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1995

GOVERNMENT OF INDIA
ATOMIC ENERGY COMMISSION

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BIBLIOGRAPHIC DESCRIPTION SHEET FOR TECHNICAL REPORT

(as per IS : 9400 - 1980)

01	Security classification :	Unclassified
02	Distribution :	External
03	Report status :	New
04	Series :	BARC External
05	Report type :	Technical Report
06	Report No. :	BARC/1995/E/014
07	Part No. or Volume No. :	
08	Contract No. :	
10	Title and subtitle :	Sulphur containing novel extractants for extraction-separation of palladium (II)
11	Collation :	46 p., 6 tabs., 6 figs.
13	Project No. :	
20	Personal author (s) :	(1) J.P. Shukla; (2) S.R. Sawant; Anil Kumar; R.K. Singh
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22	Corporate author(s) :	Bhabha Atomic Research Centre, Bombay-400 085
23	Originating unit :	Radiochemistry Division, Bhabha Atomic Research Centre, Bombay
24	Sponsor(s) Name :	Department of Atomic Energy
	Type :	Government
30	Date of submission :	August 1995
31	Publication/Issue date	September 1995

contd...(ii)

(ii)

40 Publisher/Distributor : Head, Library and Information Division,
Bhabha Atomic Research Centre, Bombay

42 Form of distribution : Hard Copy

50 Language of text : English

51 Language of summary : English

52 No. of references : 52 refs.

53 Gives data on :

60 Abstract : Extraction performance of palladium (II) by sulphur containing extractants has unequivocally established their strong extraction ability toward this thiophilic 'soft' metal. Hence a comprehensive investigative study was initiated by us to examine selective reversible extraction-separation of trace and macro amounts of palladium (II) from both aqueous nitric acid as well as hydrochloric acid media into 1,2-dichloroethane by 1,10-dithia-18 crown-6 (1,10-DT18C6), S₅-pentano-36 (S₅-P-36) and bis (2-ethylhexyl) sulphoxide (BESO) dissolved in toluene. From the study of aqueous phase acidity, reagent concentration, period of equilibration, diluent, strippant and diverse ions, conditions are established from its quantitative and reversible extraction. Recovery of Pd(II) from loaded thiocrown and sulphoxide phase is easily accomplished by using sodium thiocyanate, ammonium thiocyanate, thiourea, sodium thiosulphate and mixture of (2M Na₂CO₃ + 0.5M NH₄OH) (only for BESO) as the strippants. The lack of interference from even appreciable amounts of contaminants like Cs-137, Ru-106, U-233 and Pu-239 may be considered as one of the outstanding advantages of the method. Application of these extractants has been successfully tested for the recovery of palladium from high active waste matrix. The extracted complex from both the thiocrowns has been characterized by elemental analyses and UV-Visible spectra, confirmed to be PdA₂.T (A = NO₃⁻, Cl⁻) from dilute (pH ~ 2) acid solutions while composition of organic species with palladium for the sulphoxide, has also been confirmed to be disolvate of the type Pd(NO₃)₂.2BESO.

70 Keywords/Descriptors : PALLADIUM COMPLEXES ;
HIGH-LEVEL RADIOACTIVE WASTES; INTERFERING ELEMENTS; SOLVENT
EXTRACTION ; CROWN ETHERS; TOLUENE; SULFOXIDES; INFRARED SPECTRA;
PALLADIUM 103; CESIUM 137; DISTRIBUTION FUNCTIONS

71 Class No. : INIS Subject Category : B1620; B1210

99 Supplementary elements :

INTRODUCTION

Solvent extraction has been developed as one of the most versatile technique particularly for the recovery and purification of strategic and precious metals (1,2). Of them, palladium is proving as one of the very important rare metals indispensable for high -technology industries as raw material of catalysts, electronic materials, etc. While the solvent extraction separation of palladium has so far been attempted with a number of extractants (3-8), but most of them contain oxygen or nitrogen as donor atoms, such as hydroxy oximes, carboxylic acids and organophosphorus compounds. Dithiozone (9), diethyl ammonium dithiocarbamate (10), 2-nitroso-1-naphthol-4-sulphonic acid (11), and synergistic mixture of 8-hydroxy quinoline + admixed with tributylphosphite (12), merit mention here. Relatively , little data is available on extractants possessing sulfur as the donor atom. Numerous studies have by now unambiguously established that S-containing extractants are highly effective and selective for Pd (II), classified as 'soft' Lewis acid (13-16). Among such extractants, long chain dialkyl sulfoxides have been gaining ever increasing importance as complexants for many radioactive, nonferrous, transition and post transition metals (17-19). Their extraction capacity for metals is comparable to and even

greater than that of tributyl phosphate(TBP). Little attention seems to have been focused on exploring their extraction characteristics particularly for thiophilic heavy metals such as Pt-group metals. Although bis(2-ethylhexyl) sulfoxide(BESO), a novel sterically hindered branched-chain solvating extractant has proved to be a powerful extractant for U, Pu, Am etc. (20-23), no effort apparently has been directed to explore its complexation behaviour with palladium.

Of late, diverse potential applications of polydentate macrocyclic polyethers("crown ethers") have also drawn much attention (24-29). The liquid-liquid extraction of alkali and alkaline earth cations by the macrocycles has been studied extensively. A thioether group, which is a soft Lewis base, reacts selectively with soft Lewis acids. Thiacrowns has sulphur atoms as coordinating groups and reacts with 'soft' class b metals acids such as Cu(I), Ag(I), Hg(II), Pd(II) etc. As a result, myriad macroheterocycles, having one or more O atoms replaced by N and/or S are reported (30) and explicitly shown to possess greater potentiality for most transition and post transition elements (31,32). In addition, the separation of these metals from each other by solvent extraction might be made more selective primarily by matching the relative sizes of

the metal cation and the intramolecular cavity of a polythioether, the choice of anion for formation of the ion-pair, and the type of the solvent used for extraction. Interest in palladium as the fission product and rare metal is primarily due to its high fission yield and value (33).

Not much data is available so far on the extraction of palladium (II) by macrocycles from aqueous acidic solutions. Neutral sulphur -containing polydentate cyclic ligands such as thiacrowns have an especially high extraction power with respect to palladium and other elements belonging to the 'soft' acid class as defined by Pearson(34). Cyclic ligands (with S,O or N donor atoms) belong to the class of reagents which form so-called host-guest complexes with metal ions. Despite the interesting properties of thiacrowns, little attention seems to have been focused on exploring their extraction characteristics particularly for thiophilic heavy metals. Sekido et al. (35,36) have studied the extraction of Pd(II) into 1,2-dichloroethane(DCE) with 1,4,8,11-tetrathiacyclotetra decane(TTCT) from picrate media at pH 4.6 . Recently, the potential of its extraction as the picrate from chloride media by a substituted dibenzo-1,10-dithia-18-crown-6 has also been demonstrated (37). Nitrogen containing derivatives of dibenzo-18-crown-6 as extracting agents for palladium proved quite ineffective mainly due to extremely slow equilibration rate (38).

Considering its strategic importance, studies have been initiated recently by us particularly to recover palladium from acidic high level radioactive wastes (HLAW) generated from nuclear fuel reprocessing operations containing palladium and other useful fission products (39). Recovery of noble metals such as Ru, Rh and Pd offers an alternative potential source of supply to meet a part of the ever-increasing platinum metals need. As a part of our on going programme to explore the usefulness of sulfoxides and thiocrowns as newer extractants for Pt metals, data on the liquid-liquid extraction of palladium (II) into toluene by bis (2-ethylhexyl) sulphoxide (BESO) and two thiocrowns of varying cavity sizes is presented over a wide range of experimental conditions, mainly from moderately acidic nitrate solutions as encountered in decontaminating HLAW's. Since Pd and other Pt-group metals are usually maintained as their chloro complexes, separation based on the selective extraction of the chloro complexes was also attempted. Effects of important experimental variables such as aqueous phase acidity, time of equilibration, aqueous to organic phase ratios, reagent concentration, strippant and nature of diluent on metal extraction were also optimised. Attempts were also made to understand the nature of the metal ion as well as nitric acid species extracted into the sulfoxide-

diluent or thiocrown-diluent phase. The Pd-S bond formation on the extraction of bivalent palladium with BESO was confirmed by IR spectra of solid complexes. Simple methods for the recycling of these extractants constitute as the noteworthy feature of the whole operation.

EXPERIMENTAL

Apparatus

A Shimadzu UV-160 UV-visible spectrophotometer with 10-mm matched quartz cells was used for recording the absorption spectra of organic extracts. IR spectra of samples in Nujol mulls between CsI discs were recorded using a Pye Unicam 9512 spectrophotometer in the range 4000-200 cm^{-1} .

Reagents

All the chemicals were of A.R. or G.R. grade unless specified otherwise. Analytical grade diluents namely benzene, chloroform, cyclohexane, o-dichlorobenzene, n-dodecane, 1,2-dichloroethane, carbon tetrachloride, solvess-100, xylene and toluene were obtained and used as such. The organic phase and aqueous acidic phase were saturated with each other prior to their use in order to prevent any volume change that may occur during extraction.

S₆-P-36 (I) was kindly gifted by Prof. R.A. Bartsch, Texas Tech Univ., U.S.A. 1,10-DT18C6(II) was procured from Aldrich, USA and used as such. Bis (2-ethylhexyl) sulphoxide

(BESO) (III), procured from Fairfield Chem. Co., U.S.A. was used after treating it with excess of 11 M HNO₃ in order to oxidise any sulphide 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 HClO₄ in dioxane(40). The structures of these extractants are shown in Fig. 1.

Tracer

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 BRIT, BARC, was used throughout the present study. Its radio chemical purity was ascertained by gamma ray spectrometry using Low Energy Photon Scintillation (LEPS) method. Pd-103 was assayed by a well type NaI(Tl) scintillation detector coupled to a single channel analyser. Uranium and plutonium were radioassayed by alpha scintillation counting. Pd-103 and Cs-137 were monitored by a well type NaI(Tl) scintillation detector coupled to a

single channel analyser. Ru-106 was determined by beta scintillation counting.

Distribution Ratio (D_{Pd}) Measurements

Equal volumes (1 ml) of aqueous Pd-103 tracer in desired acid concentration and the extractant dissolved in an organic diluent, were pipetted into a 15 - ml glass stoppered equilibration tube and shaken mechanically for nearly 20 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_{Pd}) defined as $D_{Pd} = \text{total concentration of Pd in the organic phase per ml} / \text{total concentration of Pd in the aqueous phase per ml}$, was thus calculated. From a knowledge of D_{Pd} , volume of aqueous phase (V_a) and volume of organic phase (V_o), the percentage of Pd extraction (% E) was then calculated : $\%E = 100 D_{Pd} / D_{Pd} + (V_a/V_o)$. All the measurements were done at least in duplicate and the agreement in D_{Pd} values obtained was within $\pm 2\%$ with excellent material balance (>95 %).

For studying the back extraction, suitable aliquot from

the loaded organic phase was withdrawn into an equilibration tube and back extracted for about 20 min with same volume of the strippant.

Uptake of nitric acid by various concentrations of BESO (0.05-0.4 M) after contacting with either 0.5 or 2 M HNO₃ was determined alkalimetrically using phenol red as the indicator.

Isolation of Solid Pd(II)-Extractant Complexes

Pd complex was prepared by solvent extraction of aqueous palladium nitrate solution (10 ml, 5 mM) at pH=2 with dodecane (10 ml) containing 10 mM of BESO, The organic layer was dried with anhydrous sodium sulphate, evaporated to dryness and the crude product recrystallized from n-hexane. Similarly, the palladium(II)-thiacrown complex was prepared by liquid-liquid extraction of 5mM aqueous palladium nitrate solution (10 ml) at pH 2 with DCE (10ml) containing 5 mM S₆-P-36. The organic layer was dried with anhydrous sodium sulphate, evaporated to dryness and the crude product recrystallized from hexane.

RESULTS AND DISCUSSION

Kinetic experiments with BESO showed that equilibrium was attained speedily after phase contact for nearly 10 to 15 min and dependent to some degree on the solvent used.

The equilibration time required for quantitative extraction depended on the metal concentration, the aqueous -organic phase volume ratios etc. A shaking time of 30-35 min was adequate for almost quantitative recovery of palladium from aqueous nitrate/chloride solutions.

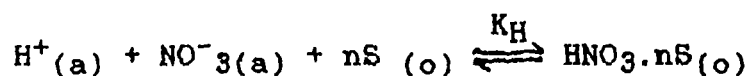
On the other hand, the kinetics of palladium (II) chloride or nitrate extraction with S₆-P-36 (I) and 1,10-DT18C6 (II) is fast, requiring only few minutes (< 5 min) of shaking to reach the observed efficiency. The important observation made in this system is that extraction efficiency is unchanged upon switching nitrate or chloride as the counter anions, and the high efficiency of extraction is not affected at all by the presence of relatively high concentrations (~2M) of hydrochloric or nitric acid. Values of D_{Pd} obtained with thiocrowns or BESO were observed to be virtually independent of the initial palladium concentration investigated in the range ($\sim 10^{-5}M$) indicating that only mononuclear species are involved in the extraction systems. Since the concentration of these extractants particularly BESO (III) (0.2M) is over several orders of magnitude higher than the concentration of Pd in the feed, the effect of change in the Pd concentration is not manifested appreciably on distribution ratios of Pd (D_{Pd}). Also D_{Pd} values, between aqueous acidic solutions and

various thiocrown solutions are as expected from the strong 'soft-soft' interaction of sulphur with divalent palladium. Contrary to this, extraction of contaminants like Pu-239, U-233, Cs-137 and Ru-106 with thiacrowns generally encountered in the recovery of Pd from PUREX process acidic wastes negligibly small (< 6%) due to their 'hard' character. But in the case of BESO, extraction of actinides such as Pu-239 and U-233 at lower molarity of nitric acid is negligible but use of higher molarity of acid may lead to significant extraction of these actinides. So, recovery of palladium from high level acidic wastes was preferred at 0.5M HNO₃.

A preliminary test of the distribution of the thiacrowns I and II between DCE and water was conducted by equilibrating solutions of each macrocycle with large volumes of water, evaporating aliquots of the equilibrated aqueous solutions, and weighing the residue. Extremely poor ($< 10^{-5}M$) aqueous solubility of both these thioethers is as expected primarily owing to weaker ability of the sulphur atoms to engage in hydrogen bonding (41,42). Weak solvation of free thiocrowns in aqueous media has been documented previously (42). The aqueous solubility of BESO-dodecane system was also reported to be very low (43).

Extraction of HNO₃ by S-Containing Extractants

Extraction of nitric acid by BESO or thiacrowns (S) can be represented by the reaction:



(where S represents sulphur containing organic extractant and the subscripts 'a' and 'o' refer to aqueous and organic phases, respectively).

for which the equilibrium constant, K_H , is given by

$$K_H = [\text{HNO}_3.n\text{S}]_{(o)} / [\text{H}^+]_{(a)} [\text{NO}^-_3]_{(a)} [\text{S}]^n_{(o)}$$

assuming that the activity coefficients of the various species do not change significantly in the concentration ranges used.

Taking logarithms on both sides of above equation and rearranging, it can be shown that

$$\log[\text{H}^+]_{(o)} - 2\log[\text{H}^+]_{(a)} = \log K_H + n \log[\text{S}]_{(o)}$$

where $[\text{H}^+]_{(o)} = [\text{HNO}_3.n\text{S}]_{(o)}$, and

$$[\text{H}^+]_{(a)} = [\text{NO}^-_3]_{(a)}$$

$[\text{H}^+]_{(a)}$ was evaluated from the value of $[\text{H}^+]_{(o)}$ and the known dissociation constant(23.5) of nitric acid (44).

$[S]_{(o)}$ was computed from the initial total S and the value of $[H^+]_{(o)}$. A plot of $\log [H^+] - 2 \log [H^+]_{(a)}$ Versus $\log [S]_{(o)}$ should be a straight line with slope, n, if the species extracted is $HNO_3 \cdot nS$. Sulphoxide, BESO considerably extract nitric acid from aqueous solutions. Nitric acid formed a solvated complex of 1:1 composition in the diluent phase where one molecule of the acid is required for one molecule of the extractant. This is in accord with our earlier observations with several other dialkyl sulfoxides (18,19). Value of K_H for $BESO \cdot HNO_3$ is thus found to be 0.41. On the other hand, experiments carried out with both thiocrowns, I and II, indicated poor extraction of nitric acid from aqueous solutions.

Variation of D_{Pd} Values With HNO_3/HCl Concentration

Pd-BESO System

To assess the dependence of the extraction capacity on the aqueous phase acidity, the extractability of palladium (II) from 8 M HNO_3 down to pH solutions into toluene by BESO from unbuffered aqueous nitrate solutions was systematically studied (Table 1). It may be seen that lowering the acidity from 8 M to 0.01 M caused an increase in percentage extraction from 72 to 82 % by 0.05 M BESO. With enhanced extractant concentration to 0.2 M, maximum extraction was accomplished at a lower acidity of about 0.01M (pH⁻²) to 0.5

M HNO₃. Therefore a good extraction efficiency can be achieved preferably at low acidity.

Extraction efficiency was noted to be unchanged by employing nitrate or chloride as the anions and the high efficiency of extraction was not affected at all by the presence of relatively high concentrations (~2 M) of nitric acid. The degree of extraction of Pd(II) with 0.2 M BESO in toluene was independent of the HNO₃ or HCl concentrations in the range 0.5-5 M though increase in acidity from 0.01 (pH=2) to 1.0 M HCl drastically reduced the % E from 94 % to 31 %. The shaking time necessary for extraction of Pd from 5 M HNO₃ was not greater than that needed with 0.5 M HNO₃. Also the D_{Pd} values, between aqueous acidic solutions and various BESO-diluent phases were generally high which was as expected from the strong 'soft - soft' interaction of sulfur with divalent palladium.

Pd-Thiacrown System

To evaluate the effect of the aqueous phase acidity, the extractability of palladium from 6 M HCl down to pH solutions (ca. 0.01 M) into DCE by compound I and compound II from unbuffered aqueous chloride/nitrate solutions was systematically studied. It may be seen that lowering the acidity from 6 M to 0.01 M caused an increase in percentage extraction from 69 to 86 % by 0.005 M S₆-P-36 (Table 2).

With enhanced extractant concentration to 0.01 M, maximum extraction was accomplished at a lower acidity of about pH 2 (0.01 M) to 0.5 M HCl or HNO₃. Similar increase in % E was noted with 1,10-DT18C6 on reducing aqueous acidity. Therefore a good extraction efficiency can be achieved preferably at low acidity.

Similarly, in case of both the macroheterocycles, the metal extraction was not affected by employing nitrate or chloride as the anion, as in case of BESO. The degree of extraction of palladium(II) with 0.005 M S₆-P-36(I) or 1,10-DT18C6 (II) in DCE showed little acid dependence on using nitric acid or hydrochloric acid in the concentration range of 0.5-5 M. The shaking time necessary for extraction of Pd from 5 M HCl was not greater than that needed with 0.5 M HCl.

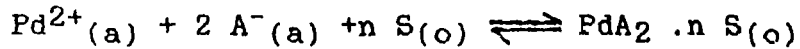
Variation of D_{Pd} Values With Extractant Concentration

Pd-BESO and Pd-Thiacrown System in HNO₃/HCl Media

The extractability of Pd(II) from 2 M HNO₃ into toluene by BESO (0.05 to 0.5 M) and thiacyclones, S₆-P-36 (0.001 to 0.01M) and 1,10 DT18C6 (0.0025 to 0.01M) increased with increasing extractant concentration. A 0.2 M BESO or 0.01M S₆-P-36 solution extracted more than 95 % of 1 mg/ml of Pd(II) in a single step. Likewise 0.05M 1,10 DT18C6 solution

extracted more than 90% of Pd(II).

Extraction of Pd(II) by BESO and thiocrowns from nitrate/ chloride (lower concentration of HCl i.e. < 0.01 M) solutions can be represented by the reaction,



where $\text{A}^{-} = \text{NO}_3^{-}$ or Cl^{-} ions,

for which the equilibrium constant, K_{ex} , is given by

$$K_{\text{ex}} = \frac{[\text{PdA}_2 \cdot n \text{S}]_{(o)}}{[\text{Pd}^{2+}]_{(a)} [\text{A}^{-}]^2_{(a)} [\text{S}]^n_{(o)}}$$

where the distribution ratio, D_{Pd} , of palladium is

$$D_{\text{Pd}} = \frac{[\text{PdA}_2 \cdot n \text{S}]_{(o)}}{[\text{Pd}^{2+}]_{(a)}}$$

and assuming $[\text{A}^{-}]$ is constant and taking logarithm on both side of the equation and rearranging, we get

$$\log D_{\text{Pd}} = \log K_{\text{ex}} + n \log [\text{S}] + 2 \log [\text{A}^{-}]$$

The plot of $\log D_{\text{Pd}}$ Vs. $\log [\text{BESO}]_{\text{free}}$ in organic phase is given in Fig 2. The line drawn through the experimental points gave a slope n , of + 2 by maintaining the extractant at low concentrations in the range between 0.05 and 0.2 M.

The slope of nearly +2 obtained for Pd(II) indicated that the extracted species in the sulfoxide diluent phase would be predominantly of the type $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{BESO}$. Similar experiments carried out with varying extractant

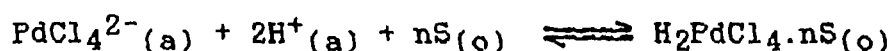
concentration in HCl medium (ca. $0.01M$ HCl) indicated the species of type, $PdCl_2 \cdot 2BESO$. This is in accord with those obtained for palladium extraction by DOSO from HCl or HNO_3 aqueous media (45). Since BESO is a neutral extractant, it follows that its role in the extraction is solely solvation of the palladium complex extracted, which itself must therefore be neutral. Similarly, the plot of $\log D_{Pd}$ Vs $\log[S_6-P-36]$ and $\log[DT18C6]$ in organic phase at fixed $2M$ HNO_3 is drawn in Fig. 3. The line drawn through the experimental points gave a slope equal to $+1.1$ for S_6-P-36 and $+0.9$ in case $1,10$ DT18C6. Here a perfect linearity with slope equal to approximately $+1$ is obtained which indicates the formation of the complexes of 1:1 composition; an ion-pair of the type, $[Pd(T)^{2+} \cdot 2NO_3^-]$, is presumably formed in the organic phase. Likewise, experiments carried out in HCl medium (ca. $0.01M$ HCl) with varying extractant concentration suggest the species of type $[Pd(T)^{2+} \cdot 2Cl^-]$.

Pd-BESO and Pd-Thiacrown System (Higher HCl Concentrations)

The extractability of Pd(II) from aqueous hydrochloric acid ($< 2M$ HCl) medium into DCE by S_6-P-36 (0.001 to 0.01 M), $1,10$ DT18C6 (0.0025 to 0.01) and BESO/ toluene (0.05 to $0.5M$) increased with increasing extractant concentration.

In the range where Cl^- ion is larger than $0.2M$, bivalent palladium predominantly exists as the species of type

PdCl_4^{2-} in the aqueous solution (46-47). D_{Pd} values are lower at higher HCl concentrations owing to inextractable nature of PdCl_4^{2-} species formed by sulphur containing organic extractants which resulted in forming unstable complexes of palladium. The extraction of Pd(II) by a thiocrown /BESO (S) from hydrochloric acid medium thus can be represented by the reaction



(subscripts 'a', 'o' refer to aqueous, organic phase respectively).

for which the equilibrium constant, K_{ex} , is given by

$$K_{\text{ex}} = [\text{H}_2\text{PdCl}_4.n\text{S}]_{(\text{o})} / [\text{PdCl}_4^{2-}]_{(\text{a})} [\text{H}^+]^2_{(\text{a})} [\text{S}]_{(\text{o})}^n$$

where the distribution ratio, D_{Pd} of palladium is

$$D_{\text{Pd}} = [\text{H}_2\text{PdCl}_4.n\text{S}]_{(\text{o})} / [\text{PdCl}_4^{2-}]_{(\text{a})}$$

Assuming $[\text{Cl}^-]$ is constant and taking logarithm on both side of the equation (1) and rearranging, we get

$$\log D_{\text{Pd}} = \log K_{\text{ex}} + n \log [\text{S}] + 2 \log [\text{H}^+]$$

The plots of $\log D_{\text{Pd}}$ versus $\log[\text{BESO}]$, $\log(\text{S}_6\text{-P-36})$ and $\log(\text{DT18C6})$ are drawn at fixed aqueous phase acidity of 2M HCl. The line drawn through the experimental points gave a

slope equal to 1.8, 0.9 and 1.2 respectively. The slope, 1.8, obtained for BESO, readily indicated a solvated species of type, $H_2PdCl_4 \cdot 2BESO$. In case of thiacrowns, slope equal to approximately +1 is obtained which suggests the formation of the complexes of 1:1 composition; an ion-pair of the type, $[Pd(T) \cdot Cl_4^{2-} \cdot 2H^+]$, is presumably formed in the organic phase. This is in accord with conclusions drawn by several other workers on the basis of previous studies pertaining to Pd(II) extractions with analogous polythiaethers.

The ionic radii of bivalent palladium are reported to be 0.64 Å and 0.86 Å corresponding to its 4 and 6 coordination numbers respectively (48). The cavity radius of both the thiacrowns, estimated by us following CPK -space filling models, works out to be 1.3-1.4 Å for 1,10-DT18C6 and 4.8- 4.9 Å for S₆-P-36. Preliminary experiments revealed that Pd²⁺ cation fits in the cavity of both the thiacrowns well. The difference in their extraction efficiency of palladium may be controlled by factors other than the cavity size alone. Consequently in this study , the cavity radius of these extractants seems to be of relatively minor importance, the main factor being the affinity of Pd²⁺ ion for the 'soft' sulphur atoms in the macroring.

Influence of Organic Diluents

Extractability and selectivity for solvent extraction of metals by organic extractants are greatly affected by the nature of organic solvents. To study the influence of several typical and commonly available aliphatic and aromatic organic solvents upon the efficiency of palladium extraction by BESO (III), extractability of palladium from 2 M HNO_3 was investigated with 0.2M BESO dissolved in varying diluents. Table 3 summarizes the data concerning the effect of diluents on the extraction of palladium. Non-polar diluents like xylene yielded less extraction compared to polar diluents, but polarizable solvents like benzene, toluene, gave remarkably high metal extraction. Among halogenated hydrocarbon solvents, 1,2 - dichloroethane and o-dichlorobenzene gave high metal extraction than chloroform. High D_{Pd} may be associated with the low dielectric constants of aliphatic hydrocarbons which favour the formation of solvated neutral Pd(II)-BESO complex. Straight lines with slope of nearly +2 obtained from plot of $\log D_{\text{Pd}}$ Vs. $\log[\text{BESO}]_{\text{free}}$ for benzene, dodecane and toluene confirm that Pd^{2+} is extracted essentially as 1:2 ion pair irrespective of organic phase medium. Toluene was however, selected as the diluent throughout the present study owing to its relative less aqueous solubility and easy availability.

To evaluate the effect of organic solvent variation upon the efficiency of palladium extraction with thiocrowns, the extractability of Pd(II) from aqueous acidic solutions by I and II dissolved into different organic solvents was examined (Table 4). The changes in extraction due to changes in solvent are small. The extraction of palladium was thus found to be practically independent of the nature of the organic solvents tested here.

Volume Ratio Studies

A study was carried out to assess whether large aqueous to organic ratios could be tolerated for the successful extraction of palladium by compd. I and compd. II under the optimum conditions. The results show that for aqueous to organic ratios up to 10:1, Pd(II) could be extracted at >95 % efficiency in a single step into DCE by 0.01 M S₆-P-36 ; and with 0.05 M 1,10-DT18C6 close to 90 % of this cation was extracted at a sufficiently large volume ratio of 20 to 1 under similar conditions. Following the standardized procedure, as little as 5.6 ug/ml of palladium (II) was recovered in a single extraction from 20 ml of the aqueous chloride solution (1M) with only 1 ml of S₆-P-36 (0.005M) and 1,10-DT18C6 (0.01M) employing DCE as the diluent. Data on loading of the organic phase containing 0.2M BESO in toluene with Pd(II) with different aqueous to organic (a:o)

ratios revealed that it could be extracted at > 90% efficiency at a:o = 10:1 in a single step; close to 80 % of this cation was extracted at a sufficiently large volume ratio of 20 to 1 under optimum conditions.

Back Extraction of Palladium

In any solvent extraction process, it becomes almost imperative to back extract the metal from the loaded organic phase. As the values of D_{Pd} with BESO were quite high from low to high concentrations of nitric acid and so its stripping becomes almost impractical with nitric acid solutions alone (Table 5). Among many strippants tried, a mixture of [2M $Na_2CO_3 + 0.5M NH_4OH$] was found to be quite effective (>95%) for stripping palladium in a single equal volume contact. The stripping of palladium was around 30 to 50% even with three equal volume contacts with solutions of 2M each of sodium carbonate and ammonia used separately. Stripping was almost complete (>95 %) within 10 to 15 min (o/a =1) with 0.2 M or higher concentrations of sodium thiosulphate.

Since the values of D_{Pd} for thiocrowns were quite high from 0.5 -6M concentrations of HCl or HNO_3 , its stripping thus became quite difficult with such acidic solutions (Table 5) alone. Pd(II)-thiocrown (S_6-P-36) complex may be very strong, so the complexing agents like

EDTA(0.2 to 0.5M) or oxalic acid(0.2M) fail to recover palladium from loaded organic phase. On the otherhand, thiacrown, 1,10 DT18C6 afforded >94% stripping with 0.5M EDTA owing to less stable complex with Pd(II). From Table 5, it is evident that on extraction from chloride media, stripping was almost complete (>95%) within 10 to 15 min (O/A=1) with 2M or higher concentrations of Na₂S₂O₃ and Mg₂S₂O₃. Other strippants removing more than 90% of the palladium studied include 0.2 M thiourea and 0.2 M or higher concentrations of NaSCN and NH₄SCN.

Characterization of the Extracted Complex

Pd-BESO System

The extracted disolvate complex is a dark brown complex, which is stable in air and not deliquescent. It is easily soluble in several common aliphatic and aromatic solvents like n-hexane, benzene, toluene including dodecane and halogenated hydrocarbons e.g. CH₂Cl₂, CHCl₃, CCl₄ and the solutions are also generally stable, but it is only slightly soluble in methanol. The complex is negligibly soluble in water and readily decomposes depositing palladium. Fig 4 depicts the absorption spectra of Pd(II) complex dissolved into toluene which is essentially similar to that extracted with TBP/toluene as the extractant. This indicate the similarity of the species involved.

The results of elemental analyses are listed below, which shows that the extracted complex has the composition:

Complex	Colour		C(%)	H(%)	N(%)	Pd(%)
Pd(NO ₃) ₂ .2BESO	Dark brown	Calc.	49.3	8.8	3.6	13.7
		Found	49.5	8.6	3.7	13.8

Pd(NO₃)₂.2BESO, which is consistent with the extracted complex in the organic phase. IR spectra, taken as Nujol mulls, show the direct proof of the BESO molecule's coordination to palladium through sulfur. A frequency shift (s) of 190 cm⁻¹ in S=O stretch towards higher frequency was observed in palladium(II) nitrate complex with BESO which definitely suggests a strong coordination through sulfur.

Pd-Thiacrown System

The extracted monosolvate complex is a dark brown complex, which is stable in air and not deliquescent. It is easily soluble in several common aliphatic and aromatic solvents like n-hexane, benzene, toluene including dodecane and halogenated hydrocarbons e.g. CH₂Cl₂, CHCl₃, CCl₄ and the solutions are also generally stable.

Figs. 5 and 6 depict the absorption spectra of Pd(II) species extracted from 0.5 M HNO₃ by TBP, S₆-P-36 and 1,10-

DT18C6 employing DCE as the diluent. The spectra are similar except a slight bathochromic shift of the peaks in the spectra of Pd(II) [260 → 300 nm] with both the thiocrowns.

The results of elemental analyses are listed below, which shows that the extracted complex has the composition:

Complex	Colour		C(%)	H(%)	N(%)	Pd(%)
Pd(NO ₃) ₂ .T	Dark brown	Calc.	42.71	7.17	3.32	12.61
		Found	42.73	7.16	3.33	12.69

Pd(NO₃)₂.T, which is consistent with the extracted complex in the organic phase.

Palladium Recovery From Synthetic Waste Solution

Extractability of Pd(II) from a process effluent containing Pu(IV) and fission products such as Ce-144, Ru-106 and Cs-137 into dichloroethane solutions of S₆-P-36 or BESO/toluene was examined. From the data summarized on thiocrown/BESO in Table 6, it is quite clear that problematic actinides like Pu(IV) and Am(III) and fission product contaminants were poorly extracted (<10%). More than 90% of Pd could be recovered in single contact (O/A=1) from 0.5M (HNO₃ or HCl) aqueous medium into DCE by 0.01M S₆-P-36 02 or 0.2M BESO/toluene. Finally, Pd could be

readily back extracted almost completely (> 98%) from the loaded thiacrown phase with an aqueous sodium thiosulphate (ca. 0.2M) solution. It is thus proved that Pd can be efficiently and reversibly extracted from HLAW solutions.

In addition to the studies cited above, potential applications of di-n-octylsulfoxide (49), alpha-benzoinoxime (50,51), and more recently CYANEX 471X (52), tested in our laboratory from the liquid-liquid extraction of palladium from dilute acidic nitrate solutions, have given very encouraging results.

CONCLUSIONS

A novel method for palladium recovery by sulphur containing extragents from aqueous acidic nitrate and chloride solutions has been developed. Feasibility of this method in its removal from high level radioactive waste is also established. The thiacrown-Pd(II) extraction system is of particular value to the analytical chemist since it offers a rapid, simple, and considerably efficient method of concentrating palladium from aqueous solutions containing only trace quantities of the element. The organic phase containing palladium can be used directly in AAS determinations in which analyst can benefit from both the solvent extraction and enhanced sensitivity of palladium. The high extraction efficiency for palladium in complex

aqueous matrices suggest potential applications of the thiocrowns in analytical chemistry as well as hydrometallurgy, which involves solvent extraction or membrane transport of the Pt-metals.

Acknowledgements

The authors wish to thank and Dr. R.H. Iyer, Head, Radiochemistry Division, Shri M.K. Rao, Director, Fuel Reprocessing Group, and Shri. M.K.T. Nair, Director, Nuclear Waste Management Group, Shri D.D. Bajpai and Shri. N. Varadarajan, PREFRE for their keen interest in this work.

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TABLE 1

Extraction of Palladium (II) into Toluene by Bis (2-ethylhexyl) Sulfoxide as a Function of Aqueous Phase Acidity

Initial Pd concentration : ca. 10^{-4} M Pd-103 tracer
 Volume ratio, O/A : 1
 Temperature : 23-25 °C (Room temp.)

		BESO , M							
		0.01		0.05		0.20		0.20	
HNO ₃						HCl			
(M)	D _{Pd}	%E	D _{Pd}	%E	D _{Pd}	%E	(M)	D _{Pd}	%E
0.01	0.89	47.1	4.49	81.8	17.62	94.6	0.01	16.42	94.3
					12.46 ^a	92.6		11.66 ^b	92.1
0.5	0.85	46.0	4.43	81.6	16.90	94.4	0.5	6.48	86.3
					12.35 ^a	92.5		5.73 ^b	85.1
1.0	0.83	45.4	4.40	80.5	16.53	94.3	1.0	0.44	30.6
2.0	0.77	43.5	4.02	80.1	13.44	93.1	2.0	0.42	29.6
3.0	0.61	37.9	3.55	78.0	13.02	92.9	3.0	0.40	28.6
4.0	0.51	33.8	3.25	76.4	12.84	92.8	4.0	0.39	28.1
5.0	0.42	29.6	3.11	75.7	11.13	91.8	5.0	0.38	27.5
6.0	0.33	24.8	3.02	75.1	11.02	91.7	6.0	ND	ND
7.0	0.25	20.0	2.72	73.1	10.81	91.5	7.0	ND	ND
8.0	0.19	15.9	2.55	71.8	10.60	91.4	8.0	ND	ND

ND, Not determined

a, Values correspond to those obtained with ca. 1 mg/ml Pd dissolved in HNO₃ and spiked with tracer Pd-103.

b, Values correspond to those obtained with ca. 1 mg/ml Pd dissolved in HCl and spiked with tracer Pd-103.

TABLE 2

Extraction of Palladium (II) into 1,2-Dichloroethane by S₆-P-36 as a Function of Aqueous Phase Acidity

Initial Pd concentration : ca. 10^{-4} M Pd-103 tracer
 Volume ratio, O/A : 1
 Temperature : 23-25 °C (Room temp.)

HNO ₃ (M)	S ₆ -P-36, M									
	0.005		0.01		HCl (M)	0.005		0.01		
	D _{Pd}	% E	D _{Pd}	% E		D _{Pd}	% E	D _{Pd}	% E	
0.01	6.23	86.1	13.58	93.1	0.01	6.32	86.3	13.05	92.9	
			12.44 ^b	92.6				13.22 ^c	93.0	
0.5	5.89	85.5	12.56	92.6	0.5	5.78	85.3	12.06	92.3	
			12.91 ^b	92.8				12.12 ^c	92.4	
1.0	5.72	85.1	11.99	92.3	1.0	5.65	85.0	11.89	92.2	
2.0	4.99	83.3	9.64	90.6	2.0	3.82	79.3	7.99	88.9	
3.0	3.84	79.3	8.33	89.3	3.0	3.24	76.4	7.14	87.7	
4.0	3.25	76.5	7.26	87.9	4.0	2.99	74.9	6.61	86.9	
5.0	2.97	74.8	5.21	83.9	5.0	2.66	72.7	4.53	81.9	
6.0	2.22	68.9	3.75	78.9	6.0	1.99	66.6	3.29	76.4	

- a. Initial Pd concentration ca. 10^{-4} M Pd-103 tracer; aqueous to organic volume ratio, 1 ; temperature = 23-25°C (room temperature).
- b. Values correspond to those obtained with ca. 1 mg ml⁻¹ Pd dissolved in HNO₃ and spiked with tracer Pd-103
- c. Values correspond to those obtained with ca. 1 mg ml⁻¹ Pd dissolved in HCl and spiked with tracer Pd-103.

TABLE 3

Influence of Organic Diluents on the Extraction of Pd(II) From Aqueous Nitric Acid Medium by BESO

Extractant : 0.2 M BESO, dissolved in an organic diluent

Aqueous phase : 2 M HNO₃ acidity

Diluent	Dielectric constant ^{a,b}	D _{Pd}	%E
Benzene	2.28	7.44	88.2
n-Dodecane	2.02	12.00	92.3
Chloroform	4.81	1.96	66.2
Carbon tetra chloride	2.24	9.22	90.2
Cyclohexane	2.10	8.00	88.8
O-Dichloro-benzene	9.93	7.32	88.0
1,2-Dichloro-ethane	10.36	4.98	83.3
Solvesso-100	—	10.00	90.9
Toluene	2.38	13.41	93.1
Xylene	2.27	3.74	78.9

a, T. Sekine, Y. Hasegawa, Solvent Extraction : Fundamental and Application, Marcel Dekkar, New York, p. 48-50 (1977)

b, C. Reichardt, Solvent Effects in Organic Chemistry, Verlag Chemie, New York, pp.270-272 (1979).

TABLE 4

Influence of Organic Diluents on the Extraction of Pd(II) From Aqueous Hydrochloric Acid Medium by Thiocrowns

Extractant : 0.005 M S₆-P-36 or 1,10-DT18C6,
dissolved in an organic diluent

Aqueous phase acidity: 1 M HCl

Diluent	Dielectric constant ^{a, b}	1,10-DT18C6		S ₆ -P-36	
		DPd	E (%)	DPd	E (%)
Benzene	2.28	0.18	15.3	4.90	83.1
Chloroform	4.81	0.22	18.0	5.39	84.4
Cyclohexane	2.10	0.19	16.0	4.81	82.8
O-Dichloro- benzene	9.93	0.21	17.4	5.01	83.4
1,2-Dichloro- ethane	10.36	0.28	21.9	5.65	85.0
n-Dodecane	2.02	0.23	18.7	5.11 (6.3) ^c	83.6 (87.6) ^c
Toluene	2.38	0.11	9.9	5.32	84.2
Xylene	2.27	0.16	13.8	4.53	81.9

a, T. Sekine, Y. Hasegawa, Solvent Extraction : Fundamental and Application, Marcel Dekkar, New York, p. 48-50 (1977)

b, C. Reichardt, Solvent Effects in Organic Chemistry, Verlag Chemie, New York, pp.270-272 (1979).

c, Values obtained by adjusting the aqueous phase acidity =2M HNO₃.

TABLE 5

Back Extraction of Palladium (II) From Loaded Organic Phase

Extractant : 0.005 M thiocrown,
0.2 M BESO
Volume ratio , org/aq : 1

Strippant ^a	Extractant					
	1,10-DT18C6		S ₆ -P-36		BESO	
	D _{Pd}	Back extd (%)	D _{Pd}	Back extd (%)	D _{Pd}	Back Extd (%)
HNO ₃ (8)	2.29	30.4	-	-	16.50	5.7
HCl(8)	2.36	29.8	-	-	16.30	5.8
Oxalic acid (0.5)	1.47	40.5	-	-	---	---
EDTA(0.5)	0.06	94.3	-	-	---	---
NaSCN(2)	0.16	86.2	0.11	90.1	---	---
NH ₄ SCN(2)	0.12	89.3	0.14	87.3	---	---
Thiourea (0.5)	0.05	95.3	0.06	94.3	---	---
Mg ₂ S ₂ O ₃ (0.2M)	0.04	96.2	0.05	95.3	---	---
Na ₂ S ₂ O ₃ (0.5)	0.02	98.0	0.01	>99.0	0.01	>99.0
Na ₂ CO ₃ (2M)	----	---	---	----	2.35	29.9
Ammonia(2M)	----	---	---	----	1.0	50.0
Na ₂ CO ₃ (1M)+ NH ₄ OH(0.5M)	----	---	----	----	0.43	69.9
Na ₂ CO ₃ (2M)+ NH ₄ OH(0.05M)	----	---	----	----	0.25	80.0
Na ₂ CO ₃ (2M)+ NH ₄ OH(0.5M)	----	---	----	----	0.05	95.2

a, Aqueous solutions of strippants were made directly by measuring the volumes approximately; concentrations are given in brackets.

TABLE 6

Recovery of Palladium from Acidic Process Effluents using S₆-Pentano-36 /DCE and BESO/Toluene as the Extractants

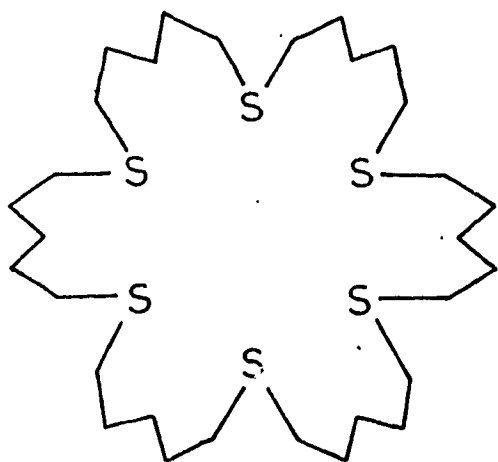
Feed : Process effluent in 0.5 M HNO₃
 Extractant concentration : 0.01 mol dm⁻³ S₆-P-36 / DCE or 0.2 M BESO/toluene
 Strippant : 0.2 M Na₂S₂O₃

Process contaminants	F.P. activity ^a in the feed (uci dm ⁻³)	F.P. activity in the organic phase		Recovery (%)	
		(uci dm ⁻³)		-----	
		S ₆ -P-36	BESO	S ₆ -P-36	BESO
Ru-106	57.2	3.4	2.2	5.9	3.9
Cs-137	2513.2	125.1	137.2	5.0	5.5
Sb-125	23.3	1.0	1.5	4.3	6.4
Ce-144	46.4	1.2	1.7	2.6	3.7
Pd-103	1.0 ^b	0.93 ^b	0.91 ^b	93.0	91.0
Pu(IV)	5.0 ^c	0.2 ^c	0.3 ^c	4.0	6.0
Am(III)	5.2x10 ^{-2c}	1.0x10 ^{-3c}	1.5x10 ^{-3c}	1.9	2.9

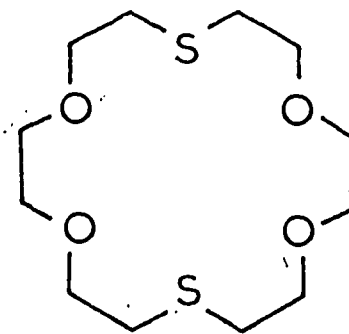
a, Activity of fission products was estimated by mutichannel analyser using a High Purity Germanium detector (HPGe).

b, Values are expressed in g dm⁻³

c, Values are expressed in mg dm⁻³.



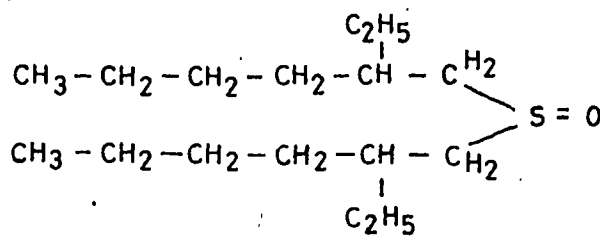
S6 - pentano - 36
(S6-P-36)



1,10-Dithia 18-Crown 6
(1,10-DT18C6)

I

II



Bis (2-ethylhexyl) Sulphoxide
(BESO)

III

FIG - 1. Structural formulae of BESO and thiacrowns used in this work.

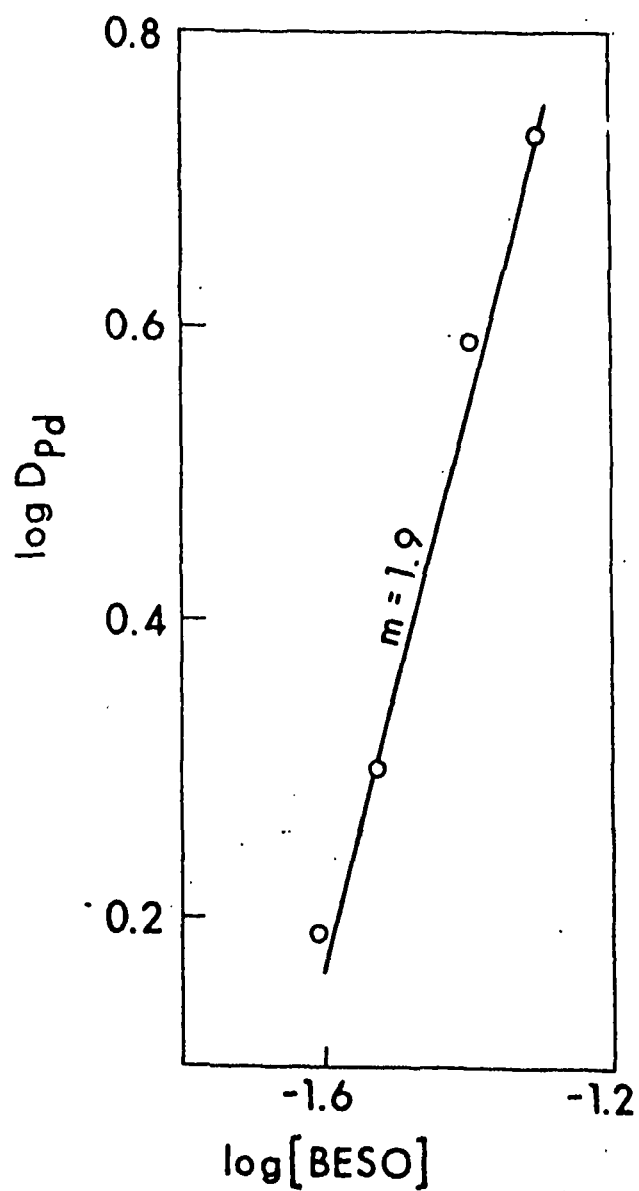


FIG. -2 Plot of extraction of Pd(II) into toluene by BESO from 2 M HNO_3 as a function of initial extractant concentration.

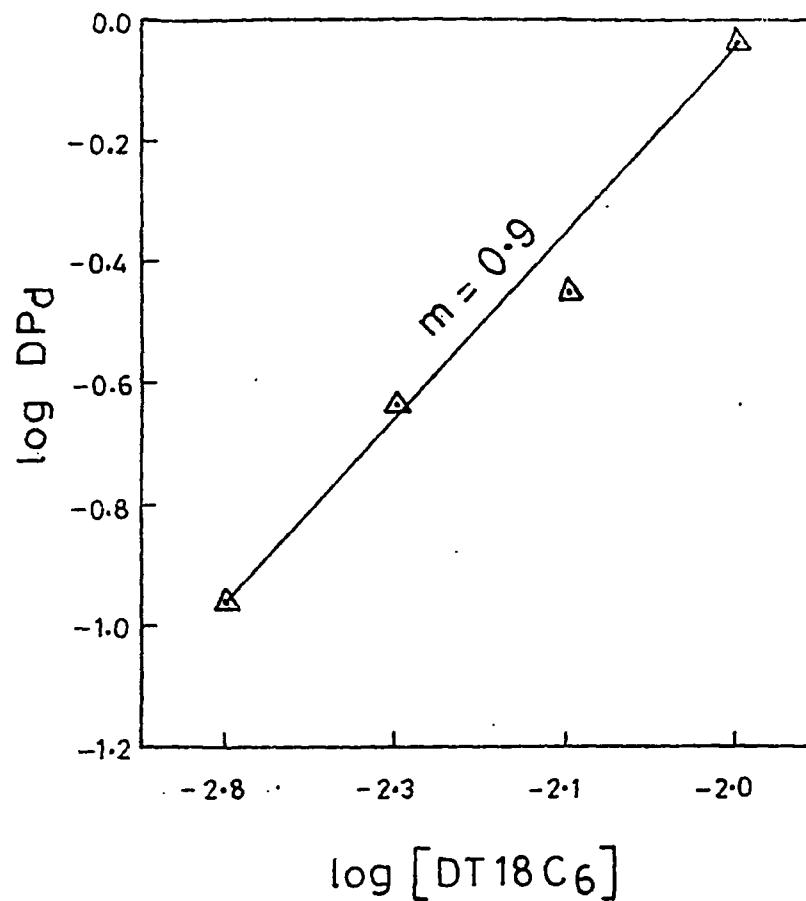
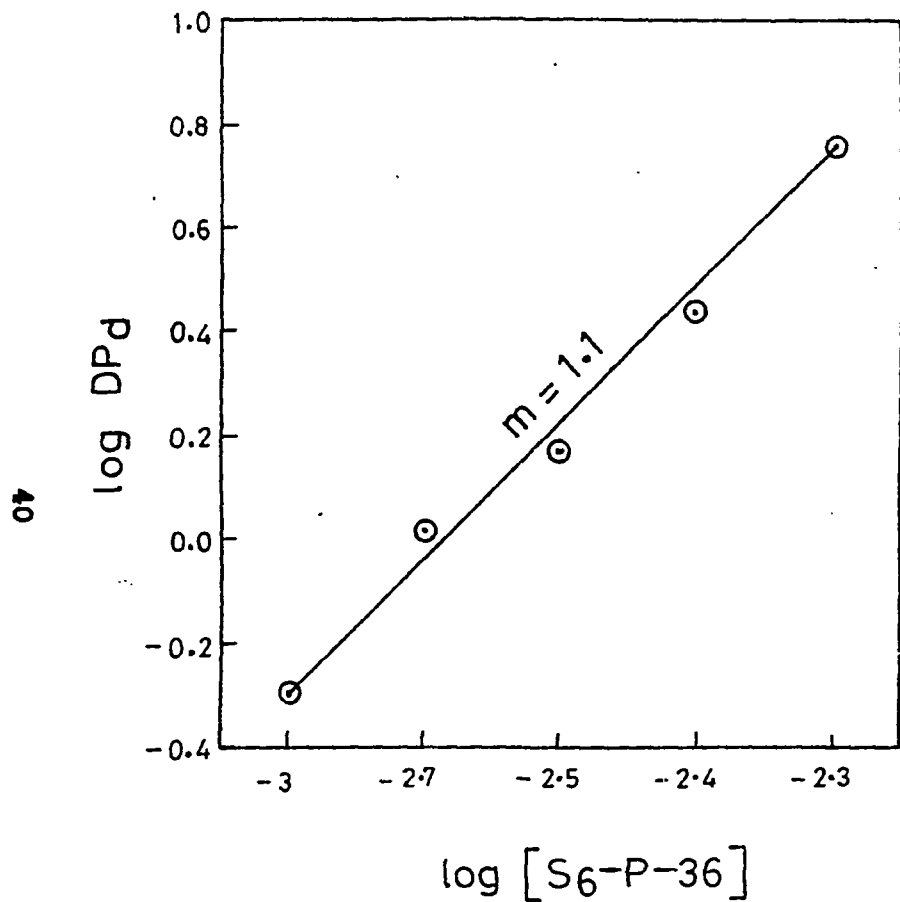


FIG.-3 Plot of extraction of Pd(II) into DCE by thiocrowns, S₆-P-36 and 1,10 DT18C₆ from 2 M HNO₃ as a function of initial extractant concentration.

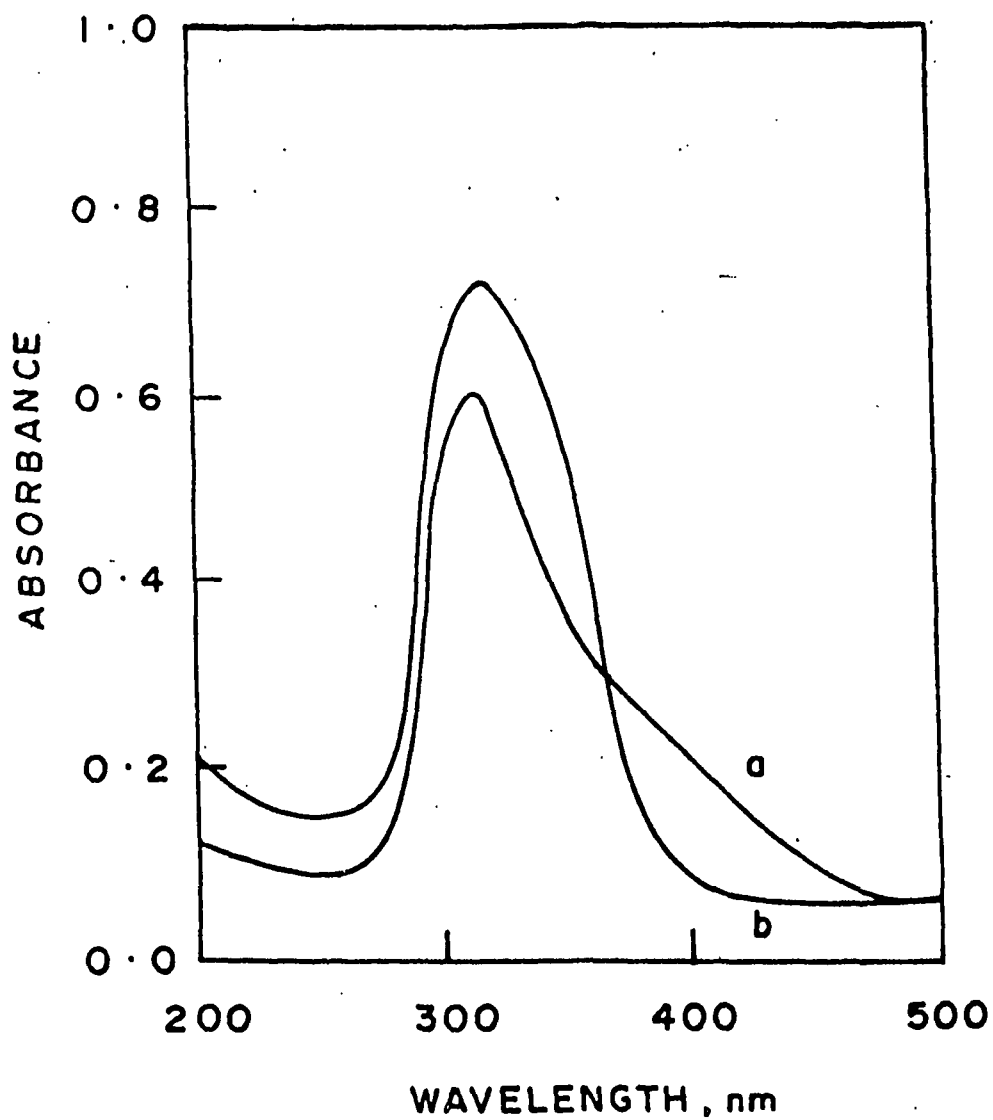


FIG.- 4 Absorption spectra of palladium (II) nitrate extracted from 0.5 M HNO_3 aqueous medium by: a) 30% TBP/toluene; b) 0.2 M BESO/toluene.

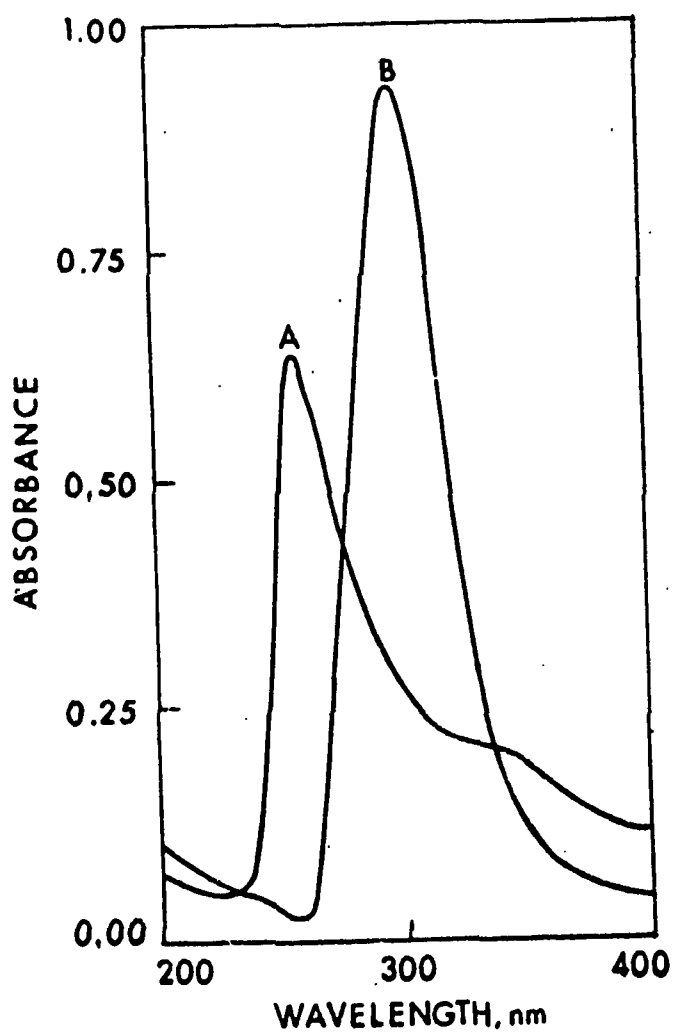


FIG.- 5 Absorption spectra of palladium (II) nitrate extracted from 0.5 M HNO_3 aqueous medium by:
a) 30% TBP/DCE; b) 0.01 M $\text{S}_6\text{-P-36}$ / DCE

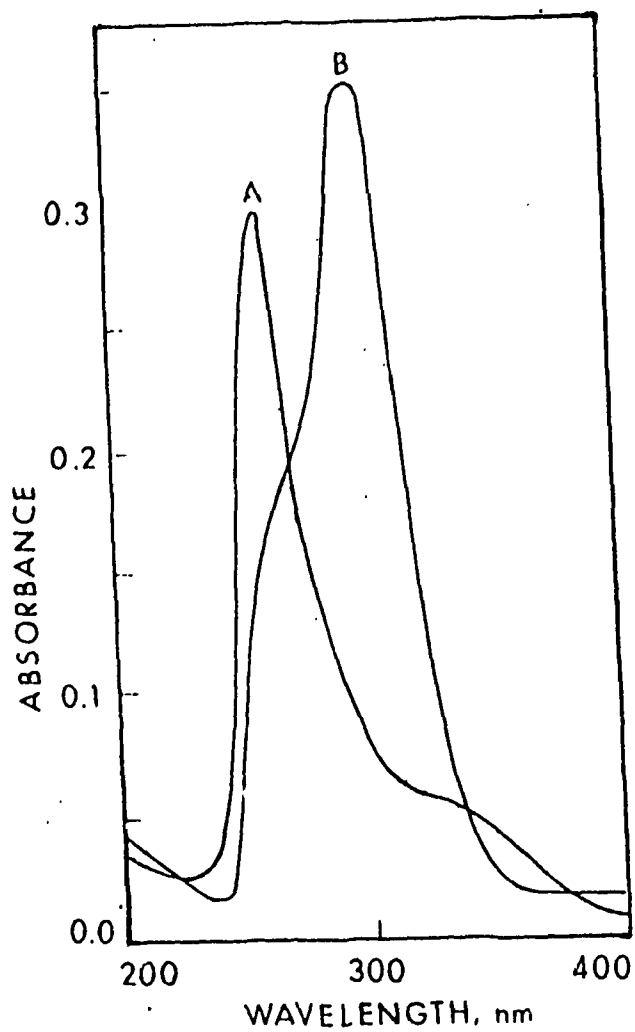


FIG.- 6 Absorption spectra of palladium (II) nitrate extracted from 0.5 M HNO_3 aqueous medium by:
a) 30% TBP/DCE; (b) 0.01 M 1,10-DT18C6/DCE

