

LLE and SLM studies for Pd(II) separation using a thiodiglycolamide-based ligand

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Abstract. The present paper deals with the liquid-liquid extraction and flat sheet supported liquid membrane studies of Pd(II) separation from nitric acid medium using a novel synthesized ligand, namely, N,N,N',N'-tetraethyl-2,2-thiodiethanthiodiglycolamide (TETEDGA). The effect of various diluents and stripping reagents on the extraction of Pd(II) was studied. The liquid-liquid extraction studies showed complete extraction of Pd(II) in ~ 5 min. The influence of nitric acid and TETEDGA concentration on the distribution of Pd(II) has been investigated. The increase in nitric acid concentration resulted in increase in extraction of Pd(II). Stoichiometry of the extracted species was found to be Pd(NO₃)₂·TETEDGA by slope analysis method. Extraction studies with SSCD solution showed negligible uptake of Pt, Cr, Ni, and Fe, thus showing very high selectivity and extractability of TETEDGA for Pd(II). The flat sheet supported liquid membrane studies showed quantitative transport of Pd(II), ~99%, from the feed (3 M HNO₃) to the strippant (0.02 M thiourea diluted in 0.4 M HNO₃) using 0.01 M TETEDGA as a carrier diluted in n-dodecane. Extraction time was ~160 min. Parameters such as feed acidity, TETEDGA concentration in membrane phase, membrane porosity etc. were optimized to achieve maximum transport rate. Permeability coefficient value of 2.66×10⁻³ cm/s was observed using TETEDGA (0.01 M) as carrier, at 3 M, HNO₃ feed acidity across 0.2 μm PTFE as membrane. The membrane was found to be stable over five runs of the operation.

Keywords: Pd(II), TETEDGA, liquid-liquid extraction, supported liquid membrane

1. Introduction

Palladium (Pd) and its compounds have been extensively used for various applications in industries like electronics, pharmaceuticals, chemical, petroleum, automotive and jewellery because of its specific physical and chemical properties like resistance to corrosion and oxidation, electrical conductivity, high melting point and extraordinary catalytic properties (Acres 1987, 1984).

Availability of Pd in the earth's crust has been found to be limited, also the continuously increasing industrial demand has attracted to exploring new options in its separation and recovery from secondary resources (Ruhela *et al.* 2010). Spent catalysts from automotive, petroleum industries and high-level waste (HLW) solution generated from reprocessing of spent nuclear fuel form major secondary resources of Pd (Ruhela *et al.* 2010, Barakat and Mahmoud 2006, Barakat 2009, Kim *et al.* 2006) that can be considered as generating wealth from waste, which in turn adds to environmental protection and resources saving.

Many extraction systems have been considered, for their possible application to Pd(II) separation and concentration. An advanced liquid-liquid extraction technique using supported liquid membrane (SLM) provides us a simple but effective separation method for metal ions. Less solvent requirement, high extraction efficiency, and moiety

selectivity, less power consumption, simultaneous extraction and stripping, absence of third phase etc., are some of its advantages over the other liquid-liquid extraction procedures.

The preliminary liquid-liquid extraction initially provides us with the first hand information for SLM studies. Successful working of a liquid membrane system predominantly lies in the choice of an extraction procedure (Bartsch and Way 1996, Boyadzhev 1990, Boyadzhev and Lazarova 1995, Kovvali and Sirkar 2003, Sirkar 2006). The technique has gradually gained considerable importance worldwide and is evident from the increasing number of scientific investigations in related topics (Sharma *et al.* 2016, Bhatluri *et al.* 2015, Nosrati *et al.* 2013, Vernekar *et al.* 2014, Jagdale *et al.* 2013, Vernekar *et al.* 2013) appropriate carrier molecule (ligand), for a particular metal to be extracted. Like in case of Pd, a soft metal ion will have affinity towards soft donor ligands containing N/S as donor atoms (Pearson 1968). Accordingly, numerous ligands have been synthesized and evaluated for their extraction efficiency towards Pd(II). A few of these are tertiary and quaternary amines such as tri-n-octylamine, tri-n-octylmethyl ammonium chloride (TOMAC), tri-n-octylmethyl ammonium nitrate (TOMAN) (Mezhov 2002a, b), α -benzoinoxime (ABO) (Dakshinamoorthy *et al.* 2008) and sulphide complexes such as, dihexyl sulphides (DHS) (Al-Bazi and Freiser 1987, Guyon *et al.* 1994), dioctyl sulphides (DOS) (Shukla 1993), dihexyl disulphide (DHDS) (Al-Bazi and Freiser 1987), dioctyl sulphoxides (DOSO) (Rizvi *et al.* 1996), bis-(2-ethylhexyl)

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membranes procured (Sterlitech) were used. Porosity of the membrane, with pore size 0.2 μm , was experimentally determined to be 65%, with an effective area of 8.03 cm^2 .

2.3 Simulated spent catalyst dissolver (SSCD) solution

SSCD solution was prepared by dissolving metal salt in concentrated nitric acid and diluting the stock solution to appropriate concentration of metal ions and acid. The concentrations of metal ions present in SSCD solution are given in Table 1.

2.4 Instruments and analysis

Quantitative determination of Pd(II) was carried out using inductive coupled plasma optical emission spectrometry (ICP-OES) (iCAP 6000 Series Thermo Scientific).

3. Method

3.1 Liquid-liquid extraction studies

Liquid-liquid extraction studies were carried out using Pd(II) solution (aq.) and TETEDGA (org.) as the ligand. Equal volumes (5 ml each) of aqueous and organic phases were taken in a vial, followed by vial shaking for ~ 5 min. similar experimental sets were carried out varying the aqueous and organic phases. Pd(II) concentration of aqueous phase before and after extraction was determined by ICP-OES. The concentration of the extracted Pd(II) in the organic phase was determined by mass balance. For the extraction studies of palladium and other SSCD solution elements, equal volume of TETEDGA/n-dodecane was equilibrated with aqueous feed solution and after phase separation, the aqueous phase was analyzed for metal ion concentration. The concentration of metal in the organic phase was calculated by mass balance. All the experiments were conducted in three sets.

From these data, the distribution coefficient, D_M , was calculated as the ratio

$$D_M = \frac{[M]_{\text{org}}}{[M]_{\text{aq}}} \quad (1)$$

where, $[M]_{\text{org}}$ and $[M]_{\text{aq}}$ are the metal ion concentration in the organic and aqueous phase, respectively. Error in D_M values was within $\pm 5.0\%$. However, for elements with very small distribution ratios in the range of 10^{-2} – 10^{-3} , the error was within $\pm 10.0\%$.

The percentage extraction of metal ion was determined by Eq. (2).

$$\%E = \left(\frac{C_0 - C_t}{C_0} \right) 100 \quad (2)$$

Where C_0 is the initial concentration of the metal ions in the feed solution and C_t is the metal ion concentration in the feed solution after time interval, t .

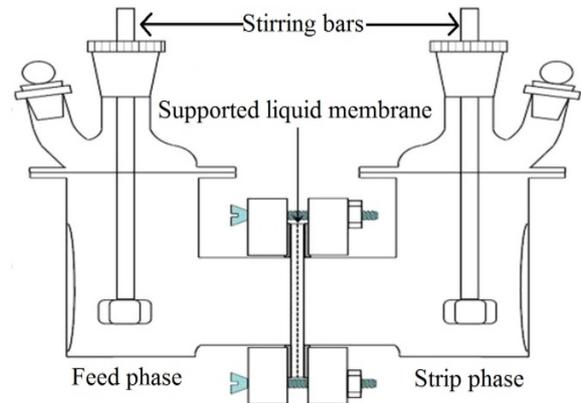


Fig. 2 Schematic diagram for flat sheet supported liquid membrane (FSSLM)

3.2 Membrane transport studies

The PTFE membrane was impregnated with the carrier solution for about 24 h thereafter removed from the solution and wiped dry with a tissue paper carefully to remove the excess carrier.

The flat sheet supported liquid membrane (FSSLM) transport experiments were carried out in a Pyrex glass cell consisting of two equal-volume compartments (Fig. 2), having volume 85 ml each with the feed and strip solutions being stirred at 300 rpm to prevent concentration polarization in the membrane interfaces and the bulk of the solutions (Izatt *et al.* 1989). The concentration of Pd(II) in feed as well as in strip solution was monitored by taking 0.1 ml samples from both sides, at regular intervals of time.

The permeability coefficient was determined by monitoring Pd(II) concentration by ICP-OES in the feed and strip phases as a function of time. The transport studies were carried out at ambient temperatures (25–30°C).

3.3 Transport equations

The transport of the metal ion across the FSSLM is considered to comprise of three major steps: (i) extraction of the metal ion from the feed phase into the organic membrane phase, (ii) diffusion of the metal-carrier complex inside the liquid membrane phase, and (iii) extraction of the metal ion from the membrane phase into the receiver phase. For effective mass transfer from the feed phase into the receiver compartment and the initial flux (J) can be calculated from the following Eq. (3), (Sriram *et al.* 2007, Danesi 1984, Danesi *et al.* 1985, Shailesh *et al.* 2006). This is initial flux at $C_{f,0}$.

$$J = P_f C_f \quad (3)$$

P_f is permeability coefficient; C_f is the concentration of the metal ion at the feed side.

In other way, the flux (J) can be calculated by the following Eq. (4).

$$J = - \left(\frac{1}{Q} \right) d \left(\frac{V_f C_f}{dt} \right) \quad (4)$$

Where V_f is the feed volume and Q is the effective surface area of the membrane used in the experiment. After combining Eq. (3) and (4), and integrating one gets,

$$\ln \frac{(V_{f,0} C_{f,0})}{(V_{f,t} C_{f,t})} = \frac{QP_{f,t}}{V_f} \quad (5)$$

where $V_{f,0}$, $C_{f,0}$, $V_{f,t}$ and $C_{f,t}$ represent the volume and concentration of feed at time 0 and after time t , respectively. If volume of the feed does not change significantly during the experiment, then Eq. (5) can be rearranged:

$$\ln \left(\frac{C_{f,t}}{C_{f,0}} \right) = - \frac{QP_{f,t}}{V_f} \quad (6)$$

Where Q is the product of geometrical surface area (A) and the porosity (ϵ). By plotting $\ln(C_{f,t})/(C_{f,0})$ against t , a linear curve is obtained. The slope of this curve can be used to calculate permeability coefficient (P) of the SLM. The percentage transport of Pd(II) (%T) across FSSLM can be calculated as:

$$\%T = \left(\frac{C_{t,r}}{C_{f,0}} \right) 100 \quad (7)$$

where $C_{f,0}$ and $C_{t,r}$ are the concentration of Pd(II) in feed and receiver compartment at time 0 and t , respectively. The data treatment that follows generally includes plots of %T vs. time. All the experiments were repeated and the accepted data were within the error limits of $\pm 5\%$.

4. Results and discussion

4.1 Liquid-liquid extraction studies

4.1.1 Effect of equilibrium time

In Fig. 3, the curve shows that shaking period of 5 min is enough for complete transfer of Pd(II) into the organic phase. At the end of the fifth minute, more than ($\sim 99\%$) of the metal ion has been already transferred to the organic phase. Prolonged shaking, however, had no further effect on the extraction.

4.1.2 Effect of nitric acid concentration

Influence of nitric acid concentration on the extraction of Pd(II) was studied by determining $D_{Pd(II)}$ at various concentration of nitric acid. Fig. 4 shows the variation of $D_{Pd(II)}$ with 0.001 M TETEDGA/n-dodecane as a function of initial nitric acid concentration. It can be seen that $D_{Pd(II)}$ increases with increase in nitric acid concentration till 3 M HNO_3 . No significant changes were observed in $D_{Pd(II)}$ on further increasing the nitric acid concentration.

4.1.3 Effect of organic diluents

The suitability of various diluents was investigated for the proposed system. Fig. 5 shows that, extraction was quantitative with n-dodecane but decreased with kerosene, hexane, toluene and chloroform. It was observed that the extractability of Pd(II) decreases with the increase in the polarity of the diluent, maximum percent extraction being

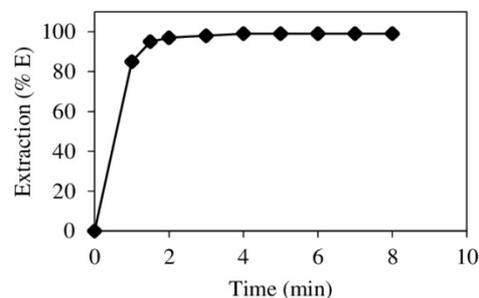


Fig. 3 Extraction behaviour of Pd(II) from aqueous solution (10^{-3} M Pd in 3M HNO_3) into organic phase (0.001M TETEDGA/n-dodecane) as a function of shaking time

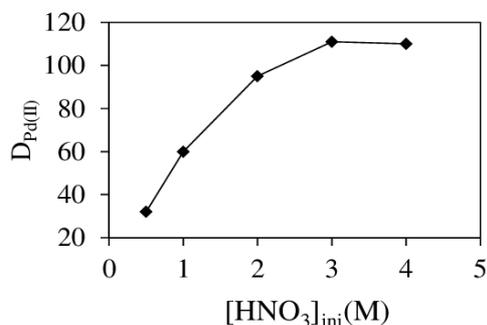


Fig. 4 Dependency of $D_{Pd(II)}$ on HNO_3 concentration. Aqueous phase: 10^{-3} M Pd(II) in 0.5 M HNO_3 to 4M HNO_3 ; Organic phase: 0.001 M TETEDGA/n-dodecane

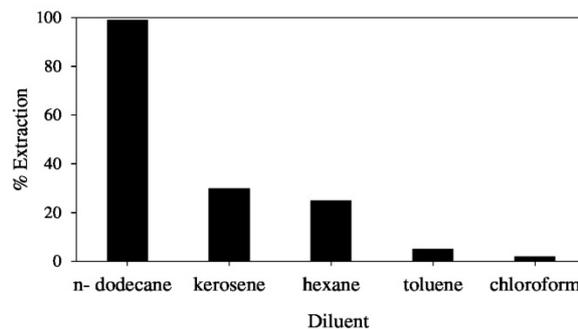


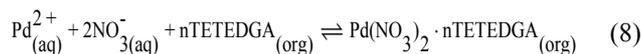
Fig. 5 Extraction behaviour of 10^{-3} Pd(II) into 0.001M TETEDGA as a function of different diluents

obtained in normal paraffinic diluent, namely, n-dodecane. Therefore, n-dodecane was the chosen diluent for analysis.

4.1.4 Effect of TETEDGA concentration on Palladium extraction

To provide an insight to the composition of Pd(II) species formed in the organic phase due to extraction, the variation of D_{Pd} as a function of ligand concentration was investigated. These results have been shown in Fig. 6.

It was observed that D_{Pd} values increase with increase in the concentration of TETEDGA. Extraction of Pd(II) by TETEDGA from nitrate solution is represented in Eq. (8).



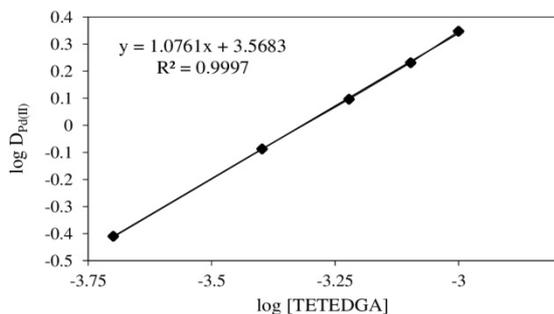


Fig. 6 Dependency of the distribution ratio of Pd(II) on TETEDGA concentration. Aqueous phase: 10^{-3} M Pd(II) in 0.5 M HNO_3 . Organic phase: 0.0002 M to 0.001 M TETEDGA/n-dodecane

where the subscripts (aq) and (org) represent the species present in the aqueous and organic phase respectively. In addition, Eq. (8) depicts that the concentration of nitric acid / nitrate ion has major role to play in the extraction of Pd(II). A plot of $\log D_{\text{Pd(II)}}$ vs. \log TETEDGA is shown in Fig. 6.

The plot is a straight line with a slope of 1.076, which indicates that the extracted species in the organic phase is $\text{Pd}(\text{NO}_3)_2 \cdot \text{TETEDGA}$.

4.1.5 Back extraction studies

The back extraction behaviour of Pd(II) using DI water, sodium thiocynide, nitric acid and thiourea solution is shown in Table 2. It is observed that dilute nitric acid alone is not suitable for recovering Pd(II) from the TETEDGA phase. Quantitative recovered of Pd in the presence of thiourea in nitric acid might be related with the fact that thiourea is soft ligand. Therefore, thiourea is effective in stripping Pd(II) from the loaded TETEDGA through the formation of Pd.thiourea complex. The organic phase obtained on equilibrating 0.001M TETEDGA/n-dodecane with aqueous phase containing 10^{-3} M Pd(II) dissolved in 3 M HNO_3 solution, were contacted with stripping solution.

4.1.6 Extraction behaviour of SSCD solution

To evaluate the feasibility of TETEDGA/n-dodecane diluents system for Pd(II) separation from spent catalyst, the extraction behaviour of elements present in SSCD solution was studied. Fig. 7 shows the distribution ratio of these elements obtained by equilibrating 0.001 M TETEDGA/n-dodecane with SSCD solution at 3.0M nitric acid concentration. The result showed very high extractability of Pd(II) with almost negligible extraction of other elements. Therefore, 0.001 M TETEDGA/n-dodecane can be used to selectively separated Pd(II) from SSCD solution.

5. Supported liquid membrane studies

5.1 Effect of feed nitric acid concentration

In Fig. 4, the liquid-liquid extraction system involving TETEDGA as ligand, $D_{\text{Pd(II)}}$ depends on the feed acid concentration. The effect of nitric acid concentration on the

Table 2 Effect of stripping reagents for 10^{-3} Pd(II) recovery from loaded 0.001 M TETEDGA organic phase

Stripping reagents	Recovery of Pd(II)
0.1 M HNO_3	0.0
5 M HNO_3	5.0
0.02 M thiourea+0.4 M HNO_3	>98
Sodium thiocynide	>10
DI water	0.0

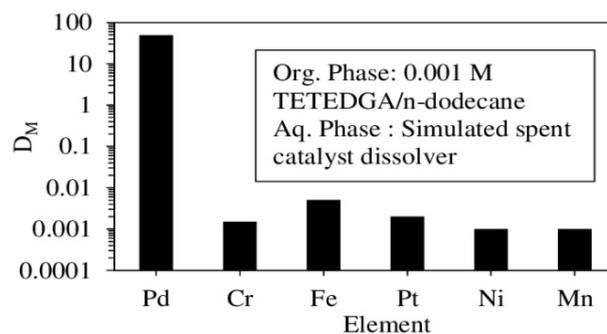


Fig. 7 Distribution behaviour of elements present in SSCD solution

Table 3 Permeability coefficient ($P_{\text{Pd(II)}}$, cm/s) and initial flux ($J_{\text{Pd(II)}}$, mol/cm² s) data for Pd(II)- TETEDGA system at different feed nitric concentration

$[\text{HNO}_3]$, M ^a	$P_{\text{Pd(II)}} \times 10^3$	$J_{\text{Pd(II)}} \times 10^6$
1	1.39	1.39
2	2.45	2.45
3	2.66	2.66
4	2.59	2.59

^a 0.01 M TETEDGA

transport of Pd(II) in the feed was investigated by dissolving 0.01 M TETEDGA carrier, in n-dodecane diluent across a 0.2 μm PTFE membrane. 0.02 M thiourea dissolved in 0.4 M HNO_3 was the strippant. From Fig. 8, it is evident that increase in nitric acid concentration resulted in increase in Pd(II) transport rate up to 3M HNO_3 , while further increase in nitric acid concentrations does not play much role in the transport profile. Near quantitative transport of Pd(II) (~99%) was observed in approximately 160 min from 3 M HNO_3 which remains constant for 4 M HNO_3 . The reason behind initial increase in transport rate from 1 M HNO_3 to 3 M HNO_3 is due to increase in nitrate ion assisted complexation of Pd with TETEDGA at the feed-membrane interface as explained in Eq. (8). When increase feed acid concentration, there was increasing nitrate ion transport of acid at 4 M HNO_3 due to formation TETEDGA· HNO_3 complex. This factor is responsible for similar transport rate observed at acidities higher than 3 M HNO_3 . After 160 min of operation, acidity of 3 M HNO_3 decreases to 2.8 M whereas the acidity of 4 M HNO_3 became 3.7 M. Higher nitrate ion transport of acid causes decrease in free carrier molecule concentration in the membrane phase as well as decreases the stripping efficiency of the receiver phase by increasing its acidity and

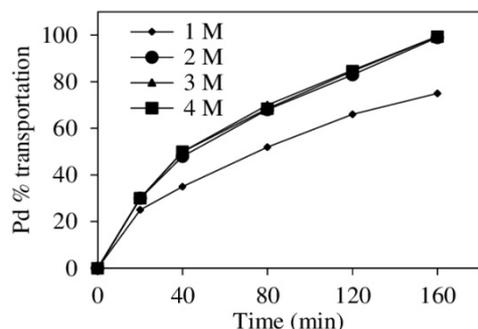


Fig. 8 Effect of HNO_3 concentration in feed solution on the transport of Pd(II); 1M-4M HNO_3 in feed solution, carrier: 0.01 M TETEDGA in n-dodecane, strippant: 0.02 M thiourea in 0.4 M HNO_3 , membrane: 0.2 μm PTFE

Table 4 Permeability coefficient ($P_{\text{Pd(II)}}$, cm/s) and percent transport (%T) data for Pd(II)-TETEDGA system at different TETEDGA concentration

[TETEDGA], M ^b	$P_{\text{Pd(II)}} \times 10^3$, cm/s	% T
0.0025	0.67	48
0.005	0.81	60
0.01	2.66	99.5
0.025	2.57	98.5

^b 3 M HNO_3

this compensates for the increasing transport rate with increasing nitrate ion concentration (Panja *et al.* 2014).

Hence, the transport rate remains the same at acidities above 3 M HNO_3 . Table 3, shows the permeability coefficient and initial flux values of Pd(II) at different feed nitric acid concentration.

5.2 Effect of carrier concentration

Pd(II) transport was studied as a function of TETEDGA concentration employing 10^{-3} M Pd(II) solution at 3M HNO_3 as feed and thiourea as strip phase (strippant). It is generally seen that transport of metal ion through FSSLM depends on the concentration of carrier molecule in the membrane phase (Huang and Juang 1987, Ansari *et al.* 2006, Panja *et al.* 2010). Therefore, to understand the effect of TETEDGA concentration on the transport of Pd(II), studies were carried out with varying concentrations of TETEDGA (0.0025 to 0.025 M in n-dodecane). Table 4 shows the variation of permeability coefficient and percent transport values of Pd (II) at different carrier concentrations. The Pd(II) transport rate initially increases with TETEDGA concentration from 0.0025 to 0.01M followed by a decrease at 0.025M. Similar trend of increase and then decrease for initial flux (J) of Pd(II) is also observed for various concentration of TETEDGA as shown in Fig. 9

Initial increase in transport rate could be increase in D value with increasing TETEDGA concentration shown in Fig 6. This increased D value results in higher concentration of Pd(II)-TETEDGA complex at the feed-membrane interface, which raises the transport rate of Pd(II). However, with increase in concentration of TETEDGA, the viscosity

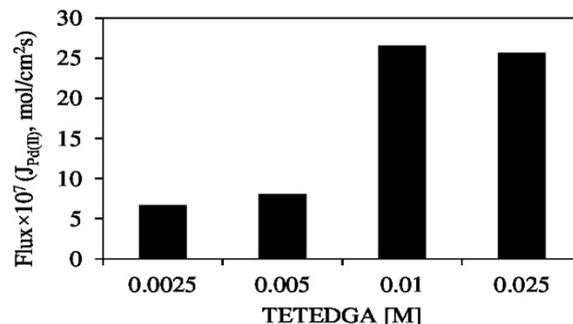


Fig. 9 Effect of TETEDGA concentration on the initial flux value of Pd(II); $[\text{HNO}_3] = 3\text{M}$, strippant: 0.02M thiourea in 0.4 M HNO_3 , membrane: 0.2 μm PTFE

Table 5 Permeability coefficient values of Pd(II) with various 'thiodiglycolamide' ligands

Ligand conc., M	Feed conc. (HNO_3), M	Permeability coefficient, cm/s	Reference
T(2EH)TDGA (0.05)	3.0	2.25×10^{-3}	[30]
DTDGA (0.025)	3.0	2.35×10^{-3}	[31]
TETEDGA (0.01)	3.0	2.66×10^{-3}	Present work

of the membrane phase also increases. An exactly similar observation has been reported in recent literature (Ruhela *et al.* 2012, Panja *et al.* 2014). Since, diffusion coefficient of the metal-carrier complex D, across the membrane phase is inversely proportional to the viscosity according to Stokes-Einstein equation.

$$D = \frac{kT}{6\pi\eta r} \quad (9)$$

Where D is the diffusion coefficient, k is the Boltzmann constant, T is the absolute temperature (K), r is the ionic radius (\AA^0) of solute and η is the viscosity of the medium. The increase in viscosity should reduce the initial flux. Therefore, with increasing TETEDGA concentration from 0.0025 M to 0.025M the membrane transport is slowed down. So 0.01 M TETEDGA was chosen as the optimum concentration in the membrane phase during further studies.

Table 5, shows the comparison of permeability coefficient values of Pd(II) with various ligands. A considerably high permeability coefficient value for Pd(II) was obtained using TETEDGA when compared to other known thiodiglycolamide ligands, thus making it one of the highly efficient ligands.

5.3 Effect of membrane pore size

The transport rate depends on the amount of carrier held in the membrane pores, pore structure / size, the membrane thickness, porosity, and tortuosity (pathway of fluid diffusion through porous media), etc. (Huang and Juang 1987). Membrane pore size plays an important role in the permeation rate of metal cations across FSSLM. With an increase in membrane pore size, porosity of the membrane increases whereas tortuosity of the membrane decreases. In order to understand the effect of membrane pore size on Pd(II) transport, two membranes with different pore sizes

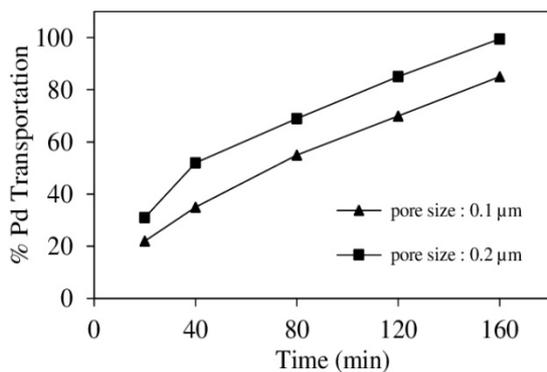


Fig. 10 Effect of membrane pore size on the transport of Pd(II); $[\text{HNO}_3] = 3 \text{ M}$ in feed solution, carrier: 0.01 M

and porosities (0.1 μm , 54% and 0.2 μm , 65%) impregnated with 0.01 M TETEDGA (in n-dodecane) were used for permeation studies. Fig. 10 shows that Pd(II) transport increased with membrane pore size suggesting that larger pore size provided easier passage for the metal cations. It has to be however noted that, too large pore size ($\geq 5 \mu\text{m}$) would lead to poor carrier holding capacity of the membrane; carrier thus leaches out of the membrane (Ruhela *et al.* 2012, Panja *et al.* 2014). From Stokes-Einstein law, the diffusion coefficient of the metal-carrier complex D, across the membrane is inversely related to the radius of the diffusing complex as per Eq. (9). Therefore, with larger pore size, the resistance faced by the metal-carrier complex will be lower; hence, the transport rate will be faster. With a change in membrane pore size, tortuosity and membrane porosity also changes. The effect of porosity and tortuosity can be expressed by the following Eq. (10)

$$D = D \left[\frac{\theta}{\tau} \right] \quad (10)$$

Where, θ and τ are the porosity and tortuosity of the membrane, respectively. Therefore, with increasing membrane pore size, porosity of the membrane increases where as tortuosity of the membrane decreases (Huang and Juang 1987)

5.4 Stability of membrane

Large scale industrial application of SLM is restricted due to its instability problem, which may primarily be caused by the cumulative effect of parameters like chemical degradation, pore blocking of membrane by precipitation of carrier, solubility of carrier or solvent in aqueous phase, leaching out of the membrane carrier by an osmotic or hydrostatic pressure gradient etc. (Ruhela *et al.* 2012). Stability of these membranes can also be adversely affected because of chemical degradation of the membrane material. For evaluating the stability of the SLM containing TETEDGA in n-dodecane, permeability experiments were carried out for five consecutive cycle in which fresh solutions of feed and receiver phase was added for each experiment. Fig. 11 shows the permeability coefficient profiles of Pd(II) over five consecutive cycles. It can be seen that there was not much decrease in permeability

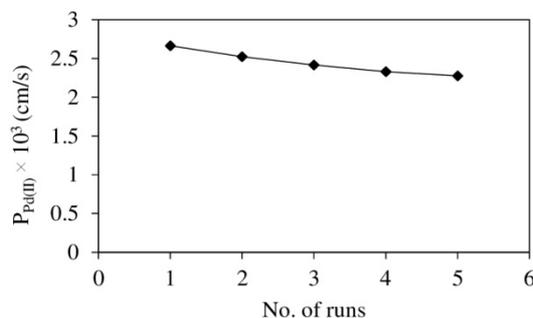


Fig. 11 Stability of SLM, number of runs versus permeability coefficient ; $[\text{HNO}_3] = 3 \text{ M}$ in feed solution, carrier: 0.01 M TETEDGA in n-dodecane, strippant: 0.02 M thiourea in 0.4 M HNO_3 , membrane: 0.2 μm PTFE

coefficient value of Pd(II) even after the 5th run. Recovery of Pd(II) for each run was more than 95%. These observations show that this SLM configuration is quite stable and can be scaled up at industrial level.

6. Conclusions

A novel ligand namely N,N,N',N'-tetraethyl 2,2-thiodiethanthiodiglycolamide (TETEDGA) has been synthesized with $\geq 99\%$ purity $\geq 95\%$ yield. Liquid-liquid extraction studies observed that extraction equilibrium was achieved in ~ 5 min, Pd(II) was quantitatively extracted in 3M HNO_3 and complete back extraction of Pd(II) was obtained in single contact using 0.02M thiourea in 0.4M nitric acid. The stoichiometry of the extracted species in to the organic phase was found to be unity. Extraction study with elements present in SSCD solution shows negligible uptake of Fe, Cr, Pt, and Ni.

The flat sheet supported liquid membrane studies showed quantitative transport ($\sim 99\%$) of Pd(II) from the feed (3 M HNO_3) to the strippant (0.02 M thiourea diluted in 0.4 M HNO_3) using 0.01M TETEDGA as a carrier diluted in n-dodecane. Extraction time was ~ 160 min. High permeability coefficient value of $2.66 \times 10^{-3} \text{ cm/s}$ and very less ligand inventory for TETEDGA in n-dodecane was observed, similar to that reported for 0.05 M T(2EH)TDGA and 0.025M DTDGA in n-dodecane. Stability of the membrane was found to be satisfactory for 5 runs of operation indicating efficient liquid membrane system.

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