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Carrier mediated transport of Pd(II) from nitric acid medium using Dithiodiglycolamide(DTDGA) across a supported liquid membrane (SLM)

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ABSTRACT

A novel ligand, namely, *N,N,N′,N′*-tetra-(2-ethylhexyl)dithiodiglycolamide (DTDGA) has been explored as a carrier across a supported liquid membrane (SLM) to study the transport behavior of Pd(II) from nitric acid medium. Almost quantitative transport of Pd(II) was observed in ~2 h time interval using 0.025 M DTDGA in n-dodecane as carrier from 4.0 M HNO_3 feed solution with 0.01 M thiourea in 0.2 M HNO_3 as strippant. During this time interval almost negligible transport of other fission products present in high level waste (HLW) solution was observed. Various parameters were optimized to achieve maximum transport rate viz., feed acidity, DTDGA concentration in membrane phase, membrane porosity etc. Highest permeability co-efficient value of 2.37×10^{-3} cm/s was observed for 0.025 M DTDGA as carrier keeping the feed acidity at 4 M HNO_3 and using 0.2 μm PTFE as membrane support. The membrane was found to be stable over six cycles of operation.

1. Introduction

Supported Liquid Membrane (SLM) technique has gained considerable importance worldwide as a separation technique [1–5]. This is evident from the increasing number of scientific investigations in this topic [6–10]. Less solvent inventory, generation of low volume of secondary waste, simultaneous extraction and stripping, no third phase problem etc. are some of the advantages of SLM over Solvent Extraction (SX) which is still followed worldwide for industrial scale applications. The prime requirement for selective transport of metal ions across a SLM is a selective and efficient carrier molecule.

Palladium has found extensive applications in various field like electric, chemical, petroleum, and pharmaceuticals industry [11,12]. Since the natural ores of palladium are very scarce, alternative sources are constantly explored worldwide. One such alternate source is high level waste (HLW) generated during reprocessing of spent nuclear fuel which contains significant amount of palladium. Owing to associated radioactivity of one of its isotope (^{107}Pd, 17% (w/w)), the recovered Pd can be used especially in those fields where the associated radioactivity (albeit weak) can be tolerated. Separation and recovery of Pd from HLW will have an added advantage of mitigating the various problem encountered during vitrification of HLW [13,14].

Recovery of PGMs (Platinum Group metals) from high level waste has been reviewed by Kolarik and coworkers [13,14]. Being a soft metal ion, Pd extraction is possible with soft donor ligands containing N/S as donor atoms. In the last two decades various ligands have been synthesized and evaluated for their extraction behavior towards Pd. Some of them are tertiary and quaternary amines (tri-n-octylamine, tri-n-octylmethyl ammonium chloride (TOMAC) and tri-n-octylmethylammonium nitrate (TOMAN)) [15,16] α-benzoinoxime (ABO) [17] dihexyl and dioctyl sulfides (DHS [18,19] and DOS[20]), dihexyl disulfide (DHDS) [18], dioctyl and bis-(2-ethylhexyl) sulfoxides (DOSO [21] and BESO [19]), triisobutylphosphinesulfide (TIPS) [21] and benzoylmethylene triphenylphosphorane (BMTTP) [22]. These ligands suffer from the problem of slow kinetics [18,19,21] poor decontamination factor [17,20], pH sensitivity [15,16], solubility [15,16,21,22] and instability in acidic medium [18–20]. Recently we have reported found that a novel ligand namely *N,N,N′,N′*-tetra (2-ethylhexyl) thiodiglycolamide (T(2EH)TDGA) [23] showed excellent extraction property towards Pd while showing very high separation factor compared to other elements present in HLW. The reason behind the high selectivity and extractability for Pd was attributed to the presence of thioetheric sulfur and amidic moiety properly placed in the molecule to chelate the metal ion through more than one donor sites. In order to further increase the

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extractability and to decrease the ligand inventory while maintaining selectivity, the incorporation of second S atom lead us to the molecule *N,N,N′,N′*-tetra(2-ethylhexyl) dithiodiglycolamide (DTDGA). This ligand showed superior extraction behavior over all other ligands reported till date for Pd extraction making it most promising extractant for separation of Pd from HLW [24]. Solvent extraction studies of Pd from nitric acid medium using DTDGA have been reported by us in an earlier communication [25] (Fig. 1).

As evident from the above discussion while a lot of literature is available relating to the liquid–liquid extraction of Pd from HLW, very few reports are available those involving SLM. There are some reports on the bulk liquid separation of Pd through bulk liquid membrane Containing Thioridazine · HCl and Oleic Acid [26], Potassium–Dicyclohexyl-18-crown-6 [27], NH_4^+-dibenzyldiaza-18-crown-6 [28] as carriers. All these studies were carried out from chloride medium. For Thioridazine · HCl and Oleic acid, optimum transport was found at source *pH* of 2 and $NaNO_2$ as stripping agent. For Potassium–Dicyclohexyl-18-crown-6 bulk liquid membrane the optimum condition for Pd transport was found to be 0.15 M KCl in source phase along with 0.8 M NH4SCN as stripping agent whereas for NH_4^+-dibenzyldiaza-18-crown-6 BLM the optimized condition was found to be 0.2 M NH_4Cl as source and 1 M KSCN as receiving phase. There is also a literature report on the SLM transport of Pd from HCl medium using tri-n-octylamine-xylene as carrier [29]. The optimized concentration of HCl and nitric acid in the source and receiving phase was found to be 5 M each respectively. All these studies have been carried out from HCl medium and most of them are most effective in lower pH medium. But HLW originated from spent nuclear fuel reprocessing is in nitric acid medium, so it was found necessary to study the transport of Pd(II) from nitric acid medium of which till date there is no literature available except the system reported by us [30].

The detailed liquid–liquid extraction studies with DTDGA has shown that this ligand is by far one of most promising one both in terms of extractability and selectivity for palladium. However, since the concentration of Pd present in HLW is very small (ppm level), application of SX for this purpose will be problematic due to generation of large volume of secondary waste which can be effectively reduced in Liquid Membrane technique in addition to lowering the ligand inventory. In view of which it was thought to use this ligand as the carrier molecule thereby combining the advantages of both the effectiveness of DTDGA and the supported liquid membrane technique. Present communication reports the transport behavior of Pd from nitric medium using DTDGA as carrier molecule across a SLM. Various parameters that affect the transport rate such as feed acid concentration, concentration of DTDGA in membrane, membrane pore size, membrane thickness etc have been investigated in detail. Stability of the membrane and selectivity over various fission products have also been reported in the communication.

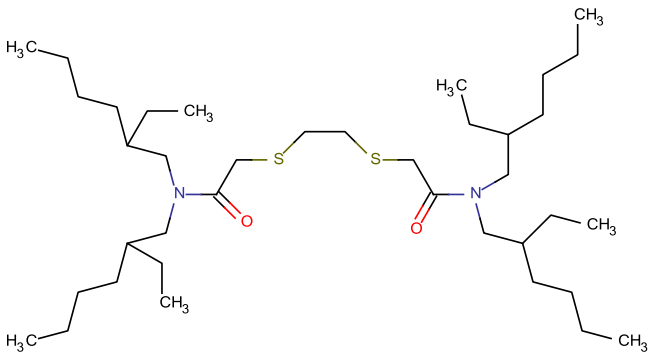

Fig. 1. Chemical structure of DTDGA.

DTDGA is a neutral extractant and so the extraction of Pd(II) takes place via anion assisted complexation. In nitric acid medium the complexation takes place via nitrate ion. The equation describing the extraction of Pd(II) from nitric acid medium by DTDGA is shown below:

$$Pd^{2+} + 2(NO_3^-) + n \cdot DTDGA(o) \leftrightarrow Pd(NO_3)_2 \cdot n(DTDGA)\ (o) \quad (1)$$

where the species with the subscript '(o)' indicate those in the organic phase and those without any subscript indicate species in the aqueous phase. For DTDGA the value of '*n*' was determined earlier in our earlier communication by both chemical (mole ratio method) as well as physical (ESI-MS) approaches [24] and the value was found to be 1 whereas for T(EH)TDGA the value of '*n*' was reported to be 2 [23]. So the nature of the extracted species was found to be different in DTDGA and T(EH)TDGA. Our earlier communication also mentioned superior extractability of DTDGA compared to T(EH)TDGA. The change of D_{Pd} (Distribution ratio of Pd) with change in feed nitric acid concentration for DTDGA was also reported by us earlier [25]. With this background of solvent extraction data we carried out the membrane transport studies of Pd using DTDGA as carrier. We have also tried to compare the advantages and disadvantages of DTDGA over T(EH)TDGA in SLM mode.

2. Experimental

2.1. Materials

DTDGA was synthesized by the reaction of potassium salt of ethane-1,2-dithiol with *N,N*-bis-(2-ethylhexyl)-2-chloroacetamide according to the procedure described earlier [24] at a yield of 95% and purity of 99.1%.

Stock solution of palladium was prepared by dissolving appropriate amount of $Pd(NO_3)_2 \cdot xH_2O$ in 4.0 M HNO_3 and the concentration of the stock solution was 1.08 g/L (1×10^{-2} M). Normally 10^{-3} M solution of Pd(II) at different nitric acid concentrations was used as feed solution by taking required aliquots from the stock solution during the membrane transport experiments. Diluted HLW solution generated during operation of PUREX process operation (Diluted in 4.0 M HNO_3) was used to study the transport properties of different fission products. The composition of the HLW solution used for the study had the following composition: U—7.54 g/L, Pu—3.12 mg/L, ^{137}Cs—8.94Ci/L, ^{106}Ru—7.01Ci/L, ^{144}Ce—28.17Ci/L, ^{90}Sr—3.26Ci/L, ^{95}Zr—0.3Ci/L. To carry out the experiment inside a Fume-hood, the activity of the solution was required to be brought down to a permissible level and for which the HLW was diluted by a factor of 10^3. Due to very low level of activity of Eu in the diluted solution, tracer solution of $^{152+154}$Eu was spiked in the solution. $^{85+89}$Sr (a gamma emitter) was spiked in the solution due to pure beta activity of the ^{90}Sr present in the HLW. The acidity was finally adjusted to 4.0 M HNO_3.

During the course of the study we used flat-sheet type PTFE hydrophobic microporous polymeric membranes, procured from Sartorius AG, Germany as membrane support. The pore size of the membranes used in all the experiments was 0.2 μm if not mentioned otherwise. The effective area of the membrane support was determined to be 4.52 cm^2 which was computed from the geometrical area and the membrane porosity (which was determined to be 51% for 0.2 μm pore size).

2.2. Methods

2.2.1. Transport studies

The details of the transport study have been earlier reported by us in our earlier communication [30]. The SLM studies were carried