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Uranium(VI) pertraction across a supported liquid membrane containing a branched diglycolamide carrier extractant: Part III☆

Mass transfer modeling

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ABSTRACT

Solvent extraction and facilitated transport of UO_2^{2+} across supported liquid membrane containing N,N,N′,N′-tetra-2-ethylhexyldiglycolamide (T2EHDGA) in *n*-dodecane as the carrier extractant and 30% *iso*-decanol as the phase modifier were investigated from nitric acid feed solutions. Extraction constants were comparable to those reported earlier for the U(VI)-TODGA extraction system at 3.0 M HNO_3 feed conditions and consequently, the transport rates were comparable with the two extractants. >80% U transport was reported in 5 h while using 3 M HNO_3 as the feed and 0.01 M HNO_3 as the receiver phase solution. Mass transport modeling of the facilitated transport of uranyl ion across PTFE supported liquid membranes was done by a developed mathematical model. Diffusion coefficients were calculated using Danesi's model as well as by lag time measurements. 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 while the membrane diffusion coefficient was calculated to be $(1.58 \pm 0.16) \times 10^{-6}$ cm^2/s.

1. Introduction

Solvent extraction methods are considered the work horse of nuclear industry for separations relevant both in the front as well as back end of nuclear fuel cycle. However, there is a growing concern for the environment and the volatile organic compound (VOC) inventory is required to be reduced drastically for this purpose. Membrane based separation methods are emerging as viable alternatives to the solvent extraction methods [1–4]. There are both pressure driven membranes and liquid membranes used for the decontamination of radioactive wastes. However, though pressure driven membrane based methods such as ultra filtration (UF) have been used for radioactive waste remediation [5,6], they lack selectivity. Supported liquid membrane (SLM) based methods which use selective organic extractants in the pores of the polymeric support, on the other hand, hold promise for the selective separation of metal ions based on the extraction efficiency of the carrier ligand. The major advantages of the SLM methods include simultaneous extraction and stripping, low solvent inventory and easy scale up options. Moreover, the drawbacks of the solvent extraction methods such as third phase formation, phase disengagement limitation and phase entrainment can be alleviated by the SLM based separation methods. However, implementation of SLM methods for plant scale application requires scaling up and modeling of the transport data can address some of those issues.

We have been extensively working on liquid membrane separation of actinides from acidic feeds using specific reagents such as CMPO (octylphenyl-N,N-diisobutylcarbamoylmethylphosphineoxide) [7], malonamides (N,N′-dimethyl-N,N′-dibutyl tetradecylmalonamide) [8] and diglycolamides such as TODGA (N,N,N′,N′-tetraoctyldiglycolamide) and T2EHDGA (N,N,N′,N′-tetra-2-ethylhexyldiglycolamide) [9–14]. Out of these extractants, diglycolamides are found to be quite promising and both N,N,N′N′-tetra-octyldiglycolamide (TODGA) and N,N,N′N′-tetra-2-ethylhexyldiglycol amide (T2EHDGA, Fig. 1) have been found promising for the transport of trivalent actinides such as Am^{3+}[9,14]. We have also reported U transport behavior across PTFE supported flat sheet liquid membranes using TODGA as well as T2EHDGA as the carrier extractants [15,16]. Though the transport rates for UO_2^{2+} were slower as compared to those for Am^{3+}, it can be applied to recover U from lean solutions. Therefore, it was required to understand the mechanism of transport and also to calculate diffusion parameters. It was also required to model the transport data for possible prediction of the U transport profiles at different acidities and T2EHDGA concentrations.

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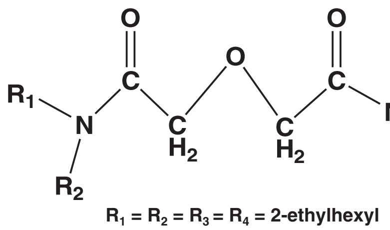

Fig. 1. Structural formula of T2EHDGA.

The present study was aimed at understanding the transport mechanism of U(VI) from HNO_3 feed solutions using T2EHDGA as the carrier extractant in the flat sheet supported liquid membrane (FSSLM) mode. Diffusion co-efficient value was calculated for the FSSLM system containing the extractant and compared with those obtained using TODGA. A mathematical model was developed and the experimentally obtained data points were compared with the theoretical lines at varying concentrations of T2EHDGA and nitric acid concentrations.

2. Experimental

2.1. Materials

Tetra(2-ethylhexyl)diglycolamide (T2EHDGA) was procured from Thermax Ltd, India and the product was characterized by GC–MS, NMR and HPLC. Microporous PTFE membranes used in the present study were procured from Sartorius, Germany and the pore sizes were determined as reported previously [9]. ^{233}U tracer was purified from the associated radiotracer impurities by ion-exchange methods reported earlier [15]. All the other reagents were of AR grade and were used without further purification. Assaying of ^{233}U was done by alpha-liquid scintillation counting.

2.2. Methods

2.2.1. Solvent extraction studies

Solutions of desired concentration of T2EHDGA prepared in *n*-dodecane (with 30% *iso*-decanol as the phase modifier) were agitated with an equal volume of the aqueous phase (containing the requisite quantity of ^{233}U 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 from both the phases. The distribution ratio (*D*) is defined as the ratio of concentration of metal ion in the organic phase to that in the aqueous phase. All distribution studies were carried out in duplicate and the data were reproducible within an error limit of ±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 optimum as reported by us earlier [9]. The micro porous membrane filters (0.45 micron pore size) were soaked in the carrier solution for 10 min prior to use. Subsequently, the submerged membrane was removed from the solution and wiped carefully with a tissue paper to remove the excess fluid on the support. Usually, the feed compartment contained 3.0 M HNO_3 while the receiver phase solution was 0.01 M nitric acid. Aliquots were removed from the feed as well as the receiver compartments in regular intervals and assay of ^{233}U was done as mentioned above. The active area for transport was measured and found to be 7.06 cm^2 while the effective area of the membrane flat sheets was determined as 4.52 cm^2. 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. Modeling of transport data

In SLM for carrier facilitated transport of metal ion, the transport takes place via the following steps, viz. a) diffusion of the metal ion from the bulk feed solution towards the membrane-feed interface; b) complexation of the metal-carrier at the feed-membrane interface; c) diffusion of the metal-carrier complex through the membrane due to concentration gradient; d) de-complexation of the metal-carrier complex at the membrane-strip interface due to non-favorable condition for complexation; e) diffusion of the stripped metal ion towards the bulk of the stripping solution; f) diffusion of the free carrier molecule towards the membrane-feed interface, and the cycle continues. The membrane transport profile is presented in Fig. 2 while the transport scheme is presented in Scheme 1. Now the membrane flux can be derived applying Fick's diffusion law with the following assumptions: i) the concentration gradient in the boundary layer and membrane phase is linear; ii) there is instantaneous dissociation of the U-T2EHDGA complex at the membrane-strip interface; iii) feed nitrate ion concentration is constant; iv) there is no transport of U(VI) in absence of T2EHDGA in the membrane phase.

Under steady state conditions, the equations describing the aqueous flux of metal ion is given by Eq. (1):

$$Ja = k_a(C_B - C_{if}) \tag{1}$$

The membrane flux of metal-carrier complex is given by Eq. (2):

$$J_{org} = k_{org}(\bar{C}\,\mathrm{if} - \bar{C}^*_{is}) \tag{2}$$

where, J_{org} is the membrane flux, k_{org} is the mass transfer coefficient, $\bar{C}if$ is the metal ion concentration in the membrane phase at feed-membrane interface while $\bar{C}^*_{is}$ is the metal ion concentration in the membrane phase at strip-membrane side interface. Considering strip reaction to be instantaneous we can write, (since $\bar{C}^*_{is} = 0$ at this condition).

$$J_{org} = k_{org}\bar{C}_{if} \tag{3}$$

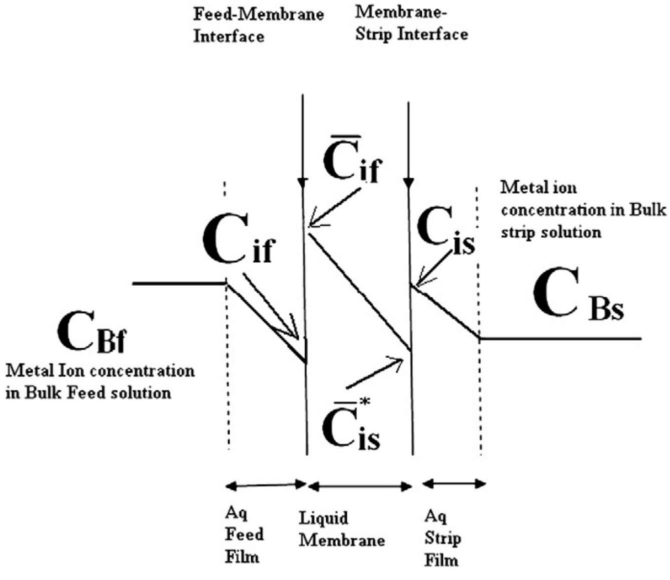

Fig. 2. Schematic presentation of the membrane transport process.