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## ABSTRACT

In continuation of our comprehensive programme on metal separations by liquid membranes, carrier-facilitated co-transport of Pd(II) from dilute acidic nitrate solutions was examined across a polymer-immobilized liquid membrane (PILM) deploying S<sub>6</sub>-pentano-36 (S<sub>6</sub>-P-36), bis-(2-ethylhexyl) sulfoxide (BESO) and bis (2,4,4 trimethyl pentyl) monothio phosphinic acid (Cyanex 302) as the novel receptors. Under the optimum conditions, micro amounts of palladium could be effectively transported using S<sub>6</sub>-P-36, BESO or Cyanex 302 as the carrier from a feed solution across an organic membrane into the product side containing an aqueous strippant. The study carried out to distinguish the driving force between H<sup>+</sup> and NO<sub>3</sub><sup>-</sup> ion for the cation transport across PILM, indicated that NO<sub>3</sub><sup>-</sup> ion not the H<sup>+</sup> ion seems to be the driving force for Pd(II) transport under the present conditions for both BESO-PILM and S<sub>6</sub>-P-36-PILM systems. On the other hand, H<sup>+</sup> ions seem to be the driving force for Cyanex 302-PILM system. Among the various aliphatic and aromatic diluents tested for S<sub>6</sub>-P-36 and BESO, the chlorinated hydrocarbons such as, chloroform, 1,2-dichloroethane and o-dichlorobenzene afforded much poor permeability compared to less polar diluents like toluene, benzene and dodecane. Similarly, toluene and dodecane are found to be suitable as diluents for Cyanex-302-PILM system. Its concentration in the source phase decreased as  $[Pd]_{s,t} = [Pd]_{s,0} \exp(-K_{obs} t)$ . The apparent rate constant (K<sub>obs</sub>) increased with increasing carrier concentration and became nearly constant above 0.02M both for S<sub>6</sub>-pentano-36 and BESO-PILM and 0.2M for Cyanex-302-PILM. With increase in nitric acid concentration from 0.1 to 4M HNO<sub>3</sub>, K<sub>obs</sub> decreased with its higher concentrations. A polytetrafluoroethylene thin film support coded as TE-35 and toluene as the membrane solvent were invariably used for all carrier systems. Among the several reagents tested, ammonium thiocyanate served most efficiently as the strippant for BESO and S<sub>6</sub>-P-36-PILM whereas thiourea proved to be efficient for Cyanex-302-PILM systems. More than 95% of palladium could be readily transported from diverse matrices through 0.05 S<sub>6</sub>-Pentano-36 or 0.2M BESO or 0.25M Cyanex-302 into a suitable dilute aqueous strippant in about 6-7 h. Recovery of palladium from acidic process effluents generated in PUREX reprocessing of spent fuels was successfully achieved.

## INTRODUCTION

The recovery of metals of value from dilute and impure solutions is a frequent requirement in the hydrometallurgical processing as well as for effluent treatment. Solvent extraction is now a well-established process in metal refining (1). Although, it has been widely used on plant scale, alternative methods have been explored to overcome several problems due to restricted selectivity, poor kinetics and many operational limitations to accomplish an efficient separation. Solvent extraction of palladium group metals (PGMs) has been extensively studied by adopting varieties of extractants, including chelating reagents having a high selectivity for some individual elements of PGMs particularly palladium (2). However, applications of these extraction systems to membrane transport of PGMs have been limited to a few cases due to their slow extraction kinetics and difficulties in stripping (3,4). In addition, the tendency to precipitate as complex species of PGMs in some systems may cause practical problems in the quantitative transport of metals (3,4). Liquid membrane transport has by now proved to be a potential alternative to conventional liquid-liquid extraction because it simultaneously combines both extraction and stripping in one step and considerably reduces solvent usage. Selective transport of a permeant through a membrane system is

primarily based on difference in permeability of the species to be separated. Permeability difference is determined by the driving force for the metal species entering and leaving the membrane, the membrane thickness, the mobility of the species and reactions or interactions with other species inside the membrane. In addition, distinct advantages of liquid membrane pertraction are the low energy requirement, low capital and operating costs, the possibility of achieving high separation factors and simple modular design (5-6). Furthermore, the technique allows the use of high cost or tailor-made reagents, because of small quantities used in the membrane supports.

Considering the strategic importance of palladium, attempts have been initiated to recover micro quantities of palladium (II) from acidic high level wastes generated from nuclear fuel reprocessing operations containing palladium and other useful fission products (7-10). In addition, recovery of noble metals such as Ru, Rh and Pd also offers an alternate potential source of supply to meet a part of the ever increasing platinum metals need.

Recently, two sulfur containing organophosphorus extractants Cyanex 301 and Cyanex 302 have been introduced by American Cyanamid Co.(11). Cyanex 302 is monothio analog of the commercial reagent, Cyanex 272 [bis(2,4,4 trimethylpentyl phosphinic acid (12). Between Cyanex 302

and Cyanex 301 tested herein, Cyanex 301 afforded very poor stripping of palladium inspite of its favorable extractability. Besides, the aqueous solubilities of Cyanex 301 and Cyanex 302 are reported to be  $7 \text{ mg L}^{-1}$  and  $3 \text{ mg L}^{-1}$  respectively (13). Guided by these facts, Cyanex 302 was chosen as the carrier owing to its low aqueous solubility, good strippability and fast kinetics.

The study carried out by Antico et.al. (14) examines the role of some new sulfur containing reagents such as  $\text{N}^2$  - substituted,  $\text{N}^2$ - phenylbenzamidines and  $\text{N}^2$  disubstituted N - benzoyl thiourea derivatives as carrier for the separation of Pd(II) by solid supported liquid membranes in the presence of thiocyanate in the feed solution. The major drawback of the study is that some of the thiourea derivatives (carriers) were decomposed in diluent itself. Further, the addition of sodium thiocyanate in source phase made the liquid membrane system more complicated.

Extraction behaviour of palladium (II) was examined recently by us using some novel S-containing extractants such as  $\text{S}_6$ -pentano-36 ( $\text{S}_6$ -P-36), bis(2-ethylhexyl) sulfoxide (BESO) and bis (2,4,4 trimethyl pentyl) monothio phosphinic acid (Cyanex 302) (15-17). Encouraged by our excellent liquid- liquid extraction results with Pd(II) and high separability from diverse ions, it is now planned to test their efficiency as ionophores in its carrier-facilitated transport. The present work examines the



permeation-separation of Pd(II) across a polymer-immobilised liquid membrane (PILM). Effects of membrane material, organic solvent, carrier concentration and aqueous phases compositions on the process efficiency for permeant transport through PILMs were studied systematically. Attempts were also made to test its applicability for the recovery of palladium from acidic process effluents generated during PUREX reprocessing operations.

### EXPERIMENTAL

#### Reagents

All the chemicals were of A.R. or G.R. grade unless specified otherwise.

S<sub>a</sub>-P-36 (I) was kindly gifted by Prof. R.A. Bartsch, Texas Tech Univ., U.S.A. BESO (II), was obtained from Fairfield Chem. Co., U.S.A. and Cyanex 302(III) was procured from American Cyanamid Co., U.S.A (now known as Cytec Industries Inc., Canada). Analytical grade diluents namely benzene, chloroform, o-dichlorobenzene, n-dodecane, 1,2-dichloroethane, solvesso-100, xylene and toluene were obtained and used as such.

BESO was used after treating it with excess of 11 M HNO<sub>3</sub> in order to oxidise any sulfide present as impurity. The mixture so obtained was treated with NaOH and then washed with distilled water till free from alkali. The product obtained was then distilled at reduced pressure (0.4

mm Hg) and the middle fraction distilling at around 140° C was collected and used for the experiments. The BESO product obtained as above was found to be more than 99.6 % pure as determined by a non-aqueous titration in acetic anhydride using standard HClO<sub>4</sub> in dioxane (18). The structures of all these ionophores used in this work are shown in Fig. 1.

### Tracers

Tracers Pu-239, U-233, Ru-106 and Cs-137 were used to study the extraction characteristics of the respective metal cations. Radiopalladium tracer (Pd-103), obtained in divalent (+2) state from the Isotope Division, BARC, was used throughout the present study. Its radio chemical purity was ascertained by gamma ray spectrometry using Low Energy Photon Spectrometry (LEPS) method. Uranium and plutonium were assayed by alpha scintillation counting. Pd-103 and Cs-137 were assayed by a well type NaI(Tl) scintillation detector coupled to a single channel analyser. Ru-106 was assayed by beta scintillation counting.

### Process Effluent

A process effluent containing plutonium (5 mg dm<sup>-3</sup>) and Am(III) (0.052 mg dm<sup>-3</sup>) and various fission products of the following composition received from reprocessing operations was employed. : Ru-106 : 57.2 uCi dm<sup>-3</sup>, Cs-137: 2513.2 uCi dm<sup>-3</sup>, Sb-125: 23.3 uCi dm<sup>-3</sup>, Ce-144 : 46.4 uCi dm<sup>-3</sup>. High purity germanium detector coupled to 4K PC

linked multichannel analyser was used for the detection and estimation of fission product nuclides such as Cs-137, Ce-144, Sb-125 and Ru-106.

#### **Distribution Ratio ( $D_{Pa}$ ) Measurements**

Equal volumes (1 ml) of aqueous Pd-103 tracer in desired nitric acid molarity and the extractant, dissolved in an organic solvent, were pipetted into a 15 -ml glass stoppered equilibration tube and shaken mechanically for nearly 40 min. Extractions were performed at room temperature (23-25°C). Preliminary experiments revealed that 20-30 min. shaking time was adequate to ensure the attainment of equilibrium. After settling for half an hour, and centrifuging if necessary, suitable aliquots from both the phases were withdrawn and radioassayed. Distribution ratio ( $D_{Pa}$ ) defined as  $D_{Pa} = \text{total concentration of Pd in the organic phase per ml} / \text{total concentration of Pd in the aqueous phase per ml}$ , was thus calculated. All the measurements were done at least in duplicate and the agreement in  $D_{Pa}$  values obtained was within  $\pm 2\%$  with good material balance (>95 %).

#### **PILM Preparation and Permeation Measurements**

The liquid membrane consisted of an organic solution of the extractant dissolved in toluene, impregnating microporous hydrophobic polytetrafluoroethylene, coded as TE-35, flat-sheet support, supplied by Schleicher and

Schuell (porosity 78% , pore size 0.2 $\mu$ m, and thickness 160  $\mu$ m ). Permeation experiments were carried in a single-stage two compartment membrane cell described elsewhere (5). To study the variation of Pd(II) concentration with time in the feed or stripping solutions, the same was periodically withdrawn and radioassayed. All experiments were performed at room temperature (25°C). Since the time lag between the decrement of the palladium fraction in the feed solution and the increment in the product solution is negligibly small in this thin membrane, the decreasing rate in the feed side is regarded as the transport rate (19). The apparent rate constant,  $K_{obs}$  ( $s^{-1}$ ) is defined as:

$$\ln \{ [Pd]_{s,t} / [Pd]_{s,0} \} = -K_{obs} \times t \quad \dots(1)$$

where  $[Pd]_{s,t}$ , and  $[Pd]_{s,0}$  denote the concentration of palladium at time  $t$  and the initial concentration, respectively and  $t$ , elapsed time, seconds, was thus computed.

#### Scanning Electron Microscopy (SEM) Study

The membrane specimens were mounted and sputtered for making them suitable for examination by recording on a scanning electron microscope. A "Stereoscan-100" coupled with image analyser "Quantimet-900" was used for studying pore size distribution and viewing of impregnation of polymeric solid support with thiocrown/toluene and the

effect of water-miscible organic solvents on polymer structure. The micro-structure was scanned at 20 KV operating voltage and 6 to 10 mm working distance in the magnification range of 30X to 12KX.

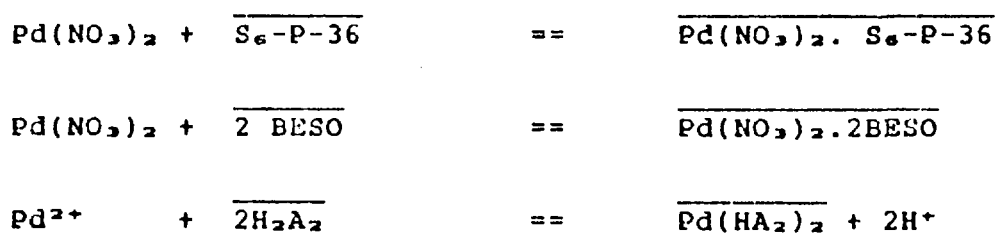
The structural changes after irradiation up to absorbed dose of 3 Mrad (impregnated with 0.05M S<sub>6</sub>-P-36/toluene for 6-8 h prior to irradiation) with membrane TE-35 (polytetrafluoroethylene) were also examined.

## RESULTS AND DISCUSSION

### Liquid-Liquid Extraction

The thiocrown, S<sub>6</sub>-P-36, BESO and Cyanex 302 studied hereby are noted to be highly effective for the solvent extraction of bivalent palladium from complex matrices; extraction better than 95% was generally accomplished in most of the instances. The kinetics of palladium (II) nitrate extraction with Cyanex 302 is relatively fast compared to both S<sub>6</sub>-P-36 and BESO, requiring only few minutes of shaking to reach the observed efficiency. Also high D<sub>PA</sub> values, between aqueous acidic solutions and the thia extractants are as expected from the strong 'soft-soft' interaction of sulfur with Pd<sup>2+</sup>. A lower concentration of S<sub>6</sub>-P-36 (0.005M) or Cyanex 302 (0.005M) was even sufficient for its quantitative recovery. Contrary to this, extraction of contaminants like Pu-239, U-233, Cs-137 and Ru-106

generally encountered in the recovery of Pd from PUREX aqueous wastes was negligibly small (< 1%) due to their 'hard' character. The extracted complex involved in thiocrown/sulfoxide systems was also characterized by elemental analyses and UV-visible spectrometry; its composition appears to be Pd(NO<sub>3</sub>)<sub>2</sub>.T from dilute (pH ~ 2) HNO<sub>3</sub> (12,13) with the thiocrown (T) while the extracted species in the sulfoxide-diluent phase is predominantly of the type, Pd(NO<sub>3</sub>)<sub>2</sub>.2BESO. On the other hand, with Cyanex 302, the species could be established as Pd(HA<sub>2</sub>)<sub>2</sub>. Cyanex 302 exists in dimeric form as H<sub>2</sub>A<sub>2</sub> (12). To sum up, the complex formation of Pd(II) with these, extractants can be represented as follows :



where the species with bar denotes the organic phase.

#### Transport of Palladium Across PILM

The solvent extraction of Pd(II) with S<sub>6</sub>-P-36, BESO, and Cyanex 302 from nitric acid solution was carried out so as to select approximate conditions for selective pertraction of Pd<sup>2+</sup> cation across PILM. The membrane transport can be performed by continuous extraction and stripping of metals on each side of PILM; in particular,

quantitative pertraction of metals may be affected by optimising the parameters like source phase acidity, ionophore concentration and type, nature and concentration of a strippant. Of different aqueous strippants tested, more than 95% of palladium could be easily recovered with  $\text{NH}_4\text{SCN}$  (1M) with carriers like  $\text{S}_6\text{-P-36}$  and BESO ; thiourea (~1M), in case of Cyanex 302.

#### Variation of $K_{\text{ext}}$ values with $\text{HNO}_3$ Concentration

To assess the dependence of the permeation behaviour on the aqueous phase acidity, the permeability of Pd(II) from 4M  $\text{HNO}_3$  down to pH 2 solutions into toluene by BESO,  $\text{S}_6\text{-P-36}$  and Cyanex 302 from aqueous unbuffered nitrate solutions was systematically studied (Table 1). It can be seen that lowering the acidity from 4M  $\text{HNO}_3$  down to pH 2 caused an appreciable increase in pertraction from around 20 to > 95 % by employing 0.2 M BESO, 0.02M  $\text{S}_6\text{-P-36}$  or 0.25 M Cyanex 302 /toluene. Values of  $K_{\text{ext}}$  of Pd(II) with 0.2 M BESO or 0.02 M  $\text{S}_6\text{-P-36}$  in toluene are almost independent of the strippant concentrations in range of 1-2 M. Figs. 2(a) and 2(b) depict plots of  $\log K_{\text{ext}}$  against  $\log D_{\text{org}}$  obtained at varying  $\text{HNO}_3$  molarities by liquid-liquid extraction of Pd(II) with  $\text{S}_6\text{-P-36}$ , BESO (Fig.2(a)) and Cyanex 302 (Fig. 2(b)) respectively. Values of  $K_{\text{ext}}$  increased with increasing distribution ratios till reached a plateau at higher  $D_{\text{org}}$  values with decreasing  $\text{HNO}_3$  concentration. As is evident

from Fig. 3-5, the percentage transport of palladium from the feed to the product side at various feed  $\text{HNO}_3$  concentrations lies in an almost symmetrical curve except in case of 4M  $\text{HNO}_3$  with all carrier ( $S_6$ -P-36, BESO and Cyanex 302 respectively) systems. At 4 M  $\text{HNO}_3$ , this may result from lower distribution ratios of Pd(II) at high nitric acid molarity and simultaneous  $\text{HNO}_3$  transport with BESO system (BESO forms complexes with  $\text{HNO}_3$  of type  $\text{BESO.HNO}_3$ ) which would cause a decline in  $K_{obs}$  values. Further, continuous transport of  $\text{HNO}_3$  through BESO system, increased the resulting nitric acid molarity in receiving phase which in turn decline the stripping fraction of palladium in product side. The palladium fraction in the feed phase decreased according to Eqn. 1. Fig.6 shows the effect of  $\text{HNO}_3$  concentration in the feed on the  $K_{obs}$  values of Pd(II) using  $S_6$ -P-36, BESO and Cyanex 302 as the ionophores.  $K_{obs}$  decreased with increasing  $\text{HNO}_3$  and declined to a value of  $1.2 \times 10^{-9} (\text{s}^{-1})$  for  $S_6$ -P-36 and  $1.8 \times 10^{-9} (\text{s}^{-1})$  for BESO and  $2.2 \times 10^{-9} (\text{s}^{-1})$  for Cyanex 302.

#### **Effect of Ionophore Concentration on Apparent Rate Constant ( $K_{obs}$ )**

Effects of the carrier concentration on the cation permeation have been extensively described and the overall picture is rather complex. The way in which its concentration affects the flux depends on whether ion-pairs



(20) or free ions (21) are present in the membrane, and whether the carrier is saturated at the source phase interface (20). Furthermore, at high carrier concentration, the same may influence the viscosity of the medium (22) and tend to form aggregates (23). The permeability of Pd(II) from dilute HNO<sub>3</sub> into toluene by S<sub>8</sub>-P-36 (0.005 - 0.04 M) and BESO (0.05 - 0.4 M) and Cyanex 302 (0.05 - 0.25 M) increased with increasing ionophore concentration. A 0.02 M S<sub>8</sub>-P-36 or 0.2M BESO solution imbibed in membrane-facilitated permeation of 1 gm dm<sup>-3</sup> of Pd(II) afforded > 95% of its recovery in about 6-7 h. The maximum K<sub>obs</sub>, 9.0 x 10<sup>-8</sup> s<sup>-1</sup>, was accomplished at 0.04 M S<sub>8</sub>-P-36 in 2 h whereas in case of sulfoxide carrier, 0.4M BESO resulted in maximum apparent constant i.e. 15.5 x 10<sup>-8</sup> s<sup>-1</sup> in 2 h of operations. Similarly maximum K<sub>obs</sub> of the order of 10.13 x 10<sup>-8</sup> (s<sup>-1</sup>) was observed at 0.25M Cyanex 302 after 2h of experimental run. Values of K<sub>obs</sub> for BESO, S<sub>8</sub>-P-36 and Cyanex 302 at varying carrier concentrations are listed in Table 2. The effect of carrier concentration on K<sub>obs</sub> across PILM at fixed HNO<sub>3</sub> for BESO, S<sub>8</sub>-P-36 and Cyanex 302, depicted in Figs. 7(a) and 7(b), showed that K<sub>obs</sub> increased with increasing carrier concentrations up to 0.02M for S<sub>8</sub>-P-36, 0.2M for BESO (Fig.7(a)) and 0.2M Cyanex 302 (Fig.(7b)) and further marginal increase at higher concentrations sufficiently large values of [Pd]<sub>m</sub>/[Pd]<sub>s</sub> after 6 h duration indicate

that for all these carrier system, efficient pertraction of Pd(II) against its concentration gradient particularly at lower nitric acid concentrations could be readily accomplished (Table 2).

The study carried out to distinguish the driving force between  $H^+$  and  $NO_3^-$  ion for the cation transport across PILM, indicated that  $NO_3^-$  ion not the  $H^+$  ion seems to be the driving force for Pd(II) transport under the present conditions for both BESO-PILM and  $S_{60}$ -P-36-PILM systems. The typical results are summarised in Table 3. On contrary,  $H^+$  ions seem to be the driving force in case of Cyanex 302-PILM system. This is in accord with the observations made by Kakoi et al. in their work performed with Pd(II) using Cyanex 301 and Cyanex 302 as the extractants (24).

#### Influence of Diluents on Permeability of Pd(II)

Both the permeability and selectivity involved in the transport of permeants by organic membrane carriers are greatly influenced by the nature and kind of an organic solvent. To assess the influence of several commonly available aliphatic and aromatic solvents on the permeation of Pd(II), its transport with BESO (0.2M),  $S_{60}$ -P-36 (0.02M) or Cyanex 302 (0.25M) in various diluents was studied maintaining the feed acidity at 1 M  $HNO_3$ . Table 4 summarizes the results concerning the effect of diluents with BESO and  $S_{60}$ -P-36 on the permeation of palladium. Among the various

diluents tested, the chlorinated hydrocarbons such as chloroform, o-dichlorobenzene, 1,2-dichloroethane afforded much poor permeability compared to diluents like toluene, benzene and dodecane which is contrary to their liquid-liquid extraction behaviour. Likewise Cyanex 302-PILM system yielded best results in diluents like dodecane and toluene whereas chlorinated hydrocarbons too proved to be detrimental for Pd(II) permeability (Table 4). The lower boiling point and high aqueous solubility of these chlorinated diluents possibly caused the fast degradation of PILM supports (25-26). The  $K_{L,M}$  values for S<sub>e</sub>-P-36, BESO and Cyanex-PILM systems in toluene are calculated to be  $9.4 \times 10^{-8} \text{ s}^{-1}$ ,  $7.9 \times 10^{-8} \text{ s}^{-1}$  and  $10.13 \times 10^{-8} \text{ s}^{-1}$  after 2h of experimental run, respectively. The dielectric constant seems to have no correlation with the permeability of Pd(II). Since the permeation of Pd(II) using dodecane is almost the same as that with toluene as the diluent, most of the studies were thus conducted using toluene as the membrane solvent owing to its easy availability, low cost and poor aqueous solubility. Based on the permeation and recovery rate of palladium, toluene was selected as the diluent throughout the present LM study.

#### **Effect of Nature and Type of Strippant on Palladium Transport**

The transport of Pd(II) across different PILM systems

is significantly dependent upon the nature and type of the strippants used on the product side of the membrane. From Table 5, it is apparent that out of several aqueous strippants such as  $\text{Na}_2\text{CO}_3$ , ( $\text{Na}_2\text{CO}_3 + \text{NH}_4\text{OH}$ ), thiourea, and  $\text{NH}_4\text{SCN}$  tested, dilute  $\text{NH}_4\text{SCN}$  (~1 M) proved to be the most efficient for back extraction purposes. Results concerning the efficiency of different strippants, evaluated with respect to Pd(II) transport are presented in Table 5. Among them, 1M  $\text{NH}_4\text{SCN}$  afforded better than 90% of its recovery across PILM with these carriers. High values of  $K_{obs}$  touched nearly  $8.6 \times 10^{-9} \text{ s}^{-1}$  for S<sub>0</sub>-P-36 and  $8.3 \times 10^{-9} \text{ s}^{-1}$  for BES0 after 1h of transport, which justified the idea of selecting dilute  $\text{NH}_4\text{SCN}$  as the strippant in the receiving phase throughout this study.

From Table 5, it is evident that out of several aqueous strippants such as  $\text{Na}_2\text{CO}_3$ , dilute  $\text{NH}_4\text{OH}$ , thiourea and  $\text{NH}_4\text{SCN}$  tested, thiourea proved to be the most efficient for Pd(II) recovery from Cyanex phase. The maximum  $K_{obs}$  exceeding  $10.13 \times 10^{-9} \text{ s}^{-1}$  with 0.25M Cyanex 302 was achieved (after 2h), indicating effectiveness of thiourea (1M) as the strippant in the receiving phase.

#### Stability of the Support and Leachability of the Carrier from PILM

Under the optimum conditions, the stability and leachability of carrier from PILM were tested (Table 6).

The feed and the product solutions were replaced each time with fresh ones. Even after 18 h of continuous use, both the carriers did not leak out of the membrane phase and further a marginal decrease only after 24 h of experimentation. The stability probably depends on the capillary forces that holds the organic membrane solvent within the pores as explained by the Young-Dupre equation (27) :  $P_c = (2\gamma/a) \cos\theta$ , where  $P_c$  denotes the capillary pressure,  $\gamma$ , the solvent water interfacial tension;  $a$ , the membrane pore size, and  $\theta$  the contact angle.

In practical applications of PILMs, their life time, viz., the membrane stability, is a matter of great importance ; however, there is very little information available on this aspect (28-30). The stability of PILMs has been extensively investigated and different degradation mechanisms have been proposed, viz. (i) chemical degradation (31), (ii) partition of the carrier and /or membrane solvent to the adjacent aqueous phases (32,29), (iii) depletion of the membrane phase under the influence of an osmotic (33); hydrostatic pressure gradient (34,35), (iv) formation of emulsions (36), or (v) inverted micelles (37,38). Takeuchi (39) et al., studied the stability of PILM systematically in terms of water leakage characteristics for both hollow-fibre and flat-sheet configurations using various polymeric membranes and organic solvents. Danesi and Rickert (30) have concluded that the probable causes of

PILM instability and progressive wettability of the support pores are induced by a lowering of the interfacial tension. The chemical resistance of PTFE membrane against toluene was periodically tested over a period of 20 days imbibed with 0.02 M  $S_6-P-36$ , 0.2 M BESO or 0.25M Cyanex 302 carrier solution. At the end of each run, the PILM support was washed and stored in toluene. The permeation of palladium across PILM was practically unaffected which showed that the TE-35 membrane possessed adequate stability in this membrane solvent even after long deployment and also the same could be easily regenerated for reuse.

#### Effect of Radiation on Polymer Supports

Apparent rate constants,  $K_{obs}$ , of Pd(II) across radiolytically degraded polymeric PTFE supports were determined in order to study the influence of gamma-radiation on their performances. No significant decrease in  $K_{obs}$  for palladium was observed for synthetic PTFE membrane like TE-35 used even with absorbed dose upto 3 Mrads . It is important to note that the total absorbed dose employed in this study was well in excess of that expected in processing actual low level waste solutions employing these as the PILM supports. Thus, their radiolytic degradation posed no serious adverse impact on the cation transport for periods corresponding to several days of continuous operations.

Scanning electron micrographs revealed that structural

changes after irradiation upto absorbed dose of 3 Mrad (impregnated with 0.02M S<sub>8</sub>-P-36/toluene for 6-8 h prior to irradiation ) with membrane TE-35 were insignificant and no serious damage to integrity of these supports took place as is clear from Figs. 8(a) and 8(b).

#### **Palladium Recovery From Synthetic Waste**

Permeability of Pd(II) from a process effluent containing Pu(IV) and fission products such as Ce-144, Ru-106 and Cs-137 across PILM containing these carriers was examined. From Table 7, it is quite evident that problematic actinides like Pu(IV) and Am(III) and fission product contaminants were poorly permeated (<10%) whereas more than 90 % of Pd could be recovered across single stage PILM from 1 M HNO<sub>3</sub> employing either 0.04 M S<sub>8</sub>-P-36, 0.2M BESO or 0.25M Cyanex 302 as the carriers and 1 M NH<sub>4</sub>SCN (for S<sub>8</sub>-P-36 and BESO) or thiourea(for Cyanex 302) as the strippants. The apparent rate constants,  $K_{app}$ , are computed to be  $9.2 \times 10^{-5} \text{ (s}^{-1}\text{)}$ ,  $8.3 \times 10^{-5} \text{ (s}^{-1}\text{)}$  and  $9.7 \times 10^{-5} \text{ s}^{-1}$  after 1 h, for S<sub>8</sub>-P-36, BESO and Cyanex 302-PILM respectively which reflect the selective pertraction of Pd(II) from such wastes.

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TABLE 1

Effect of HNO<sub>3</sub> Concentration on Pertraction of Pd(II) Across FILM

Initial feed concentration : 1.0 gm dm<sup>-3</sup> Pd in HNO<sub>3</sub>  
 Carrier concentration : 0.02 M S<sub>2</sub>-P-36/toluene (I)  
 : 0.20 M BESO/toluene (II)  
 : 0.25 M Cyanex/toluene (III)  
 Strippant : 1 M NH<sub>4</sub>SCN for both S<sub>2</sub>-P-36  
 : 1M Thiourea for Cyanex 302  
 Source to receiving phase volume ratio : 1

Feed (HNO <sub>3</sub> ) (M)	Time (h)	Apparent rate constant, $K_{app}$ x10 <sup>-6</sup> (s <sup>-1</sup> )			[Pd] <sub>1</sub> /[Pd] <sub>2</sub> after 6h			Recovery of Pd after 6h (%)		
		I	II	III	I	II	III	I	II	III
1	2	3	4	5	6	7	8	9	10	11
0.01	1	-	10.7	-	-	13.2	-	-	98.7	-
	2	-	9.1	-						
	3	-	12.0	-						
	4	-	11.9	-						
	5	-	11.7	-						
	6	-	12.3	-						
0.1	1	6.9	8.0	8.61	8.4	7.0	18.97	95.1	94.6	26.3
	2	8.6	8.2	10.13						51.5
	3	8.2	10.1	8.98						62.4
	4	7.4	8.4	8.61						71.1
	5	7.4	7.5	12.78						89.8
	6	8.8	9.4	13.89						95.4
0.5	1	-	-	7.50	-	-	12.90	-	-	24.3
	2	-	-	9.03	-	-				51.8
	3	-	-	9.17	-	-				63.6
	4	-	-	8.82	-	-				72.4
	5	-	-	9.50	-	-				82.0
	6	-	-	12.31	-	-				93.8

contd...

1	2	3	4	5	6	7	8	9	10	11
1.0	1	9.1	6.2	8.33	7.5	3.5	10.47	94.8	70.3	91.2
	2	8.1	6.4	9.31						
	3	6.6	6.6	8.06						
	4	6.6	6.2	8.82						
	5	7.4	5.8	9.50						
	6	8.5	6.8	11.16						
2.0	1	6.9	3.6	7.22	7.2	3.0	6.55	87.8	73.1	86.7
	2	8.3	3.8	9.03						
	3	6.4	3.6	7.78						
	4	5.6	3.0	8.33						
	5	3.8	3.3	9.22						
	6	8.2	3.5	9.44						
3.0	1	2.6	3.2	3.89	2.0	1.7	1.43	68.7	41.2	58.8
	2	1.6	2.9	3.61						
	3	3.8	2.4	4.25						
	4	4.8	2.3	4.38						
	5	3.7	2.1	4.22						
	6	4.0	2.0	4.12						
4.0	1	2.0	2.6	2.50	0.6	0.4	0.41	35.3	28.3	27.7
	2	1.2	1.8	2.22						
	3	1.2	1.4	7.41						
	4	1.1	1.5	5.28						
	5	1.3	1.5	1.50						
	6	1.3	1.3	1.52						
5.0	1	1.7	1.4	-	0.4	0.3	-	25.6	20.4	-
	2	1.5	1.1	-						
	3	1.2	1.0	-						
	4	1.0	0.8	-						
	5	1.0	0.8	-						
	6	1.0	0.7	-						

**TABLE 2**

**Pertraction of Pd(II) across FILM as a Function of Carrier Concentration ( S<sub>e</sub>-P-36, BESO and Cyanex 302 )**

Initial feed concentration : 1.0 gm dm<sup>-3</sup> Pd in 1M HNO<sub>3</sub> for S<sub>e</sub>-P-36/toluene, 0.1M HNO<sub>3</sub> for BESO/toluene and Cyanex 302/toluene

Carrier concentration : 0.005 M S<sub>e</sub>-P-36/toluene(I)  
: 0.05 M BESO/toluene(II)  
: 0.05 M Cyanex/toluene (III)

Strip pant : 1 M NH<sub>4</sub>SCN for both S<sub>e</sub>-P-36 and BESO

Source to receiving phase volume ratio : 1

Carrier concentration (M)	Time (h)	Apparent rate constant, $K_{app} \times 10^{-3}$ (s <sup>-1</sup> )			[Pd] <sub>p</sub> /[Pd] <sub>s</sub> after 6h			Recovery of Pd after 6h (%)			
		I	II	III	I	II	III	I	II	III	
1	2	3	4	5	6	7	8	9	10	11	12
I	0.005	1	2.0	10.7	2.50	1.2	3.4	1.02	55.1	70.2	50.2
II	0.05	2	3.1	7.8	3.86						
III	0.05	3	2.7	6.2	2.87						
		4	1.5	5.4	2.94						
		5	1.9	5.3	2.83						
		6	3.2	4.6	3.29						
I	0.01	1	6.6	9.5	2.22	2.5	6.5	2.64	75.2	77.3	72.4
II	0.10	2	6.3	8.0	3.06						
III	0.10	3	5.8	7.0	5.00						
		4	6.7	7.5	5.42						
		5	6.2	8.2	5.50						
		6	5.5	9.1	6.06						

contd...

	1	2	3	4	5	6	7	8	9	10	11	12
I	0.02	1	7.0	8.4	5.56	7.5	8.1	3.80	94.8	90.3	79.6	
II	0.20	2	8.6	8.3	5.42							
III	0.15	3	8.2	10.5	5.74							
		4	7.4	8.4	6.18							
		5	7.4	7.5	6.89							
		6	8.6	9.8	7.22							
I	0.03	1	7.2	15.6	5.28	8.0	8.5	7.57	92.3	94.3	88.4	
II	0.30	2	8.6	15.3	5.14							
III	0.20	3	7.8	12.8	6.39							
		4	7.5	14.1	7.92							
		5	7.4	14.7	10.17							
		6	9.4	13.9	9.81							
I	0.04	1	8.0	16.2	8.61	11.2	13.0	18.99	96.3	97.1	95.5	
II	0.40	2	9.0	15.5	10.13							
III	0.25	3	8.2	14.6	8.98							
		4	8.1	15.2	8.61							
		5	7.8	13.4	12.78							
		6	7.5	14.6	13.89							

TABLE 3

Apparent Rate Constants ( $K_{app}$ ) and Pertraction of Pd(II)  
At a Fixed  $[(NO_3)^-]$  Concentration in the Source Phase

Aqueous feed composition : 0.5 M  $NO_3^-$  (  $HNO_3$  +  $NH_4NO_3$  )  
1.0 gm Pd  $dm^{-3}$  in feed

Carrier concentration : 0.02 M  $S_6$ -P-36/toluene  
Strip pant : 1 M  $NH_4SCN$  for both  $S_6$ -P-36  
and BESO PILM systems

Source to receiving phase  
volume ratio : 1

$NH_4NO_3$ + $HNO_3$ (M)	Time (h)	Apparent rate cons- tant, $K_{app}$ $\times 10^{-6}$ ( $s^{-1}$ )		$[Pd]_p/[Pd]_a$ after 6h		Recovery of Pd after 6h (%)	
		$S_6$ -P-36	BESO	$S_6$ -P-36	BESO	$S_6$ -P-36	BESO
0.5M $HNO_3$	1	7.2	7.3	7.9	7.6	94.1	93.9
	2	8.5	8.2				
	3	7.9	7.9				
	4	7.5	7.7				
	5	6.8	7.1				
	6	6.7	6.9				
0.45M $NH_4NO_3$ + 0.05M $HNO_3$	1	9.9	5.9	7.3	6.6	92.4	90.4
	2	9.3	7.1				
	3	8.0	9.4				
	4	7.5	8.4				
	5	7.7	7.4				
	6	8.8	8.2				
0.4M $NH_4NO_3$ 0.1M $HNO_3$	1	10.3	8.0	7.7	6.4	95.2	91.1
	2	8.8	8.1				
	3	8.0	9.9				
	4	7.7	8.4				
	5	7.1	9.9				
	6	8.8	8.4				
0.25M $NH_4NO_3$ + 0.25M $HNO_3$	1	10.3	7.6	7.3	6.1	93.8	89.8
	2	8.8	7.6				
	3	8.0	9.9				
	4	7.7	8.2				
	5	7.1	7.8				
	6	8.8	8.3				



**TABLE 4**

**Effect of Diluents on the Pertraction of Pd(II) Across PILM**

Initial feed concentration : 1.0 gm dm<sup>-3</sup> Pd in 1M HNO<sub>3</sub> for S<sub>2</sub>-P-36/toluene and 0.1M HNO<sub>3</sub> for BESO/toluene and Cyanex 302/toluene

Carrier concentration : 0.02 M S<sub>2</sub>-P-36 (I)  
: 0.20 M BESO (II)  
: 0.25 M Cyanex-302 (III)

Strippant : 1 M NH<sub>4</sub>SCN for both S<sub>2</sub>-P-36 and BESO-PILM systems and 1M thiourea for Cyanex 302-PILM system

Source to receiving phase ratio : 1

Diluent	Time (h)	Apparent rate constant, K <sub>app</sub> x10 <sup>-3</sup> (s <sup>-1</sup> )			[Pd] <sub>o</sub> /[Pd] <sub>a</sub> after 6h			Recovery of Pd after 6h (%)		
		I	II	III	I	II	III	I	II	III
1	2	3	4	5	6	7	8	9	10	11
Benzene	1	8.8	7.6	2.2	3.7	7.9	0.18	79.2	91.2	9.5
	2	8.0	8.8	2.0						
	3	6.8	9.5	1.6						
	4	5.7	8.5	1.8						
	5	6.0	8.9	1.7						
	6	7.2	9.1	1.6						
Chloroform	1	2.1	8.7	-	0.2	1.6	-	16.2	60.1	-
	2	1.4	5.0	-						
	3	1.3	4.1	-						
	4	1.1	3.7	-						
	5	0.8	4.1	-						
	6	0.7	4.2	-						
1,2 Dichloroethane	1	1.2	-	-	0.8	-	-	47.2	-	-
	2	1.5	-	-						
	3	1.1	-	-						

contd...

	1	2	3	4	5	6	7	8	9	10	11
		4	1.0	-	-		-	-		-	-
		5	0.9	-	-		-	-		-	-
		6	0.6	-	-		-	-		-	-
<b>Dodecane</b>	1		2.3	2.6	6.94	6.5	3.3	7.83	92.2	81.1	88.8
	2		1.5	2.1	8.75						
	3		4.3	3.0	8.70						
	4		4.2	4.8	8.13						
	5		4.9	5.7	10.56						
	6		5.7	6.8	10.23						
<b>o-Dichlorobenzene</b>	1		2.3	5.5	2.50	0.3	0.5	0.63	20.2	35.6	40.1
	2		1.3	3.1	3.33						
	3		1.1	2.3	2.50						
	4		1.0	2.1	2.78						
	5		1.0	1.7	2.38						
	6		0.9	1.8	2.36						
<b>Toluene</b>	1		8.7	7.7	8.61	7.5	7.0	18.97	94.8	90.7	95.4
	2		9.4	7.9	10.13						
	3		8.5	10.2	8.98						
	4		7.7	8.4	8.61						
	5		7.5	7.4	12.78						
	6		8.3	9.6	13.89						
<b>Xylene</b>	1		2.0	-	3.33	0.1	-	0.43	12.2	-	30.1
	2		1.2	-	1.94						
	3		7.7	-	1.76						
	4		7.3	-	1.46						
	5		6.5	-	1.61						
	6		5.4	-	1.67						
<b>Solve- sso-100</b>	1		-	2.9	2.42	-	1.2	0.18	-	55.1	11.2
	2		-	4.2	2.13						
	3		-	3.5	1.86						
	4		-	3.7	1.92						
	5		-	3.4	2.00						
	6		-	3.6	1.95						

TABLE 5

Effect of Different Strippants on Pertraction of Pd(II) Across PILM

Initial feed concentration : 1.0 gm dm<sup>-3</sup> Pd in HNO<sub>3</sub>

Carrier concentration : 0.02 M S<sub>2</sub>-P-36/toluene (I)  
 : 0.20 M BESO/toluene (II)  
 : 0.25 M Cyanex/toluene (III)

Source to receiving phase : 1  
 volume ratio

Strip- pant	Time (h)	Apparent rate constant, $K_{app}$ $\times 10^{-3}$ (s <sup>-1</sup> )			[Pd] <sub>D</sub> /[Pd] <sub>F</sub> after 6h			Recovery of Pd after 6h (%)		
		I	II	III	I	II	III	I	II	III
Na <sub>2</sub> CO <sub>3</sub> (2M)	1	1.7	1.1	1.1	0.1	0.1	0.1	12.6	10.0	10.0
	2	1.0	1.0	1.0						
	3	7.7	3.3	3.3						
	4	7.3	2.1	2.1						
	5	6.4	2.0	2.0						
	6	6.0	3.0	3.0						
Na <sub>2</sub> CO <sub>3</sub> (2M) + NH <sub>4</sub> OH (0.05)	1	2.1	1.4	1.4	0.2	0.1	0.1	8.2	12.9	8.2
	2	1.2	0.9	0.9						
	3	8.7	0.8	0.8						
	4	6.6	0.7	0.7						
	5	6.5	0.5	0.5						
	6	5.9	0.5	0.5						
Na <sub>2</sub> CO <sub>3</sub> (2M) + NH <sub>4</sub> OH (0.5M)	1	2.6	1.4	1.4	0.21	0.2	0.1	17.6	17.7	7.0
	2	1.5	1.2	1.2						
	3	1.1	1.0	1.0						
	4	9.7	0.7	0.7						
	5	8.4	0.7	0.7						
	6	8.6	0.7	0.7						
Thio- urea (1M)	1	4.2	1.0	8.6	1.6	0.1	18.97	65.2	9.23	95.8
	2	5.4	0.9	10.1						
	3	5.2	0.7	9.0						
	4	4.5	0.7	8.6						
	5	5.0	0.6	12.8						
	6	4.5	0.5	13.9						
NH <sub>4</sub> SCN (1M)	1	7.0	7.8	2.6	7.5	8.7	0.2	94.8	97.2	17.7
	2	8.6	8.3	1.5						
	3	8.2	10.0	1.1						
	4	7.4	8.3	2.7						
	5	7.4	7.7	2.4						
	6	8.6	9.4	2.0						

**TABLE 6**

**Leachability and Degradation of PILM using A Flat-Sheet Polytetrafluoroethylene Support (TE-35)**

**Aqueous feed composition** : 1.0 gm dm<sup>-3</sup> Pd in 1M HNO<sub>3</sub>

**Carrier concentration** : 0.02M S<sub>8</sub>-P-36/toluene (I)  
0.2 M BESO/toluene (II)  
0.25M Cyanex 302/toluene (III)

**Stripant** : 1 M NH<sub>4</sub>SCN for S<sub>8</sub>-P-36  
and BESO-PILM and 1M thiourea  
for Cyanex 302-PILM

**Source to receiving phase** : 1  
**volume ratio**

**Support** : TE-35 (PTFE)

Number of days	Time elapsed (h)	Apparent rate constant, $K_{app}$ x10 <sup>-6</sup> (s <sup>-2</sup> )			[Pd] <sub>p</sub> /[Pd] <sub>a</sub> after 6 h			Recovery of Pd after 6h (%)		
		I	II	III	I	II	III	I	II	III
1	1	6.9	7.1	8.3	7.6	7.4	10.2	93.1	92.9	92.3
	3	7.3	7.2	8.0						
	6	6.7	6.8	11.2						
6	145	9.5	5.3	8.1	7.5	6.8	8.8	91.8	90.2	90.6
	147	8.1	9.2	8.2						
	150	8.3	8.0	10.6						
10	241	9.7	7.8	7.9	7.3	6.2	6.7	90.2	91.1	89.2
	243	8.2	9.5	7.6						
	246	8.4	7.9	8.2						
15	361	7.9	7.2	7.1	6.2	5.7	6.2	89.2	86.8	88.1
	363	7.2	7.7	7.2						
	366	6.1	7.5	7.6						

**Table 7**  
**Permeation of Palladium and Various Fission Product Contaminants**  
**Through PILM using S<sub>e</sub>-P-36, BESO and Cyanex 302 as Carriers**

**Feed** : Process effluent spiked with Pd-103 in  
 1 M HNO<sub>3</sub>

**Carrier concentration** : 0.04M S<sub>e</sub>-P-36/toluene (I)  
 0.2 M BESO/toluene (II)  
 0.25M Cyanex 302/toluene (III)

**Strippant** : 1 M NH<sub>4</sub>SCN for I and II and  
 1 M thiourea for III

Fission product	F.P. activity <sup>a</sup> in the source phase (uci dm <sup>-3</sup> )	F.P. activity in the receiving phase (uci dm <sup>-3</sup> )			Permeant permeation (%)		
		I	II	III	I	II	III
Pd-103	1.0 <sup>b</sup>	0.9 <sup>b</sup>	0.9 <sup>b</sup>	0.9 <sup>b</sup>	94.0	95.0	96.2
Ru-106	57.2	2.7	1.6	1.9	4.7	3.6	4.1
Cs-137	2513.2	104.3	93.4	98.6	4.2	3.9	3.1
Sb-125	23.3	1.3	1.2	1.1	5.6	5.2	4.9
Ce-144	46.0	2.6	2.3	1.8	5.7	5.1	3.4
Pu(IV)	5.0 <sup>c</sup>	0.1 <sup>c</sup>	0.1 <sup>c</sup>	0.1 <sup>c</sup>	2.0	1.8	1.6
Am(III)	5.2 <sup>d</sup>	0.8 <sup>e</sup>	0.6 <sup>e</sup>	0.9 <sup>e</sup>	1.5	1.3	1.1

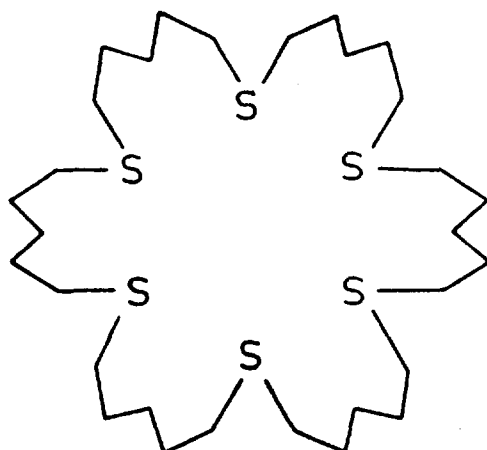
a, Activity of fission products was estimated by multichannel analyser using a High Purity Germanium detector (HPGe).

b, Concentration expressed in gm dm<sup>-3</sup>

c, Concentration expressed in mg dm<sup>-3</sup>.

d, x 10<sup>-2</sup> mg dm<sup>-3</sup>

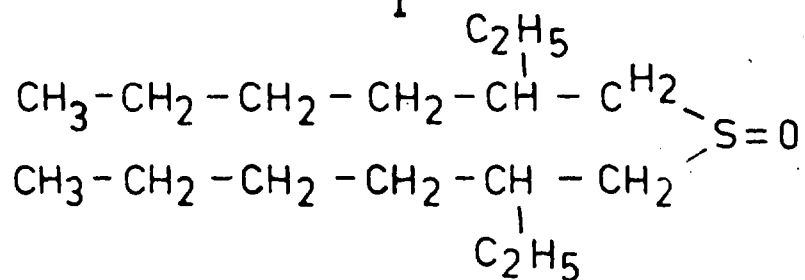
e, x 10<sup>-3</sup> mg dm<sup>-3</sup>



S6 - pentano - 36

(S6-P-36)

I



Bis ( 2 ethylhexy ) Sulfoxide

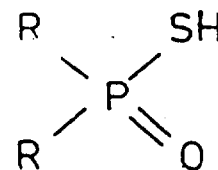
( B E S O )

II

Bis, 2,4,4 trimethyl pentyl  
mono thio phosphinic acid

( Cyanex 302 )

R-2,4,4 trimethyl pentyl



III

Fig.1. The structures of ionopores used in present study.

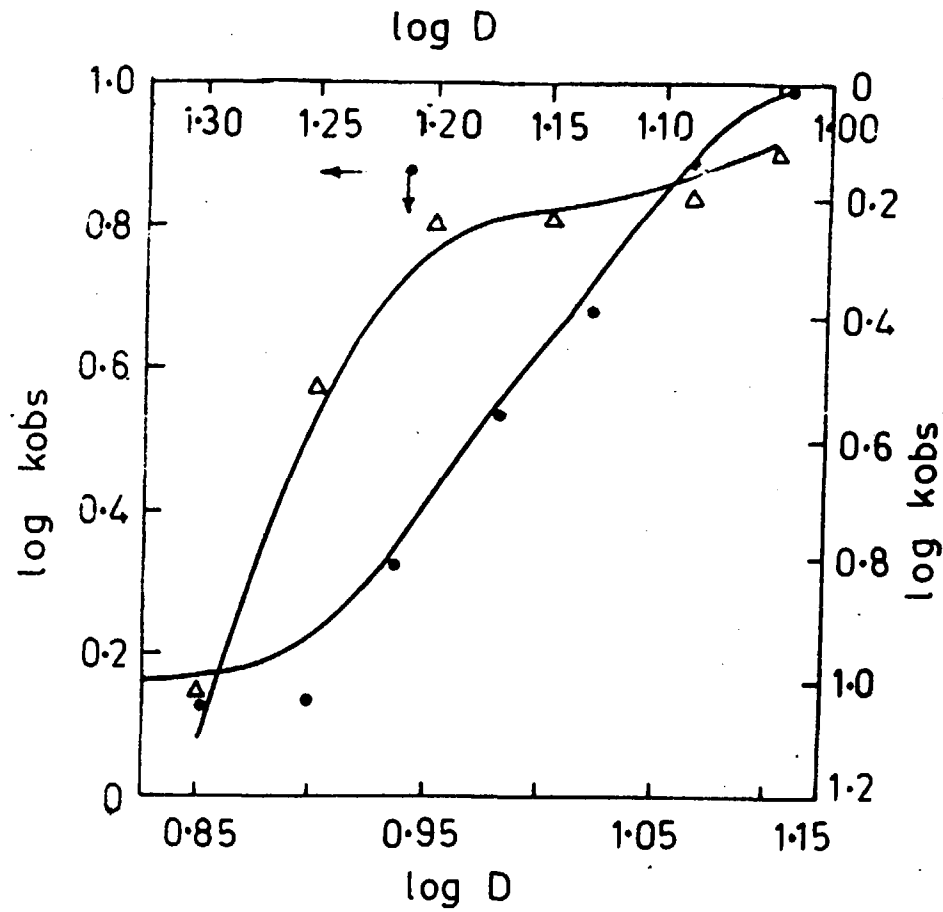


FIG. 2(a) Effect of  $\log D_{p,d}$  on apparent rate constant,  $K_{app}$ , of Pd(II) using  $S_4$ -P-36 and BESD as an ionophore, Source phase:  $1.0 \text{ gm dm}^{-3}$  in  $\text{HNO}_3$ , Receiving phase:  $1.0 \text{ M NH}_4\text{SCN}$ ; Carrier concentration:  $0.02 \text{ M } S_4$ -P-36 in toluene and  $0.2 \text{ M BESD}$  in toluene

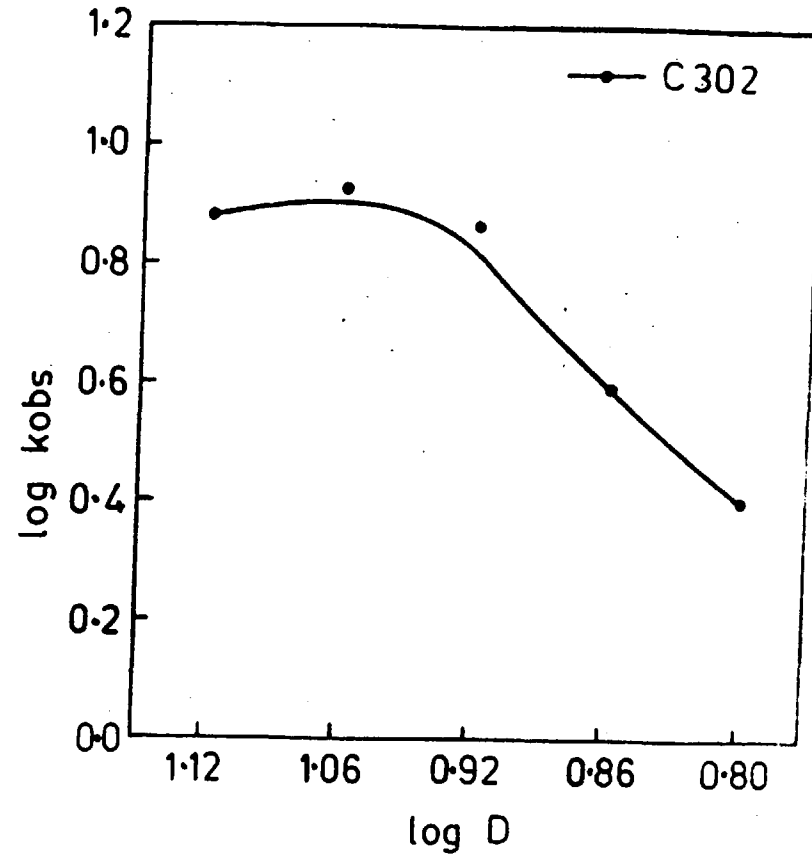


FIG. 2(b). Effect of  $\log D_{p,d}$  on apparent rate constant,  $K_{app}$ , of Pd(II) using Cyanex 302 as ionophore, Source phase:  $1.0 \text{ gm dm}^{-3}$  in  $\text{HNO}_3$ , Receiving phase:  $1.0 \text{ M Thiourea}$ ; Carrier concentration:  $0.25 \text{ M Cyanex 302}$  in toluene

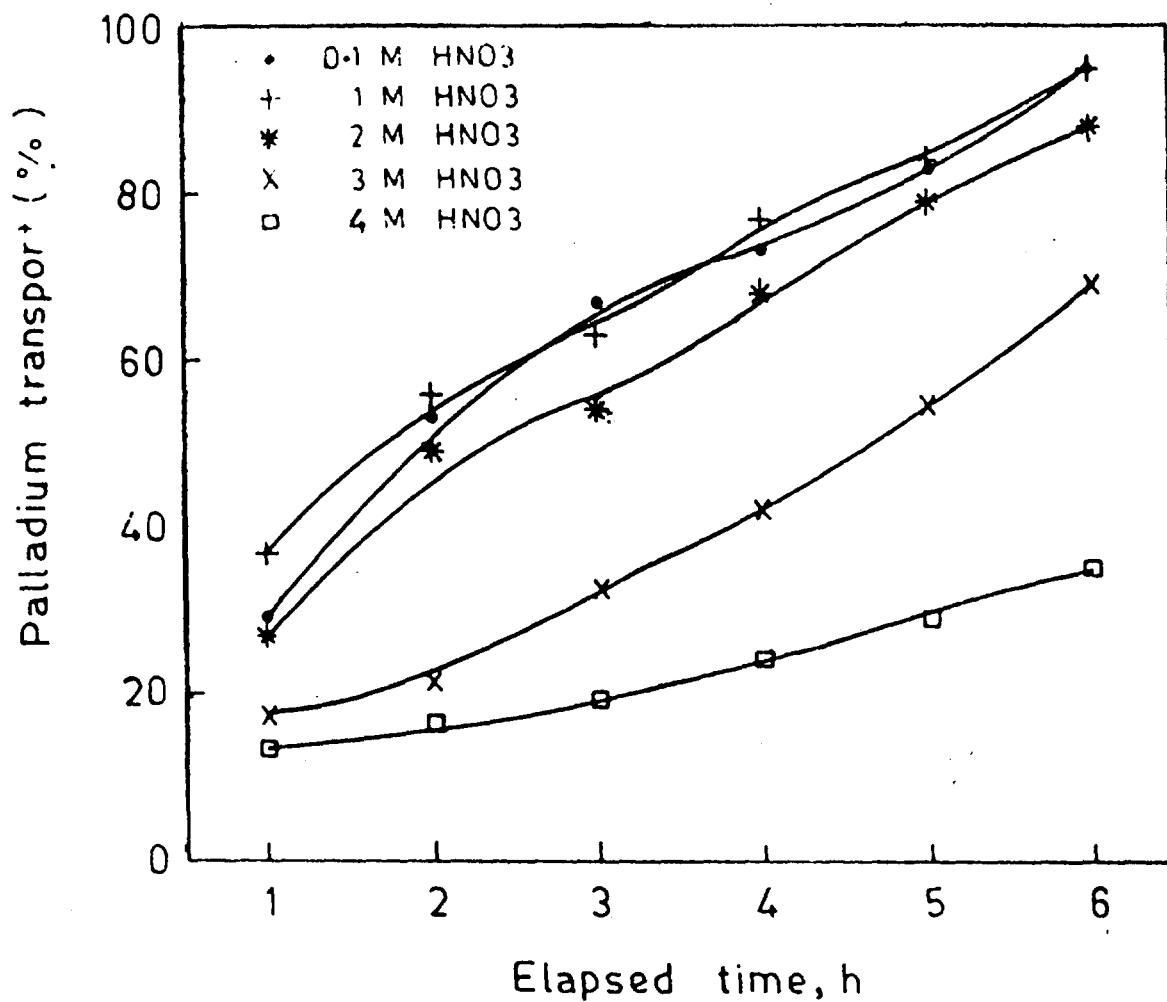


FIG. 3. Effect of HNO<sub>3</sub> on transport of Pd(II) across PILM using S<sub>6</sub>-P-36 as the carrier ; Receiving phase : 1.0 M NH<sub>4</sub>SCN; Carrier concentration: 0.02 M S<sub>6</sub>-P-36 in toluene



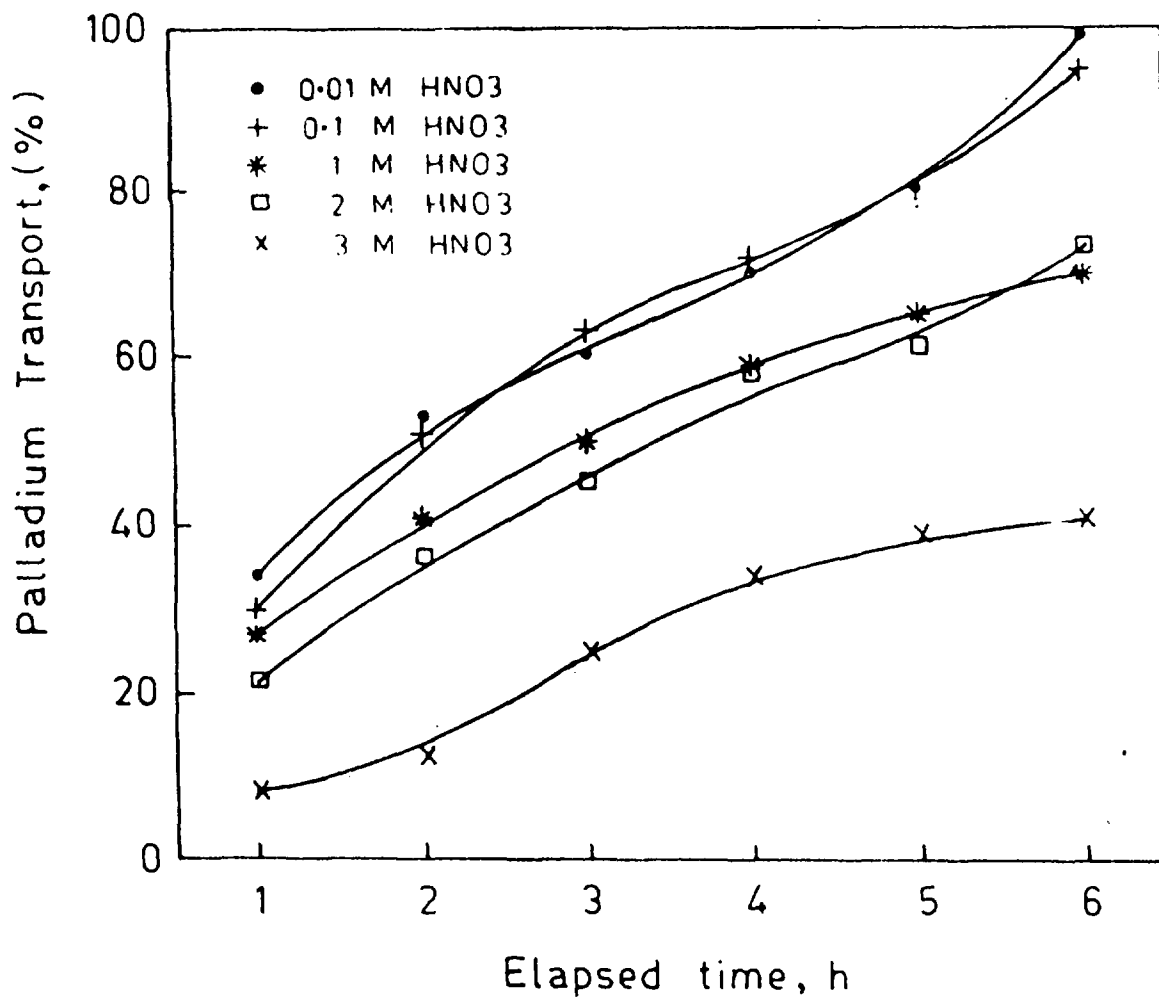


FIG. 4. Effect of HNO<sub>3</sub> on transport of Pd(II) across PILM using BESO as the carrier; Receiving phase: 1.0 M NH<sub>4</sub>SCN; Carrier concentration: 0.2 M BESO in toluene

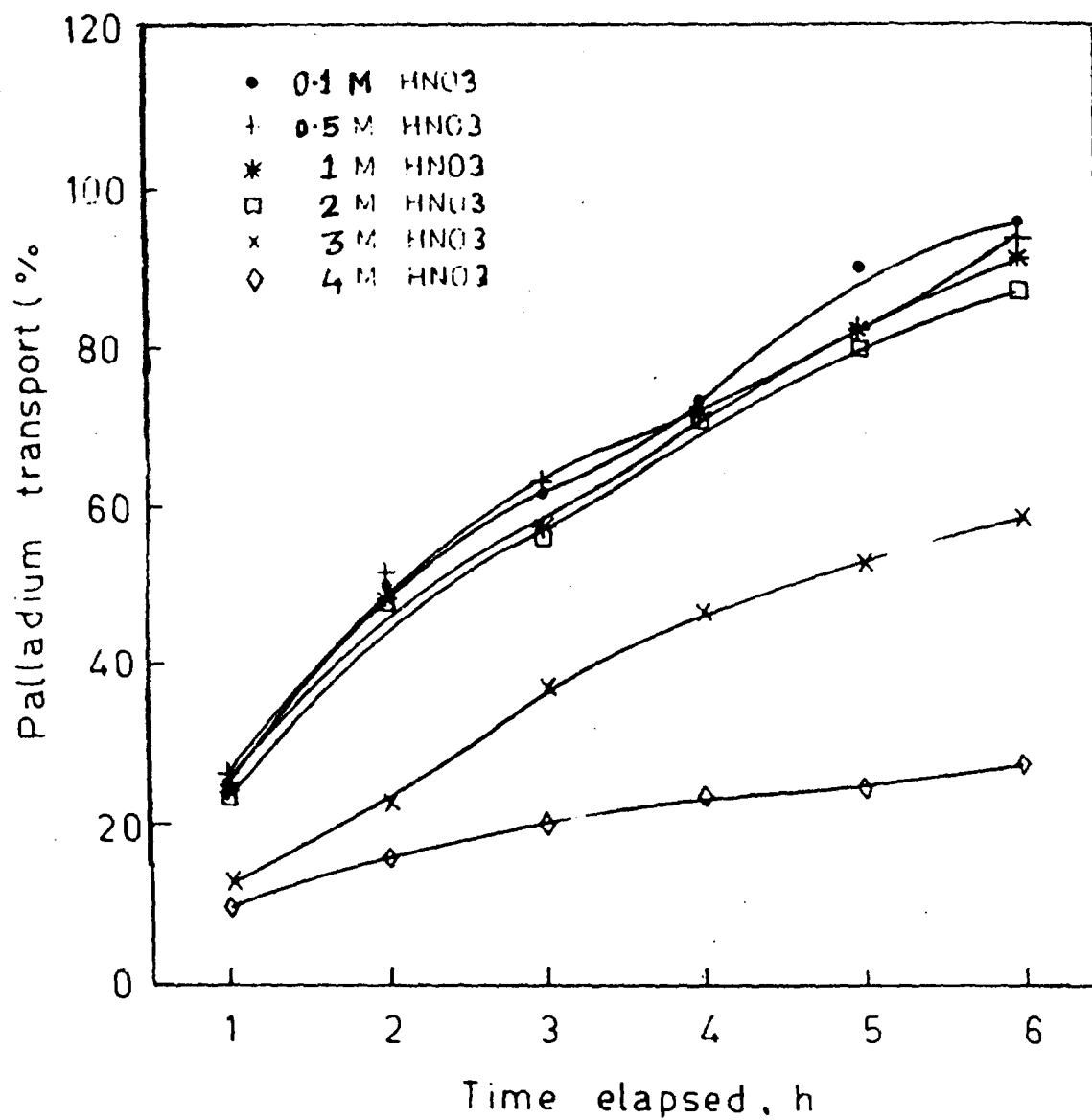


FIG. 5. Effect of HNO<sub>3</sub> on transport of Pd(II) across PILM using Cyanex 302 as the carrier; Receiving phase : 1.0 M Thiourea; Carrier concentration: 0.25 M Cyanex 302 in toluene

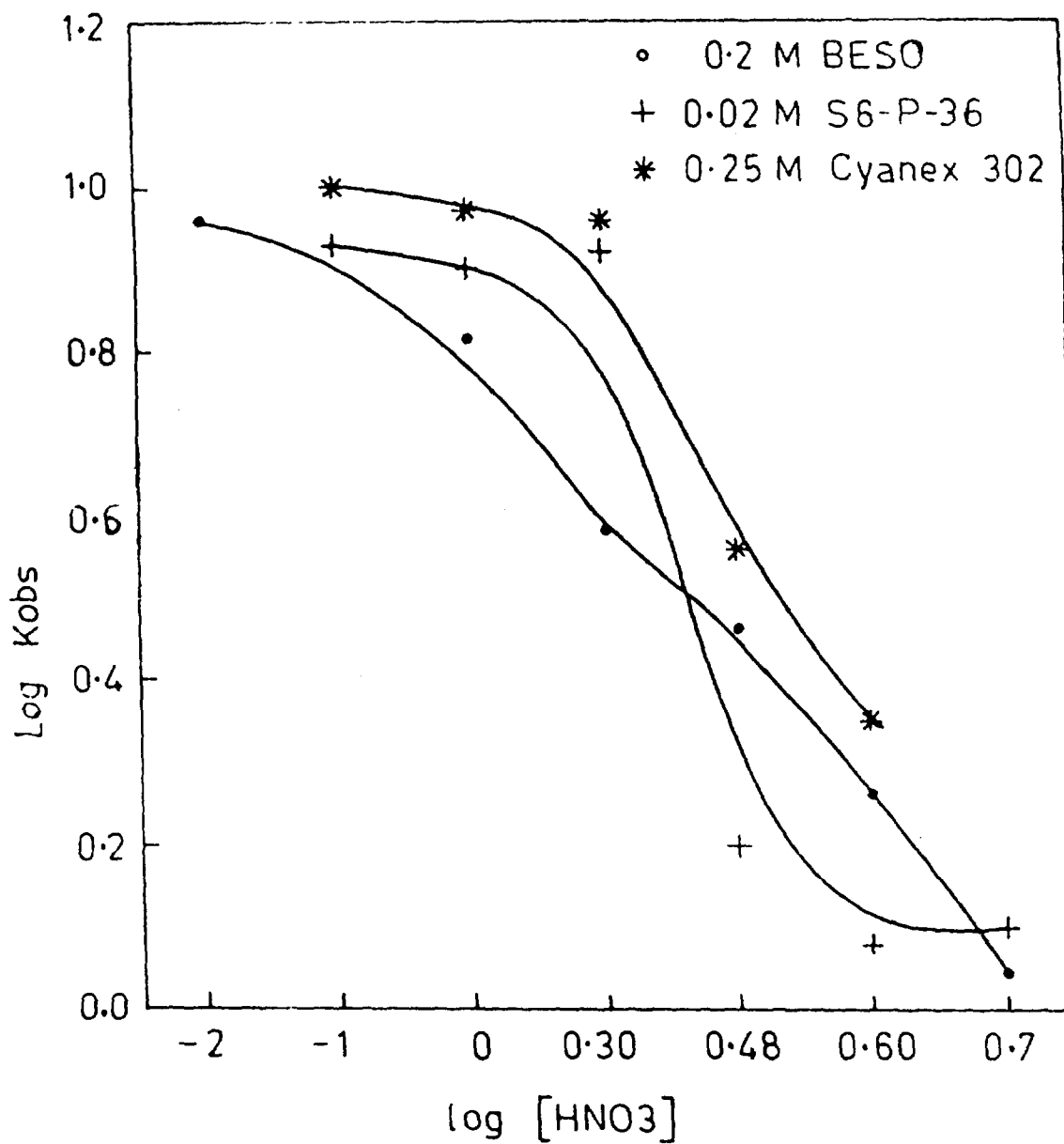


FIG. 6. Effect of HNO<sub>3</sub> on permeation of Pd(II) across PILM using Ss-P-36, BESO and Cyanex 302 as the carrier; Receiving phase: 1.0 M NH<sub>4</sub>SCN for BESO and Ss-P-36-PILM and 1.0 M Thiourea for Cyanex 302-PILM; Carrier concentration: 0.02 M Ss-P-36, 0.2 M BESO and 0.25 M Cyanex 302 in toluene

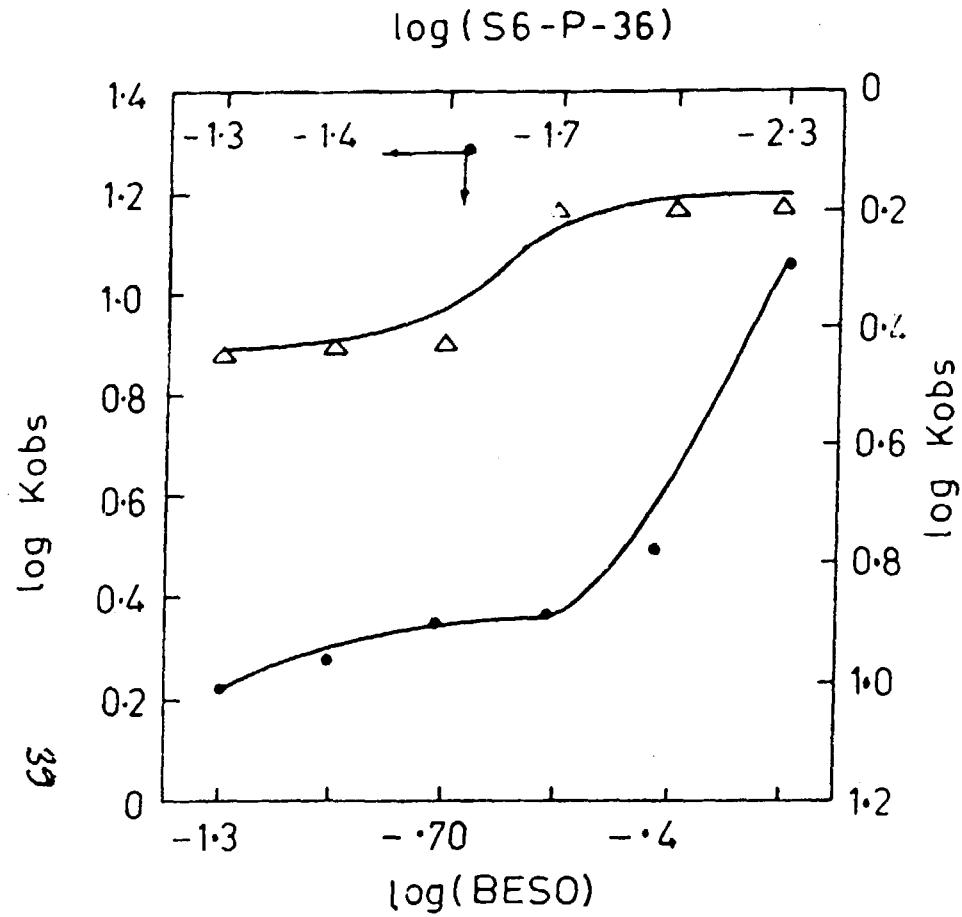


FIG. 7(a). Effect of ionophore concentration on  $K_{obs}$  of Pd(II) across PILM using S<sub>6</sub>-P-36 and BESO as the carriers, Receiving phase: 1 M NH<sub>4</sub>SCN for both S<sub>6</sub>-P-36 and BESO-PILM

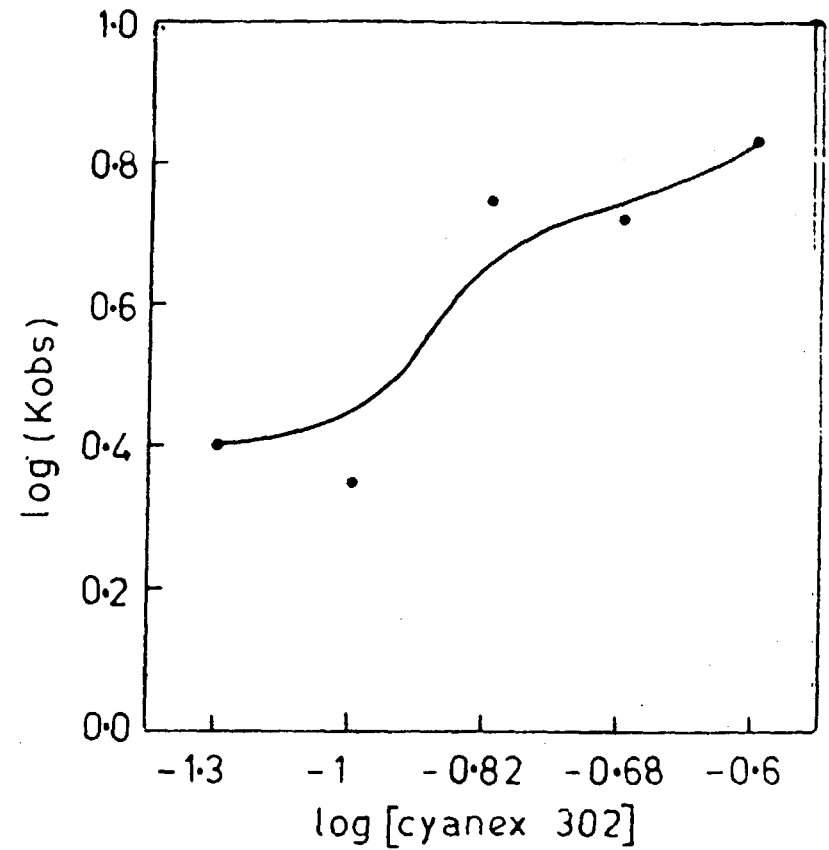


FIG. 7(b). Effect of ionophore concentration on  $K_{obs}$  of Pd(II) across PILM using Cyanex 302 as the carrier; Receiving phase: 1.0 M thiourea

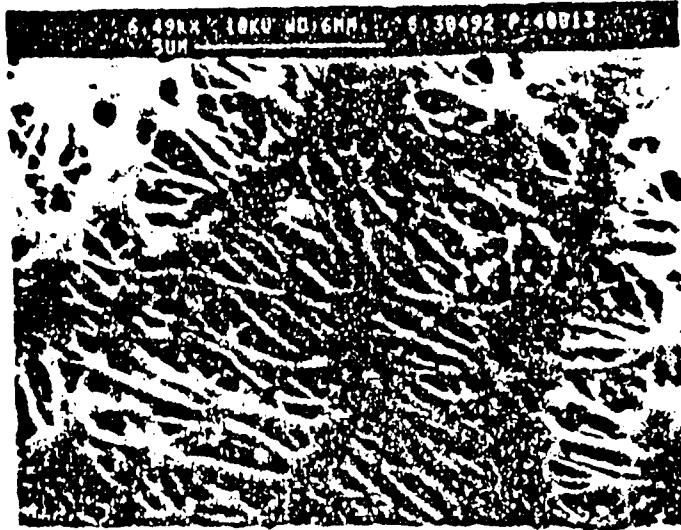


FIG. 8(a) Electron micrograph of TE-35 showing TDN prior to irradiation, magnification level = 6.49 k. TDN: Three Dimensional Network.

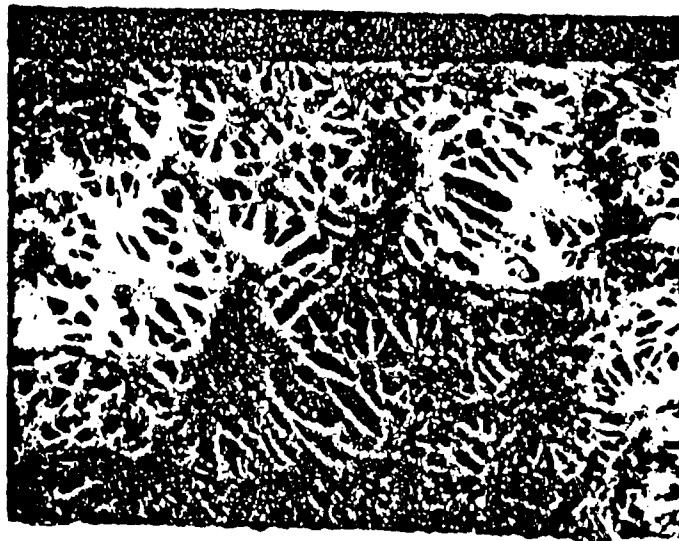


FIG.-8(b) Electron micrograph of TE-35 showing effects of radiation after irradiating up to 3 Mrads; magnification level = 4.97 k.

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