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Facilitated transport of Pd(II) through a supported liquid membrane (SLM) containing *N*,*N*,*N*′,*N*′-tetra-(2-ethylhexyl) thiodiglycolamide T(2EH)TDGA: A novel carrier

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HIGHLIGHTS

- Pd(II) was quantitatively transported (~99.9%) within 2 h from 3.0 M HNO_3 medium using 0.05 M T(2EH)TDGA.
- Pd(II) uptake was very selective over other metal ions present in high level waste solution.
- The membrane was found to be stable for several consecutive cycles.
- Palladium transport was found to be diffusion controlled, the diffusion co-efficient value determined to be 3.56×10^{-5} cm^2/s.

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ABSTRACT

A novel carrier, *N*,*N*,*N*′,*N*′-tetra-(2-ethylhexyl) thiodiglycolamide, T(2EH)TDGA has been studied for transport of Pd(II) from nitric acid medium across a supported liquid membrane (SLM). Pd(II) was found to be almost quantitatively transported (~99.9%) within 2 h from 3.0 M HNO_3 medium using 0.05 M T(2EH)TDGA in *n*-dodecane as carrier and 0.01 M thiourea in 0.2 M HNO_3 as strippant. Pd(II) transport was also studied against various parameters like feed acidity, carrier concentration, membrane pore size, etc. Palladium transport was found to be diffusion controlled and the diffusion co-efficient value was found to be 3.56×10^{-5} cm^2/s. Selectivity of T(2EH)TDGA for palladium over other fission products was found to be quite high, with the separation factors for Pd, with respect to different fission products being $>10^3$. With respect to leaching out of carrier from the membrane support, the membrane was found to be stable for six consecutive cycles. Thus, T(2EH)TDGA can be used as an efficient carrier of Pd(II) from nitric acid medium.

1. Introduction

The platinum group metals (PGMs) namely palladium, rhodium and ruthenium have found extensive applications in chemical, pharmaceutical, electronic and petroleum industries [1,2]. The natural abundance of these metals in the earth crust is very low and those present in mines are also likely to be consumed in another few decades. Therefore, in order to meet the growing demand of these metals, it becomes imperative to seek alternate resources. High level waste (HLW) solutions originating from reprocessing of spent fuel by PUREX process contains significant amount of PGMs [2–4]. Therefore, there is an increasing interest towards recovering these metal ions from HLW. Furthermore, the separation of PGMs from waste could also indirectly exclude some problems associated with vitrification prior to long term disposal [5,6].

Recovery of PGMs from HLW has been extensively studied with particular interest in separation of palladium. Kolarik and coworkers have reviewed, in detail, the methods and materials reported to date for the separation and recovery of fission PGMs from spent nuclear fuel [3,4]. Since the target metal palladium is a soft acid, its selective extraction is possible with soft donor based extractants containing N/S atoms. Based upon this presumption several extractants, namely, tertiary and quaternary amines [7,8], α-benzoin oxime (ABO) [9], dioctyl sulphides [10], trialkylphosphine sulphide (TIPS) [11], bis-(2-ethylhexyl) sulphoxide (BESO) [12] and benzoylmethylene triphenylphosphorane (BMTTP) [13], have been developed at various laboratories. Recently, a novel ligand of the class thiodiglycolamides, namely, *N*,*N*,*N*′,*N*′-tetra(2-ethylhexyl)thiodiglycolamide (T(2EH)TDGA) has been synthesized in our laboratory and studied for extraction behavior of palladium

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from simulated high level waste (SHLW) solution [14,15]. The extractant has shown very high extractability and selectivity for palladium over other metal ions present in SHLW. Hydrolytic and radiolytic stabilities of the extractant have shown promises to be used in processing of genuine HLW to recover palladium [16].

Liquid–liquid extraction has been the most widely used technique to process HLW. But for low concentration of metal ions this method is not suitable due to generation of large volume of secondary waste and handling of large volume of inflammable diluents. Moreover, the use of exotic reagents used for very selective separations necessitate a drastic reduction in the extractant inventory. Thus, it is imperative to look for alternative methods which can reduce the ligand inventory as well as generate small volume of secondary waste. In this regard, membrane based methods are becoming increasingly popular [17,18], not only due to low ligand inventory, but also because of easy scaling up option employing hollow fiber supported liquid membranes [19,20] and alleviation of problems such as third phase formation and phase entrainment.

A prime requirement for a successful liquid membrane system is the choice of a selective and efficient carrier for the species to be separated. Among various extractive ligands used in extraction of palladium from HLW, T(2EH)TDGA was found to be most promising in view of its high extractability and selectivity over other metal ions [14,15]. However, this extractant has not been studied for membrane systems till now. It is therefore of interest to investigate the transport of palladium using T(2EH)TDGA as carrier through supported liquid membrane (SLM).

The current study deals with a detailed investigation of the transport of Pd(II) from nitric acid feed solutions using T(2EH)TDGA/*n*-dodecane as a carrier incorporated in a flat-sheet supported liquid membrane (FSSLM). Various parameters like feed acidity, carrier concentration, membrane pore size, membrane thickness, etc. which effect the transport of Pd(II), have been studied in detail. Experiments have also been carried out to see the transport behavior of different fission products from diluted HLW solution. Stability of the membrane against the leaching of the extractant has also been investigated.

2. Experimental

2.1. Synthesis of T(2EH)TDGA

T(2EH)TDGA was synthesized by the condensation reaction of sodium sulphide nonahydrate with corresponding *N*,*N*-di-(2-ethylhexyl)-2-chloroacetamide according to the procedure described earlier [14]. The purity of product was 98.5% and yield of the reaction was 85.0%. Solutions with desired concentration of T(2EH)TDGA were prepared by dissolving appropriate amount of T(2EH)TDGA in *n*-dodecane.

2.2. Reagents

Throughout this study, flat-sheet type PTFE hydrophobic microporous polymeric membranes were used which were procured from Sartorius AG, Germany. The membrane thickness was measured using the procedure given elsewhere [21]. Pore size of membrane used in all the experiments was 0.45 μm if not mentioned otherwise. The porosity of membrane with pore size 0.45 μm was determined as 64% with an effective area (computed from the geometrical area and the membrane porosity) of 4.52 cm^2. Palladium nitrate solution was prepared by dissolving appropriate amount of $Pd(NO_3)_2{\cdot}xH_2O$ in nitric acid. The concentration of palladium and nitric acid in the inactive stock solution was 1.06 g/L (1×10^{-2} M) and 4.0 M respectively. Aliquots from these solutions were used for different experiments. Normally 10^{-3} M solution of Pd(II) at different nitric acid concentrations was used as feed solution for membrane transport experiments. For transport studies of various fission products, HLW solution generated from PUREX process was diluted in 3.0 M HNO_3 and was used as feed in membrane experiment. High level waste (HLW) originated from research reactor fuel reprocessing plant from a particular batch having the composition of uranium (predominantly ^{238}U) – 8.56 g/L, plutonium (predominantly ^{239}Pu) – 2.19 mg/L, ^{137}Cs – 9.29 Ci/L, ^{106}Ru – 7.99 Ci/L, ^{144}Ce – 27.75 Ci/L, ^{90}Sr – 4.0 Ci/L, ^{95}Zr – 0.2 Ci/L was used. In view of high activity of HLW, it was diluted by a factor of 10^3 to bring down the activity to a measurable level. Consequently, the activity of the radionuclide $^{152+154}Eu$ became too low to determine and hence, had to be spiked. Owing to pure β activity of ^{90}Sr present in the diluted solution, $^{85+89}Sr$ was spiked where a gamma emitter, namely, ^{85}Sr was used as a tracer. The acidity was finally adjusted to 3.0 M HNO_3.

2.3. Membrane studies

The SLM studies were carried out using a Pyrex glass cell consisting of two compartments having volume 16 mL each with the feed and strip solutions being stirred at 5 Hz (300 rpm) to prevent concentration polarization in the membrane interfaces and in the bulk of the solutions [20]. PTFE membranes were kept in T(2EH)TDGA/*n*-dodecane solution for 18 h prior to use. T(2EH)TDGA/*n*-dodecane solutions in each transport experiments were pre-equilibrated with feed nitric acid solution. The pores were immediately and apparently quantitatively filled with the carrier solution by capillary action. Subsequently, the submerged membrane was removed from the solution and wiped carefully with a tissue paper to remove the excess carrier. Assay of Pd(II) in the feed as well as in the receiver phase was carried out at different time intervals to calculate the permeability coefficients. Transport of hydrogen ion was monitored by volumetric titrations. The transport studies were carried out at ambient temperatures (24–26 °C).

2.4. Instruments

Quantitative determination of palladium was carried out using Atomic Absorption Spectrophotometry technique (AAS Avante 1.31, GBC). Detection limit for palladium was 0.06 μg/mL. Error in palladium analysis was within ±2.0%. The activity of the radionuclides during HLW experiment was assayed with a high purity germanium detector coupled to a 4096 channel analyzer. Energies used for the various radionuclides were as follows: ^{106}Ru – 621 keV, ^{137}Cs – 662 keV, ^{144}Ce – 133 keV, ^{241}Am – 59 keV, ^{152}Eu – 121.8 keV and $^{85+89}Sr$ – 514 keV. Uranium analysis was carried out spectrophotometrically using Br-PADAP as chromogenic reagent.

2.5. Transport equations

Transport process in the supported liquid membranes mainly involves three 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 conditions that the distribution coefficient is much larger at the feed–membrane interface as compared to the membrane–receiver interface. Under steady state condition, by ignoring the concentration of the metal ion in the receiver phase one can get the flux (J) [21] from the following equation:

$$J = P_f C_f \quad (1)$$