \left(\frac{C_{r,t}}{C_{f,0}} \right) \quad (4)$$

where, $C_{r,t}$ is the concentration of the metal ion in the receiver phase at a given time ' t '.

3. Results and discussion

3.1. Solvent extraction studies

3.1.1. Effect of phase-modifier concentration

T2EHDGA was found to form third phase at higher acidities and under loading conditions and a phase modifier was required to mitigate this problem [10]. Out of the various reagents used as phase modifier, *iso*-decanol was found to be the most suitable due to its relatively low acid uptake [11]. The composition of the solvent was 0.2 M T2EHDGA in *n*-dodecane with or without 30% *iso*-decanol considered suitable for actinide partitioning [11]. In the present study, the distribution behaviour of U(VI) was investigated at varying concentrations of nitric acid. For comparison purpose, the solvent extraction data with 0.1 M TODGA in *n*-dodecane is also reported (Table 1). It is clear from the table that, the extraction efficiency of T2EHDGA decreased in presence of 30% *iso*-decanol. This behaviour is similar to other analogous diglycolamide extractants, such as TODGA, which also show lower extraction efficiency in the presence of phase modifiers [24]. It is expected that the diglycolamides form reverse micelle aggregates in non-polar medium such as *n*-dodecane [25]. By adding a polar phase modifier such as *iso*-decanol, the aggregate formation is expected to be affected. Though the polarity increase helps in increasing the limiting organic concentration (LOC) of the extracted complex (thereby suppressing the third phase formation), the D values show a decreasing trend, probably as a result of the deaggregation of the reverse micelles.

The solvent extraction data presented in Table 1 also show that increasing the nitric acid concentration increases the D value of U. However, the D values of T2EHDGA increased more sharply with nitric acid concentration as compared to TODGA. When NaNO₃ was used in the feed in the absence of nitric acid, the D_U values were significantly enhanced and this was most prominent at lower NaNO₃ concentration. To the contrary, in the TODGA system, an entirely opposite trend was observed, i.e., the D values were lower

Table 1

D_U with varying feed nitrate concentration in the absence and presence of phase modifier.

[HNO ₃ /NaNO ₃] in the feed	$D_{U(VI)}$	
	0.2 M TEHDGA	0.2 M TEHDGA + 30% <i>iso</i> -decanol
1 M NaNO ₃	12.17	3.17
2 M NaNO ₃	13.89	5.49
3 M NaNO ₃	16.37	10.18
4 M NaNO ₃	22.45	13.85
6 M NaNO ₃	33.62	21.14
1 M HNO ₃	0.82 (1.01) ^a	0.19
2 M HNO ₃	2.74 (2.08) ^a	–
3 M HNO ₃	7.63 (4.99) ^a	2.51
4 M HNO ₃	12.25 (5.92) ^a	–
6 M HNO ₃	TP ^b (7.31) ^a	9.56

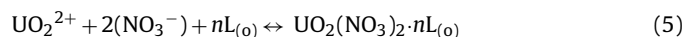
^a Values in parentheses refer to those with 0.1 M TODGA as the extractant.

^b Third phase formation.

in the presence of NaNO₃ as compared to those in the presence of HNO₃. These results suggest that the presence of NaNO₃ may be responsible for breaking the TODGA aggregates thereby causing the drastic decrease in the D_U values. On the other hand, an entirely opposite trend was observed with T2EHDGA, i.e., the D_U values increased in the presence of NaNO₃, the reason for which is yet to be understood.

3.1.2. Effect of T2EHDGA concentration

Extraction of U was also studied by varying the concentration of T2EHDGA in *n*-dodecane with 30% *iso*-decanol as the phase modifier. Zhu et al. have discussed extraction of solvated species of the type UO₂(NO₃)₂· n L where L represented the diglycolamide extractant [9]. The extracted species conform to the following extraction equilibrium:



where the subscript '(o)' indicates species in the organic phase and those without any subscript indicate species in the aqueous phase. The T2EHDGA concentration variation experiments indicated a dependence of ~ 1 when $\log D$ was plotted against $\log [T2EHDGA]$ (Fig. 1), suggesting that the extracted species is UO₂(NO₃)₂·T2EHDGA_(o). Similar species was reported by us for the extraction studies involving TODGA [21]. However, Sharma et al. [10], reported a species of the type UO₂(NO₃)₂·2T2EHDGA_(o) which is in sharp contrast to the species reported by us. On the other hand, a recent structural analysis of a uranyl diglycolamide extract from nitrate medium [26] conform to the presence of a single tridentate diglycolamide unit which is in conformity with our observation.

3.2. Transport studies

3.2.1. Effect of the phase modifier concentration

The effect of the modifier (*iso*-decanol) concentration on the U extraction has been mentioned above. However, the influence of the modifier on the diffusion of the extracted complex across the membrane is not clearly known. Therefore, the transport behaviour of U(VI) was investigated for 0.2 M T2EHDGA as the carrier extractant in *n*-dodecane containing 0–40% *iso*-decanol as the phase modifier. Feed acidity was maintained at 3 M HNO₃ and 0.01 M HNO₃ was used as the strippant in the receiver phase. As shown in Fig. 2, the transport rates decreased with increasing concentration of *iso*-decanol. We found that after 300 min $\sim 81\%$ U was transported when 0.2 M T2EHDGA was used as carrier without any *iso*-decanol. This was found to decrease to $\sim 64\%$ when 40% *iso*-decanol was used as the phase modifier. The permeability coefficients are calculated and are listed in Table 2.

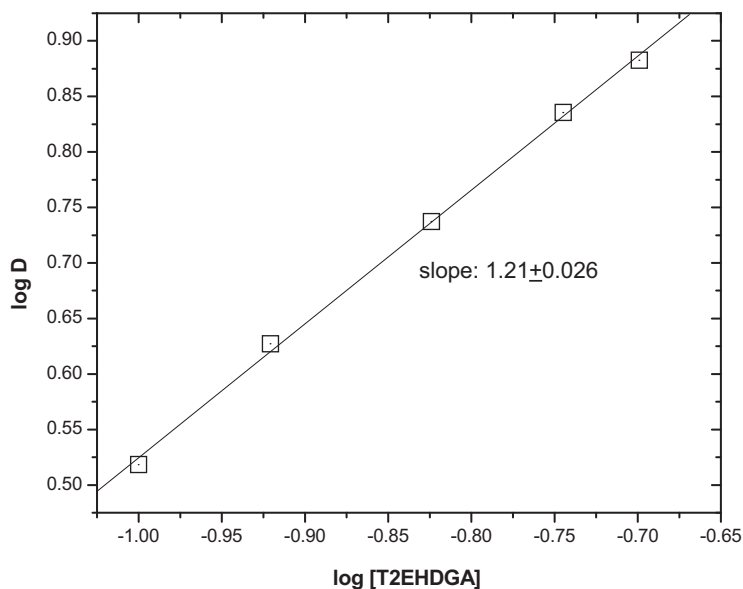


Fig. 1. Dependence of D_U on the concentration of [T2EHDGA]. Aqueous phase: 3 M HNO_3 .

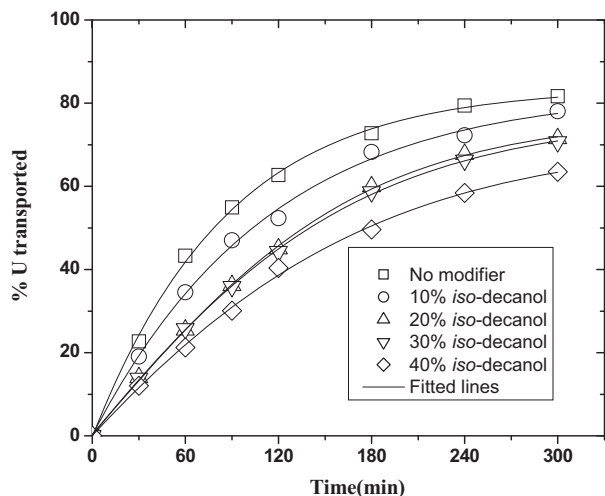


Fig. 2. Transport of U (VI) using 0.2 M T2EHDGA in *n*-dodecane with varying concentration of phase modifier. Feed: 3 M HNO_3 ; receiver: 0.01 M HNO_3 .

The acid transport from the feed to the receiver side was estimated by volumetric method using standard alkali and phenolphthalein indicator. As indicated in Table 2, the acid transport was close to 6% in the absence of any phase modifier while, in the presence of phase modifier the acid transport increased only marginally and was 7% even with 40% *iso*-decanol. This was probably beneficial in the transport of uranyl ion and in spite of significant decrease in the D_U values (about 4 times in the presence of 40% *iso*-decanol) the decrease in the P was only by a factor of two. The dynamic viscosity, on the other hand, showed a significant increase

with increasing *iso*-decanol fraction and might be responsible for the decrease in the transport rates. These results indicated that the diffusion of the metal–carrier complex is more important in deciding transport rates as compared to the D_U values. This also suggests that the transport is a diffusion controlled process similar to other SLM systems studied earlier [19–21].

3.2.2. Effect of the feed acidity

Acidity of the feed solution plays an important role in the carrier facilitated metal ion transport by several factors. Firstly, the acid provides the counter anion in the solvated extraction mechanism and the transport rate increases with increasing feed acidity. Secondly, if the acid interacts with the carrier extractant, then with increasing feed acid concentration, a decrease in the free ligand concentration leads to a decrease in U transport rate. Finally, if there is co-transport of acid, then the receiver phase acidity can increase, resulting in inefficient stripping. The transport profiles of U as a function of the feed nitric acid concentration are presented in Fig. 3. As indicated in the figure, the transport of U(VI) increased from 0.5 M HNO_3 to 3 M HNO_3 for 0.2 M T2EHDGA as the carrier. As per Eq. (5), the transport of U(VI) takes place via nitrate assisted complexation of U(VI) with T2EHDGA. In other words, the higher the feed acidity, the higher will be the complexation and hence the transport rate. However, the possibility of the formation of T2EHDGA· HNO_3 complex can result in lower free T2EHDGA concentration, which can lead to lower U(VI) transport rates. T2EHDGA is expected to form adducts such as T2EHDGA· HNO_3 and the equilibrium constant (K_H) is given as:



Table 2
Transport data as a function of the phase modifier fraction in the carrier extractant. Support: 0.45 micron PTFE; extractant: 0.2 M T2EHDGA; feed: 3 M HNO_3 ; receiver: 0.01 M HNO_3 .

Modifier concentration	Permeability coefficient (cm/s)	% T (5 h)	% Acid transport (5 h)	Dynamic viscosity (cP)	D_U
Nil	$(3.80 \pm 0.32) \times 10^{-4}$	81.7	5.67	2.0010	7.63
10%	$(3.41 \pm 0.25) \times 10^{-4}$	78.1	6.33	2.3329	3.79
20%	$(3.23 \pm 0.06) \times 10^{-4}$	71.5	6.67	2.9141	3.54
30%	$(3.20 \pm 0.13) \times 10^{-4}$	70.7	6.33	3.8501	2.51
40%	$(2.04 \pm 0.09) \times 10^{-4}$	63.5	7.00	4.8625	1.90

Table 3Transport parameters as a function of the nitrate ion concentration in the feed. Support: 0.45 micron PTFE; extractant: 0.2 M T2EHDGA; receiver: 0.01 M HNO₃.

[HNO ₃], M	Permeability coefficient (cm/s) × 10 ⁴	[NaNO ₃], M	Permeability coefficient (cm/s) × 10 ⁴
0.5	0.11 ± 0.01	–	–
1.0	0.36 ± 0.02	1.0	0.19 ± 0.02
2.0	1.94 ± 0.08	2.0	0.80 ± 0.11
3.0	3.37 ± 0.29	3.0	0.93 ± 0.06
6.0	3.86 ± 0.23	6.0	2.70 ± 0.30
8.0	4.16 ± 0.33	–	–

The value of K_H of T2EHDGA is reported as 1.8 ± 0.3 as compared to 4.1 ± 0.4 for TODGA [27]. Therefore, though there is a decrease in the availability of free T2EHDGA for complex formation with U(VI) with increasing acid concentration, it is to a much lesser extent as compared to TODGA. It is shown in Fig. 3 that when the feed acidity increases from 3 M to 6 M HNO₃, the transport rate decreases, while it increases again if the feed acidity is increased to 8 M HNO₃.

It is clear from the above discussion that there is a possibility of higher transport of acid for higher feed acidity which may lead to an increase in the acidity of the receiving phase. It was observed that the acidity of the strip phase increased from 0.2 M for 1 M HNO₃ feed to 0.4 M for 6 M HNO₃ feed acidity after 5 h. As a consequence of increasing acidity in the receiving phase, stripping efficiency decreased and this led to lower transport rate at higher acidity. For trivalent and tetravalent ions we found that when the acidity of the feed phase increased from 3 M HNO₃ to 6 M HNO₃ transport rate decreased quite significantly for both T2EHDGA and TODGA. However, for the hexavalent ions, there is a consistency in the transport rate when feed acidity increased from 3 M HNO₃ to 6 M HNO₃ (Table 3). This is due to the fact that only two nitrate ions are required to form an extractable complex for hexavalent ions whereas for trivalent and tetravalent ions this number is three and four, respectively.

The transport of U with varying nitric acid concentration in the feed can be summarized as follows: (1) with increasing nitric acid concentration U extraction is expected to increase due to the availability of nitrate ion for complexation and formation of the extracted species (Eq. (5)); (2) with increasing nitric acid concentration (beyond 3 M) the T2EHDGA·HNO₃ adduct formation becomes predominant and this leads to a decrease in extraction and hence transport rates; (3) with increasing nitric acid concentration the extraction mechanism may change (beyond 6 M HNO₃) and this can result in higher extraction of U and hence higher transport rates.

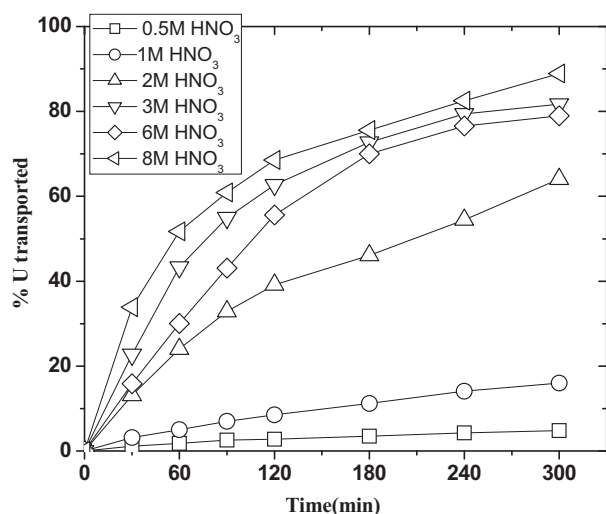


Fig. 3. Transport of U(VI) using varying concentration nitric acid in the feed. Carrier: 0.2 M T2EHDGA in *n*-dodecane containing 30% *iso*-decanol; receiver: 0.01 M HNO₃.

The net result of this three processes is an initial increase in transport up to 3 M HNO₃, slight decrease up to 6 M HNO₃ and further increase at 8 M HNO₃.

In order to discount the effect of nitric acid on the decrease in transport rates at higher acidities while trying to understand the effect of nitrate ion, transport experiments were carried out from feed solutions having varying nitrate ion concentration at a fixed H⁺ ion concentration (0.1 M). The results, as shown in Fig. 4, clearly show the effect of acid transport on the transport rate of U(VI). There was a continuous increase in U(VI) transport rate with increasing nitrate ion concentration from 1 M to 6 M. This is reflected in the permeability data (Table 3). Here neither was any adduct formation for T2EHDGA nor any transport of acid causing acidity of the receiver phase to increase. As a result, the transport rates increased with the nitrate ion concentration in the feed. However, though the transport rates were steep in the initial phase (up to 2 h) for 6 M NaNO₃ as the feed, a plateau was observed afterwards; while a continuous increase in the transport rate was observed with 6 M HNO₃ and marginally higher transport (79%) as compared to 6 M NaNO₃ (74%) was observed after 5 h.

3.2.3. Effect of T2EHDGA concentration

As indicated in Eq. (5), an increase in the T2EHDGA concentration can cause an increase in the distribution coefficient leading to an increase in the transport rates. The effect of T2EHDGA concentration on the transport rate of U was investigated using 3 M HNO₃ as the feed and 0.01 M HNO₃ as the strippant in the receiver phase. In a blank experiment, no U transport was observed when the membrane was dipped in dodecane without T2EHDGA. As shown in Fig. 5, the transport rates increased with increasing concentration of T2EHDGA up to 2.0 M TEHDGA. However, on further increasing the concentration of T2EHDGA to 0.3 M, a marginal decrease in the transport rate was observed. The transport data indicated ~58% and 81% transport of U(VI) in 5 h for 0.05 M and 0.2 M

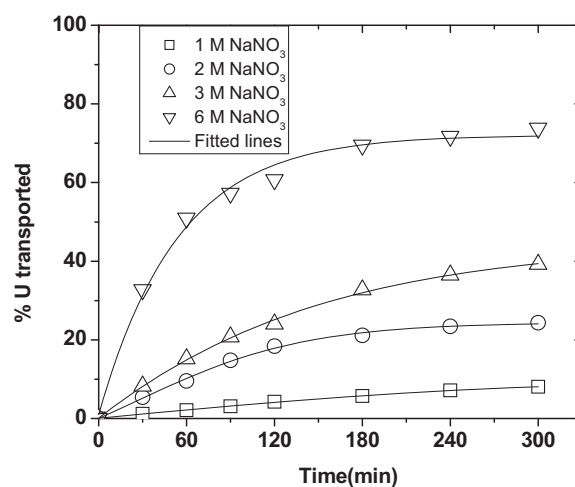


Fig. 4. Transport of U(VI) using varying concentration sodium nitrate in the feed. Carrier: 0.2 M T2EHDGA in *n*-dodecane containing 30% *iso*-decanol; receiver: 0.01 M HNO₃.

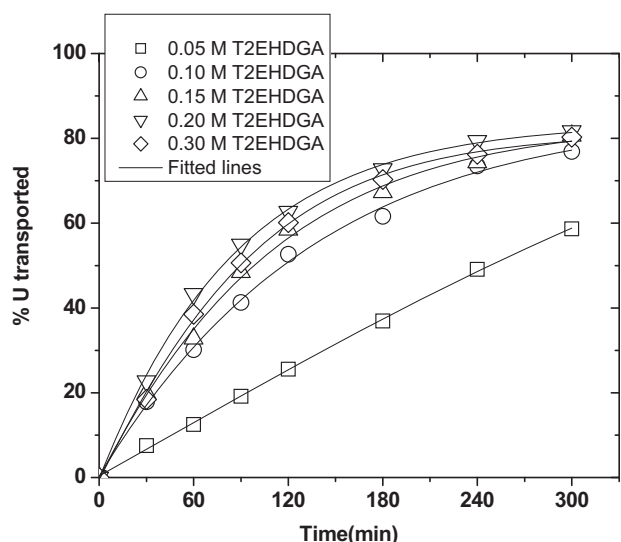


Fig. 5. Transport of U(VI) using varying concentration of T2EHDGA; feed: 3 M HNO₃; receiver: 0.01 M HNO₃.

T2EHDGA, respectively, which marginally decreased to ~80% with 0.3 M T2EHDGA. However, the permeability coefficients showed an increasing trend with increasing T2EHDGA concentration and a slight decrease at 0.3 M T2EHDGA and beyond. For the U–TODGA transport system, the effect of carrier concentration on the P value was studied up to 0.2 M TODGA and a saturation effect was seen [21]. On the other hand, a peak value at 0.10 M TODGA was reported for both trivalent (Am(III)) and tetra-valent (Th(IV)) actinide ions [20,28]. However, for the Am–T2EHDGA transport system, the transport behaviour was similar to the present system [19]. The linear increase up to a higher carrier concentration in case of T2EHDGA as compared to TODGA is probably due to the difference in their aggregation behaviour. Moreover, unusual behaviour in case of U diglycolamides is attributed to the mono solvate species leading to relatively easier diffusion compared to the tri- or tetra-solvates in case of the tetra- and tri-valent actinides, respectively. However, at higher carrier concentration, the viscosity effects play a dominating role, seriously hindering the diffusion process of even the U–T2EHDGA mono solvates.

Babcock et al. [29] assigned the following reasons for the “maximal phenomenon” such as: (i) concentration gradient of the metal–carrier complex, (ii) viscosity of the complex and (iii) hindered diffusion of the metal complex due to the aggregation of the carrier. As already discussed above (Fig. 1), it is quite clear that with increasing T2EHDGA concentration, the distribution ratio of U(VI) is increased (as observed in the solvent extraction studies above) leading to an increase in the concentration of the U–T2EHDGA complex in the membrane–feed interface. This phenomenon causes an increase in the transport rate of U(VI) while increasing the T2EHDGA concentration from 0.05 M up to 0.20 M as evident from Fig. 5. Beyond 0.2 M T2EHDGA, the viscosity effects predominate. The viscosity of 0.1 M T2EHDGA is 1.62 mPa/s which rises to 2.35 mPa/s for 0.3 M T2EHDGA. This increase in viscosity plays a negative role on the transport rate of U(VI) metal as explained by Stokes–Einstein equation,

$$D_0 = \frac{kT}{6\pi R\eta} \quad (7)$$

where, k is the Boltzmann constant, T is the absolute temperature, r is the ionic radius of solute and η is the viscosity of the organic phase equilibrated with the aqueous phase, and D_0 is the diffusion coefficient of the complex across the membrane. Clearly, D_0 is inversely proportional to the viscosity of the carrier solution. Hence,

Table 4

Stability data for the liquid membrane with 0.2 M T2EHDGA in *n*-dodecane with 30% *iso*-decanol as the phase modifier as the carrier extractant. Feed: 3.0 M HNO₃; receiver: 0.01 M HNO₃.

Stability period	% T (5 h)	$P \times 10^4$ (cm/s)
1 day	81.6	3.36 ± 0.11
5 days	80.6	3.29 ± 0.07
10 days	78.9	3.17 ± 0.09
15 days	76.7	3.04 ± 0.06

an increase in the organic phase viscosity caused a decrease in diffusion of the U(VI)–T2EHDGA complex which is reflected in the decreased the transport rates of U(VI).

3.2.4. Membrane stability

The stability of the liquid membrane was evaluated over a period of 15 days and the same liquid membrane was repeatedly used with fresh feed and receiver phase solutions. Though the transport rates and the P values changed only marginally after 15 days of use, and showed a gradual decrease. The average value of P was found to be $(3.22 \pm 0.16) \times 10^{-4}$ cm/s and the data are presented in Table 4. The decrease in the stability of the SLM could be attributed to the erosion of part of the *iso*-decanol used as the phase modifier from the membrane due to the finite solubility of the alcohol in water. This corroborates our earlier conclusion that diluents play a significant role in the stability of the membranes [30,31].

4. Conclusions

From the present studies, the following conclusions can be drawn. Unlike the literature reports, the extracted species was found to contain one T2EHDGA molecule. The lowering in the extraction and transport rates in the presence of the phase modifier is probably due to change in its aggregation behaviour due to a change in the polarity of the medium. The increase in the feed nitric acid concentration increased the transport rates. While increasing the carrier extractant concentration led to an increase in the transport rates a decrease occurred at 0.3 M T2EHDGA concentration which is ascribed to viscosity effects. The membrane transport mechanism is diffusion controlled. The transport rates of uranyl ion obtained in the present system with T2EHDGA as the carrier extractant compared very well with those reported earlier with the TODGA system and hold promise for application in the removal of U from acidic wastes including the PUREX raffinate and high level waste.

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