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Separation and recovery of palladium(II) from nitrate solutions using dithiodiglycolamide (DTDGA) derivatives as novel extractants

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ABSTRACT

The feasibility of using four novel dithiodiglycolamides (DTDGA) derivatives, namely, N,N,N′,N′-tera-octyl-dithiodiglycolamide (TODTDGA), N,N,N′,N′-tetra-2-ethylhexyl-dithiodiglycolamide (TEHDTDGA), N,N,N′,N′-tetra-n-hexyl-dithiodiglycolamide (THDTDGA), and N,N,N′,N′-tetra-iso-butyl-dithiodiglycolamide (TIBDTDGA) as agents for the selective extraction of palladium(II) from nitrate solutions was investigated. The extraction of nitric acid was also studied. A systematic investigation has been carried out on the detailed extraction properties of palladium(II) with these extractants from nitrate media. The quantitative extraction of palladium(II) with TODTDGA and THDTDGA from HNO_3 is observed at ~ 4 M. The extraction of palladium(II) from an aqueous nitrate solution in the presence of metal ions, such as Zr(II), Nd(III), Fe(III), Mn(II), Sr(II), Ni(II), Cr(II), Pt(IV) and Cs(I) was carried out using TODTDGA and THDTDGA in binary and multicomponent mixtures. The investigated DTDGA showed great extractability and selectivity for palladium than the other investigated metal ions, which showed negligible extraction values. The extraction ability of DTDGA remains almost constant for five successive cycles of extraction/back-extraction, indicating excellent stability and re-utilization of these extractants.

Keywords: Dithiodiglycolamides; Structure effect; Nitric acid; Palladium; Solvent extraction; Selective recovery

1. Introduction

Selective recovery and separation of metal ions from different industrial wastes are gaining importance because of the increasing demand for environmental concerns. Palladium(II) is an important element from an industrial point of view [1,2]. With the expansion of industrial activities during this century, the selective separation of palladium from undesired impurities is an important issue in the production of pure Pd(II), which has a wide range of applications in various industry field like catalysis, fuel cells electronics, pharmaceuticals, jewelry, dental alloys, telecommunications, petroleum industry, etc. [3,4]. In general, the natural abundance of platinum-group metals in the earth crust is very low and likely to be consumed in a few decades.

To overcome the situation, the recovery of palladium from wastes has become hot subject for technical and economic reasons [1,5,6]. The sufficient recovery of metal ions is possible only if the separation/recovery process is easy and effectively selective. In fact, solvent extraction process plays an important role in the recycling of the platinum-group metals (PGMs), and thus a good effort has been continuously devoted to the development of novel effective extractant molecules [1–6].

A survey of the literature showed that a large number of reagents [1–7] have been used for the extraction of palladium(II), particularly those addressing the treatment of hydrometallurgical solutions coming from secondary sources. Several well-known and/or commercial extractants such as; Cyphos®IL-101 [8], dialkyl sulfoxides [9], 4-acylpyrazolone [10], 2-hydroxy-4-sec-octanpyl diphenyl-ketoxime [11], Acorga®Clx50, 8-hydroxyquinoline,

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tributylphosphate (TBP), Aliquat 336, Cyanex 923 [4,12–15] have been used extensively for the extraction of palladium(II) from hydrochloric acid solutions. In general, these extractants have several limitations such as slow kinetics of extraction, poor solubility in aliphatic diluents, chemical stability, and used effectively only at lower acidic concentration, etc.

To overcome the situation, it becomes imperative to look for other classes of extractants. In fact, during the last ten years, a considerable amount of work appeared in literature, reporting the development of amide compounds to efficiently and selectively recover Pd(II) and other PGMs from chloride solutions [1,16]. With this aim, thiodiglycolamide, Fig. 1(a), was recently introduced for the separation of palladium(II) from hydrochloric acid solutions [17–19]. Very recently, dithiodiglycolamides (DTDGA), Fig. 1(b), class have come to play an important role as novel selective extractant for Pd(II). Ruhela et al., [20] investigated the extraction behavior of N,N,N′,N′-tetra-2-ethylhexyl-dithiodiglycolamide (TEHDTDGA) towards various elements present in high level liquid waste (HLW). Das et al., [21] evaluated of TEHDTDGA for separation and recovery of palladium from simulated spent catalyst dissolver solution. They found that, TEHDTDGA has shown remarkable extractability and selectivity for palladium over other metal ions present in hydrochloric acid solutions. Dithiodiglycolamide (DTDGA) contains two thioetheric sulfur atoms and amidic moiety properly, that can vigorously capture the metal ions, and act as a multidentate ligand [22]. This produces a very stable complex through the bonding through more than one donor sites as well as enhanced the high selectivity and extractability for palladium compared with thiodiglycolamide or other extractants. These attractive features make them worthy candidates for further investigations to assess their possible use in different solutions. Although, a considerable amount of work has been reported on the removal of palladium(II) using TEHDTDGA from chloride solutions, there is no literature available on the solvent extraction of palladium using these extractants from nitrate solutions except the TEHDTDGA/n-dodecane/HNO_3 system [23]. In addition, there is no information in the literature regarding the effect of structure of dithiodiglycolamides on the extraction behavior palladium. The nature of alkyl chain substituent plays an important role for coordinating properties of amides extractants as explored by us [1,24,25]. In our previous works [1,25–27], we reported on the synthesis of different cyanamides, diamides and diglycolamides and their extraction ability for selected PGMs and base metal ions from nitrate and chloride solutions.

Very recently, we synthesized and investigated some new thiodiglycolamides [19], Fig. 1(a), for the separation of selected platinum-group and base metal ions from nitric acid solutions. These new “S” donor ligands showed remarkable selectivity for palladium over other investigated metal ions. We now report on the synthesis and evaluation of new four different related structure substituted dithiodiglycolamides (DTDGA), which contains two sulfur atoms, Fig. 1(b), namely, TODTDGA, TEHDTDGA, THDTDGA and TIBDTDGA for extraction of Pd(II), Zr(II), Nd(III), Fe(III), Mn(II), Sr(II), Ni(II), Cr(II), Pt(IV) and Cs(I) from nitric acid medium. A systematic investigation was carried out on the extraction of Pd(II) with both TOTDGA and TEHTDGA in n-dodecane. Except TEHDTDGA, the three ligands TODTDGA, THDTDGA and TIBDTDGA is novel synthesized and used in the present study. In addition, to define the influence of the individual substituents on the extraction ability of dithiodiglycolamides, the influence of alkyl group (R) on the extraction % of Pd(II) from different acids solutions (HNO_3, HCl or H_2SO_4) was also studied.

2. Experimental

2.1. Synthesis of dithiodiglycolamides extractants

The four dithiodiglycolamides (TIBDTDGA, THDTDGA, TEHDGA, and TODTDGA) chosen for this study were synthesized by the condensation reaction of sodium sulfide nonahydrate with the corresponding N,N-di-isobutyl-chloroacteamide, N,N-dihexyl-chloroacteamide, N,N-di-(2-ethylhexyl)-chloroacetamide, and N,N-dioctyl-chloroacteamide, respectively, by using a method similar to that described in Refs. [19,20]. The purity of the synthesized DTDGA was found to be more than 98% and the yield of the product was ≥85%. Solutions with desired concentration of DTDGA were prepared by dissolving appropriate amount of DTDGA in diluents namely; toluene, benzene, n-hexane, n-dodecane, dichloromethane, cyclohexane and carbontetrachloride.

2.2. General extraction procedure

Equal volumes of aqueous and organic phases were equilibrated by shaking for 15 min with vigorous shaking in

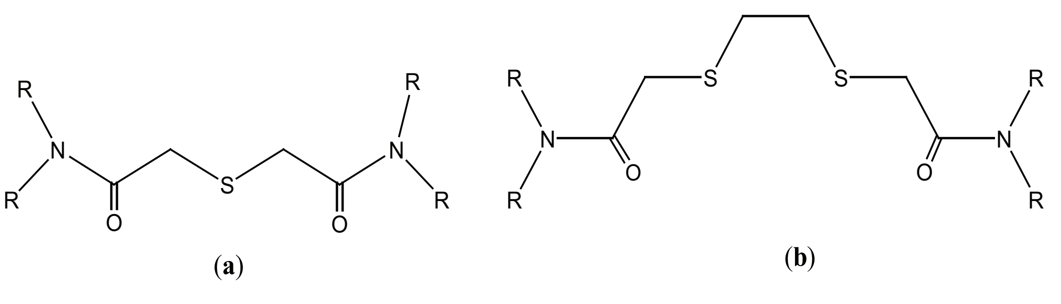

Fig. 1. Chemical structure of (a) thiodiglycolamide (TDGA), (b) dithiodiglycolamide (DTDGA).

a temperature controlled water bath adjusted to the desired temperature. After phase separation by centrifugation, the aqueous phase was analyzed for metal ion concentration. The distribution ratio (D_M) of the metal ion was determined as the ratio of metal ion concentration in organic phase to that in aqueous phase, Eq. (1):

$$D_M = [M]_{\text{org}}/[M]_{\text{aq}} \tag{1}$$

Percentage extraction of metal ion was determined by the following equation:

$$\%E = D_M/(D_M + 1) \times 100 \tag{2}$$

where M is the metal ion [Pd(II), Zr(II), Nd(III), Fe(III), Mn(II), Sr(II), Ni(II), Cr(II), Pt(IV) and Cs(I)]. All the extraction experiments were conducted in triplicate. Unless otherwise indicated, n-dodecane was used as diluent for DTDGA. Aqueous metal solutions were prepared by dissolving the corresponding metal nitrate in nitric acid solutions. The stock solutions of the metal ions being studied Pd(II), Zr(II), Nd(III), Fe(III), Mn(II), Sr(II), Ni(II), Cr(II), Pt(IV) and Cs(I)] were diluted to obtain the desired concentrations for the working solutions. Normally 1 × 10^{-3} M of metal nitrate at various nitric acid concentrations was employed as feed solution. The amount of the metal ion in the organic phase was determined by subtracting the aqueous concentration from the initial aqueous concentration of the metal ion. The concentrations of Pd(II), Zr(II), Nd(III), Fe(III), Mn(II), Sr(II), Ni(II), Cr(II), Pt(IV) and Cs(I) in the aqueous phases were determined before and after extraction by atomic absorption spectrometry (AAS, Perkin– Elmer-400) and ICP-AES 8100, Shimadzu. For the acid extraction, the DTDGA solutions of concentration 0.0001–0.01 M in n-dodecane were equilibrated with 1 M HNO_3 for 15 min. After the phase separation, the acidity in the organic and aqueous phases was determined as previously reported [28]. The extracted species in the organic phase were investigated by using FTIR (Thermo Scientific Nicolet-6700), with the spectra recorded in the range 400–4,000 cm^{-1}. All the chemicals used in this work were of analytical reagent grade and were used without any purification.

2.3. Back extraction studies

For the back-extraction studies, the organic phase was loaded with 1 × 10^{-3} M Pd(II) in 3 M nitric acid. A certain volume of the loaded organic solutions was mixed with equal volume of aqueous solution containing the strippant using a mechanical shaker for 15 min [19].

2.4. Extractant re-utilization

To gain insight on the stability or regeneration characteristics and feasibility of reusing DTDGA extractants, an organic phase containing TODTDGA or TEHDTDGA in n-dodecane was subjected to five successive extraction-stripping contacts with fresh solutions of palladium(II) in nitric acid and with thiourea in 0.1 M HNO_3, respectively [26].

3. Results and discussion

Some preliminary experiments were carried out in order to investigate the quantitative extraction of palladium(II) ions by DTDGA in the absence of other metal ions. The optimum conditions for the extraction of palladium(II) were established by varying the experimental parameters, such as HNO_3 concentration, extractant concentration, and the equilibration time. n-dodecane was chosen as the diluent for the investigated DTDGA extractants. For all the synthesized DTDGA, no third phase formation was observed after extraction; good and fast phase separation was also attained for all the extraction experiments that were conducted.

3.1. Effect of structure

The nature of N substituent (alkyl group, R) plays an important role on the extraction ability of the diamides. The dithiodiglycolamides (DTDGA) considered were synthesized with different substituting groups. On the other hand, the presence of long chain alkyl groups (hexyl or octyl) or branched alkyl group (isobutyl or 2-ethylhexyl) bonded to the nitrogen atoms act as electron donating, thus giving the molecular structure a more basic character. The extraction of Pd(II) from 2 M of different acids (HNO_3, HCl or H_2SO_4) solution by 0.002 M of the different dithodiglycolamides in n-dodecane has been studied, Table 1. On the other hand, the extraction of Pd(II) was found to suffer a notable decrease when increasing in the alkyl chain length from C_6H_{12} to C_8H_{17}.

It was also found that, the extraction of Pd(II) is slightly affected by the branching of the alkyl group (isobutyl or 2-ethylhexyl) compared with the corresponding linear symmetrical alkyl chain dithiodiglycolamides (THDTDGA and TODTDGA). In general the sequence for the extraction of Pd(II) with investigated dithiodiglycolamides (DTDGA) in all acids systems studied is the following: TEHTDGA >THTDGA > TOTDGA.

Similar conclusions were previously reported for the extraction of Pd(II) and some metal ions with thiodiglycolamides [19]. In all studied systems, the results clearly demonstrate the superior extraction of Pd(II) in nitric acid or hydrochloric acid solutions, while poor values were obtained in case of sulfuric acid solution, as shown in Table 1.

On the other hand, the sequence of the studied systems (HNO_3, HCl or H_2SO_4) for the extraction of pd(II) is the following (at 2 M from each): $HNO_3 \geq HCl >> H_2SO_4$.

Table 1
Influence of alkyl group (R) on the extraction % of Pd(II) from 2 M (HNO_3, HCl or H_2SO_4) solution by 0.002 M different synthesized dithiodiglycolamides (DTDGA) in n-dodecane at 25°C ± 0.5°C, relative error about ± 1.0%

DTDGA	Alkyl group (R)	Extraction (%)		
		HNO_3	HCl	H_2SO_4
TODTDGA	n-C_8H_{17}	97.39	97.13	6.64
TEHDTDGA	$CH_2CH(C_2H_5)C_4H_9$	98.53	96.83	7.83
THDTDGA	n-C_6H_{13}	98.07	97.80	7.23
TIBDTDGA	$CH_2CH(CH_3)_2$	96.96	96.23	7.01

3.2. Kinetic of the recovery of palladium(II) from multicomponent mixtures

The extraction percentage was determined for palladium (II) by contacting the mixtures of Zr(II), Nd(III), Fe(III), Mn(II), Sr(II), Ni(II), Cr(II), Pt(IV) and Cs(I) at 4 M HNO_3 with TODTDGA in n-dodecane. The contact time was varied from 1 to 30 min, as shown in Fig. 2.

The kinetic study showed that the extraction of palladium(II) from aqueous phase was realized in a short period of time (4–5 min). Our results are in good agreement to these reported for the extraction of palladium(II) with thiodiglycolamide from nitric acid [19] or hydrochloric acid solutions [17]. It is important to observe that, the equilibrium for Pd(II) in the presence of Zr(II), Nd(III), Fe(III), Mn(II), Sr(II), Ni(II), Cr(II), Pt(IV) and Cs(I) was obtained at same time (3–5 min). Moreover, the same result was observed using concentrations of $5 \cdot 10^{-3}$ M instead of $1 \cdot 10^{-3}$ M of all metal ions investigated. On the other hand, these results confirm the selective recovery of palladium(II) by TODTDGA in the presence of multicomponent mixtures metal ions in the aqueous solution.

3.3. Extraction of nitric acid

Studies regarding the extraction of nitric acid by TODTDGA can be an important contribution to a better knowledge on behavior of these new extractants towards palladium(II) and other metal ions. Based on the basic nature of DTDGA compounds, TODTDGA was found to extract nitric acid into the organic phase. The basicity of TODTDGA can be attributed to the presence of carbonyl group of two amidic moieties attached to the two sulfur atoms through methylene bridge. The extraction of nitric acid by TODTDGA diluted in n-dodecane was investigated at the initial concentration of 1 M HNO_3 at 25°C, Fig. 3.

The general equilibrium for HNO_3 extraction by TODTDGA is as follows:

$$H^+ + NO_3^- + n\ TODTDGA_{(o)} = HNO_3{\cdot}nTODTDGA_{(o)} \qquad (3)$$

The equilibrium constant (K_H) for the above equation can be written as follows:

$$K_H = \frac{[HNO_3 \cdot n\ TODTDGA]_{(o)}}{\gamma^2 \pm \left[H^+\right]_{(aq)} \left[NO_3^-\right]_{(aq)} \left[TODTDGA\right]^n_{(o)}} \qquad (4)$$

where the square brackets indicate molar concentration and the subscript (*o*) and (*aq*) represent the organic and aqueous phase, respectively. In Eq. (4), the activity coefficient (γ±) of different species was negligible in the concentration range used [29]. Rearranging Eq. (4) in the logarithm form,

$$\log[H^+]_{(o)} - 2\log[H^+]_{(aq)} = \log K_H + n\log[TODTDGA]_{(o)} \qquad (5)$$

where $[H^+]_{(aq)} = [NO_3]_{(aq)}$ and $[HNO_3{\cdot}nTODTDGA]_{(o)}$ instead of $[H^+]_{(o)}$, because the ionic form is certainly not the more probable form in organic diluents. The plot of $\log[H^+]_{(o)} - 2\log[H^+]_{(aq)}$ vs. $\log[TODTDGA]_{(o)}$, gives straight lines with slope 0.25, as shown in Fig. 3. The calculated value of K_H was found to be 0.63 ± 0.08. The higher values of K_H as well as a formation of different nitric acid-diamide adducts were reported for other diamides (under different extraction conditions) [29,30].

3.4. Choice of the diluents

The effect of seven different aromatic and aliphatic diluents namely; toluene, benzene, n-hexane, n-dodecane, dichloromethane, cyclohexane and carbontetrachloride on the extraction behavior of palladium by TEHTDGA or TOTDGA from 3 M HNO_3 was investigated, Table 2. It was found that the different aromatic and aliphatic diluents used have slightly effect on the extraction percentage (%E) of Pd(II) with the synthesized dithiodiglycolamides (DTDGA).

In general, the extraction sequence of Pd(II) as related to different diluents is; n-dodecane ≥ n-hexane > benzene > toluene > dichloromethane ≥ carbontetrachloride > cyclohexane. This sequence is generally parallel to the sequence of the slightly lowering in carbonyl stretching frequency,

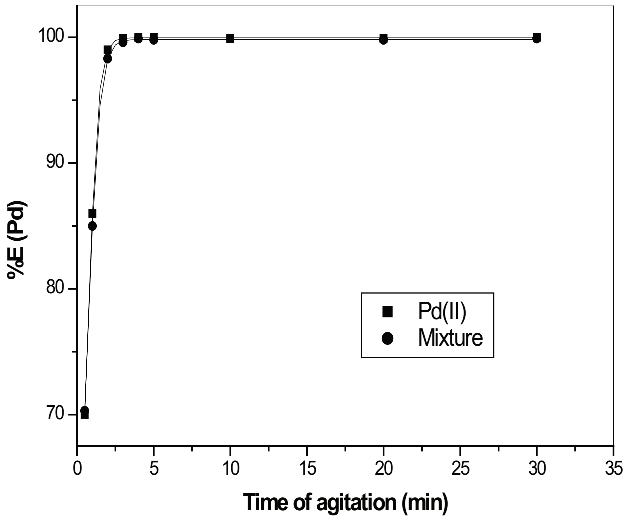

Fig. 2. Extraction of Pd(II) from 4 M HNO_3 as a function of time.

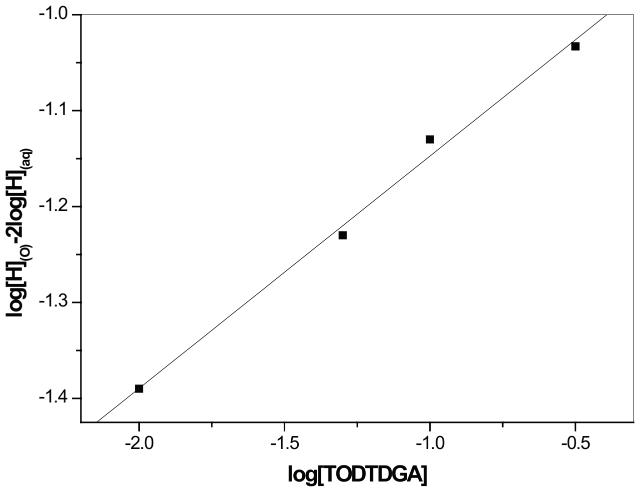

Fig. 3. Extraction of 1M nitric acid with different molarities of TODTDGA in n-dodecane at 25°C ± 0.5°C.

Table 2
Effect of diluents on the extraction (%) of Pd(II) with 0.002 M DTDGA from 3 M nitric acid at 25°C ± 0.5°C; relative error about ± 0.03%

Diluent	TODTDGA		TEHDTDGA	
	$\nu_{C=O}$	E (%)	$\nu_{C=O}$	E (%)
Toluene	1635	97.87	1635	98.19
Benzene	1636	98.63	1635	98.98
n-hexane	1638	99.21	1639	98.61
n-dodecane	1639	99.33	1639	98.80
dichloromethane	1634	97.26	1634	97.79
carbontetrachloride	1633	97.91	1633	97.69
cyclohexane	1632	96.98	1632	97.44

$\nu_{C=O}$, observed in different aliphatic and aromatic diluents studied as shown in Table 2. Mowafy et al. [19,24] reported on the effect of different aromatic and aliphatic diluents namely, benzene, toluene, n-hexane and n-dodecane, on the extraction of Pd(II) in nitric acid medium by some thiodiglycolamides (TDGA) or other diamides. They found that aromatic and halogenated diluents gave slight lower distribution ratios than n-hexane and n-dodecane diluents, which parallel to our findings for the extraction of Pd(II) with dithiodiglycolamides used in the present work.

3.5. Effect of acid concentration on the extraction of palladium(II)

Fig. 4 shows the percentage extraction of palladium(II) with TODTDGA and TEHDTDGA in n-dodecane as a function of nitric acid concentrations. It was found that the extraction of Pd(II) is dependent on the nitric acid concentration until ~4 M, after which a constant value was obtained. On the other hand, the extraction of Pd(II) becomes nearly quantitative for both TODTDGA and TEHDTDGA from ~4 M HNO_3.

Although both TOTDGA and TEHTDGA have the same number of carbon atoms (no. of carbon atoms = 36), the 2-ethylhexyl group in TEHDTDGA was found to enhance the extraction of Pd(II) compared with the long chain octyl group in TODTDGA, as shown in Fig. 4. So far, no available work was reported on the effect of structure or introduction of branched radicals on the N atoms of these novel ligands (DTDGA). These results are of the same behavior as those obtained for the extraction of Pd(II) thiodiglycolamides derivatives (TOTDGA and TEHTDGA) from nitric acid solutions [19]. However, as suggested before the significant extractability of Pd(II) with branched dithiodiglycolamide (TEHDTDGA), may be attributed to their lower degree of steric hindrance as well as electro-indicative effect to the coordination of the Pd(II), compared with the dithiodiglycolamide with a long chain attached to the nitrogen atom (TODTDGA). In this concern, Mowafy et al. [1,24,25,28] investigated the extraction of selected actinide and lanthanides metals ions with different substituting long chain monoamides, diamides, or diglycolamides. They found that the longer alkyl chain suppressed the extraction of different metal ions.

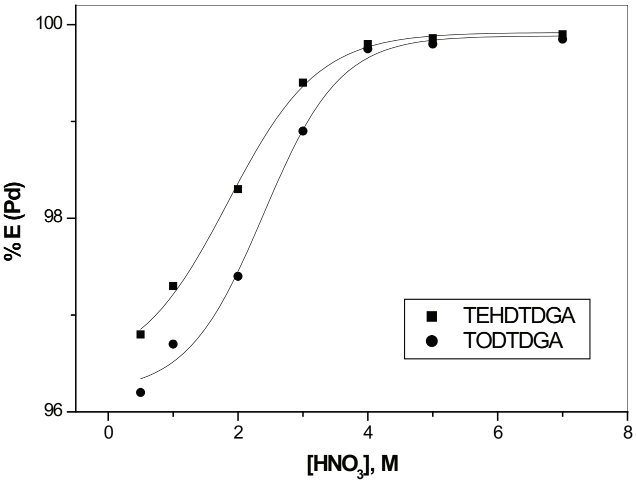

Fig. 4. Extraction of Pd(II) from different molarities of nitric acid solutions with 0.002 M TODTDGA and TEHDTDGA in n-dodecane at 25°C ± 0.5°C.

Palladium was nearly quantitative extracted at 3–4 M nitric acid with thiodiglycolamides (TDGA) as previously reported [19]. Das et al. [21] reported that the extraction of Pd(II) TEHDTDGA increase with increasing hydrochloric acid concentration up to 3 M HCl, after which remained constant on further increase in acidity. These results indicated that the nitric acid play a role in the extraction palladium.

To get an insight on the role of nitric acid in the extraction reaction, the distribution ratio of palladium, D_{Pd}, was determined at fixed ionic strength of 3.5 M $(H,Na)NO_3$, as shown in Fig. 5. It was found that the distribution ratio of palladium, D_{Pd}, remain unchanged with nitric acid variation. On the other hand, the obtained results indicated that nitric acid molecule itself does not participate in the species formation. Therefore, the increase in the extraction of Pd(II) with increase nitric acid concentration, Fig. 4, can be attributed to the salting out effect of nitrate ion, which participates in complex formation.

Our results are in good agreement with those reported for the extraction of palladium(II) from nitrate solutions with T(2EH)TDGA [17].

3.6. Composition of Pd(II) extracted species

To get an insight on the nature of the extracted species in the organic phase, the effect of initial dithiodiglycolamides concentration in n-dodecane on the distribution ratios of pd(II) was investigated. Fig. 6 shows the effect of TODTDGA and TEHDTDGA concentrations diluted in n-dodecane on the distribution ratios of Pd(II). The relations between log-D_{Pd} and log[TODTDGA]$_{ini}$ or log[TEHDTDGA]$_{ini}$ showed straight lines of slopes of 1.08 ± 0.03 and 1.14 ± 0.05, respectively, which are close to 1.

Based on these findings, we can suggest that palladium(II) extracted species (Pd: DTDGA) is 1:1. The present results are within that reported by other for palladium with other similar extraction system [20].

Experiments were also carried out on evaluate loading studies of the investigated DTDGA (TODTDGA and

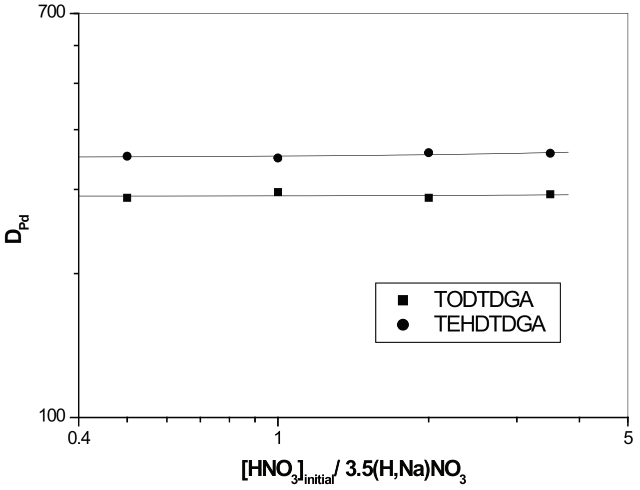

Fig. 5. Extraction dependence of D_{Pd} in 3.5 M (H,Na)NO_3 with 0.002 M DTDGA in n-dodecane at 25°C ± 0.5°C.

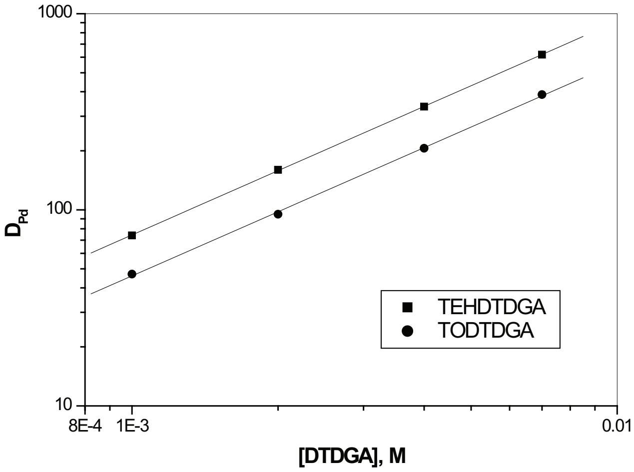

Fig. 6. Variation of the distribution ratio of pd(II) as a function of the TODTDGA or TEHDTDGA concentration in n-dodecane at 25°C ± 0.5°C, $[HNO_3]$ = 3 M.

TEHDTDGA) by using equal volume of 2 × 10^{-3} M of TODTDGA or TEHDTDGA in n-dodecane and 1 × 10^{-3} M Pd(II) in 3.5 M nitric acid at 25°C ± 0.5°C. It was found that 2.11 × 10^{-3} ± 0.03 M Pd(II) and 2.13 × 10^{-3} ± 0.02 M Pd(II) for TODTDGA and TEHDTDGA, respectively, were loaded in two repeated contacted, after which there is no loading was obtained. These results also indicated that the stoichiometry of the palladium(II) extracted species (Pd: DTDGA) is 1:1. In addition, identical ratio was obtained using higher concentrations of palladium(II) (2 · 10^{-3} M and 4 · 10^{-3} M).

3.7. Extraction of palladium(II) from binary solutions

The separation of palladium(II) from Zr(II), Nd(III), Fe(III), Mn(II), Sr(II), Ni(II), Cr(II), Pt(IV) and Cs(I) in binary mixtures was carried out using TODTDGA and TEHDTDGA, Table 3.

Table 3
Binary separation of Palladium(II) from Zr(II), Nd(III), Fe(III), Mn(II), Sr(II), Ni(II), Cr(II), Pt(IV) and Cs(I) by 0.002 M TODTDGA or TEHDTDGA in n-dodecane at 25°C ± 0.5°C; $[HNO_3]$ = 5 M

Composition	Molar ratio	% Recovery of Pd(II) or M(I, II, III or IV)			
		TODTDGA		TEHDTDGA	
		Pd(II)	M(I, II, III or IV)	Pd(II)	M(I, II, III or IV)
Palladium(II) : zirconium(II)	1 : 1	99.8	~NE	99.9	~NE
	1 : 2	99.8	<0.01	99.8	~NE
	1 : 5	99.7	<0.01	99.8	<0.01
Palladium(II) : manganese(II)	1 : 1	99.9	~NE	99.9	~NE
	1 : 2	99.8	<0.01	99.9	~NE
	1 : 5	99.7	<0.01	99.7	<0.01
Palladium(II) : nickel(II)	1 : 1	99.9	NE	99.9	~NE
	1 : 2	99.7	<0.01	99.8	~NE
	1 : 5	99.7	<0.1	99.7	<0.01
Palladium(II) : strontium(II)	1 : 1	99.9	<0.01	99.9	~NE
	1 : 2	99.8	<0.03	99.9	~NE
	1 : 5	99.7	<0.03	99.7	<0.01
Palladium(II) : iron(III)	1 : 1	99.9	<0.02	99.9	<0.01
	1 : 2	99.8	<0.03	99.9	<0.02
	1 : 5	99.7	<0.04	99.7	<0.05
Palladium(II) : neodymium(III)	1 : 1	99.8	<0.03	99.9	<0.02
	1 : 2	99.8	<0.03	99.9	<0.03
	1 : 5	99.7	<0.05	99.7	<0.03
Palladium(II) : cesium(I)	1 : 1	99.9	~NE	99.9	~NE
	1 : 2	99.8	<0.01	99.9	~NE
	1 : 5	99.7	<0.03	99.7	<0.04
Palladium(II) : chromium(II)	1 : 1	99.9	~NE	99.9	~NE
	1 : 2	99.8	~NE	99.9	<0.01
	1 : 5	99.7	<0.01	99.7	<0.01
Palladium(II) : platinum(IV)	1 : 1	99.9	<0.01	99.9	<0.03
	1 : 2	99.8	<0.03	99.9	<0.03
	1 : 5	99.7	<0.04	99.7	<0.04

Note; 1:1 = 0.001M Pd(II): 0.001M M(I, II, III or IV); 1: 2 = 0.001 M Pd(II): 0.002M M(I, II, III or IV); 1: 5= 0.001 M Pd(II): 0.005M M(I, II, III or IV), M(I, II, III, IV) = Cs(I), Zr(II), Mn(II), Sr(II), Ni(II), Cr(II), Nd(III), Fe(III) and Pt(IV), NE= not extraction.

For all the binary metal ion mixtures, palladium(II) was nearly quantitative extracted for both TODTDGA and TEHDTDGA in the presence of each of the above ions in a binary mixture. On the other words, the metal ions mixed with palladium were not extracted into the organic phase. This readily facilitate the separation of palladium(II) from theses metal ions. As shown in Table 3, the extraction of palladium(II) was not affected by the amount of metal ions in the binary mixtures used.

3.8. Selectivity patterns

To gain an insight into the selectivity pattern of DTDGA for palladium from multicomponent mixtures of

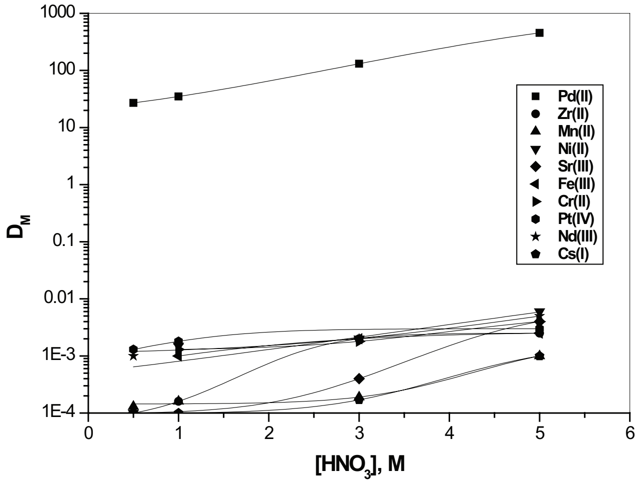

Fig. 7. Selective extraction of 0.001 M Pd(II) from multicomponent mixtures of 0.001 M of each of Zr(II), Nd(III), Fe(III), Mn(II), Sr(II), Ni(II), Cr(II), Pt(IV) and Cs(I) by 0.002 M TODTDGA in n-dodecane from different HNO_3 concentrations.

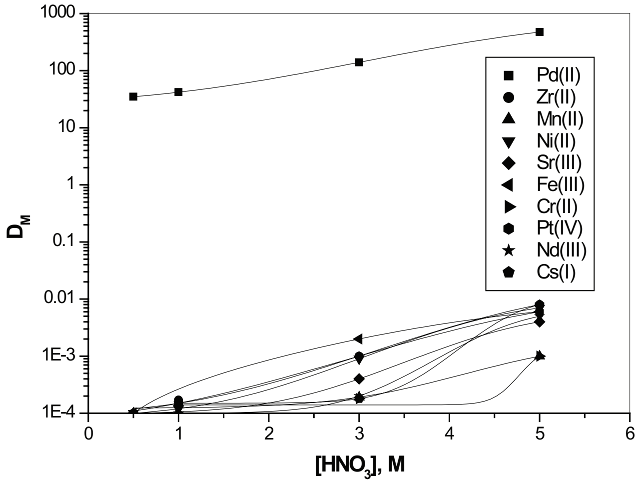

Fig. 8. Selective extraction of 0.001 M Pd(II) from multicomponent mixtures of 0.001 M of each of Zr(II), Nd(III), Fe(III), Mn(II), Sr(II), Ni(II), Cr(II), Pt(IV) and Cs(I) by 0.002 M TEHDTDGA in n-dodecane from different HNO_3 concentrations.

metal ions, the separation of palladium from mixture of Zr(II), Nd(III), Fe(III), Mn(II), Sr(II), Ni(II), Cr(II), Pt(IV) and Cs(I) using TODTDGA or TEHDTDGA in n-dodecane were tested as shown in Figs. 7 and 8. It was found that the extraction of Pd(II) with TEHDTDGA or TODTDGA becomes nearly quantitative. These results clearly demonstrate the superior extraction of palladium(II) over other associated multi-component metal ions when extracted with TODTDGA or TEHDTDGA. On the other hand, the quantitative extraction of palladium from various metal ions in nitric acid solution may be obtained in a single contact. It is very interesting to consider the high selectivity of both TEHDTDGA and TODTDGA in view of a practical application, considering that no significant contamination of the organic phases occurs.

Table 4
Extraction of palladium(II) from 5 M HNO_3 in five successive extraction-stripping cycles by TODTDGA in n-dodecane; relative error about ± 0.07%

Extraction-stripping cycles	% of Extraction	
	TODTDGA	TEHDTDGA
1	99.64	99.89
2	99.51	99.85
3	99.40	99.71
4	99.32	99.79
5	99.16	99.68

3.9. Stripping of palladium(II) and extractant re-utilization

The back extraction of Pd(II) from 0.002 M TODTDGA or TEHDTDGA in n-dodecane using different concentrations of nitric acid (0.01 and 0.1 M) was carried out. The amount of the recovered palladium was found to be not more than ~50% in all studied systems. On the other hand, nitric acid alone is not suitable as stripping agent for palladium from the loaded organic solution. Experiments performed with the loaded organic phase showed that palladium was quantitatively re-extracted (~100%) by 0.01 M thiourea in 0.1 M nitric acid. Therefore, thiourea is efficient striping of palladium from loaded organic phase. The results obtained are agreement with that reported for the back extraction of palladium with thiodiglycolamides from nitric acid medium [19] or with TEHDTDGA from hydrochloric acid medium [21].

Experiments were also carried out on evaluate the stability and feasibility of reusing DTDGA extractants for the selective recovery of palladium(II) from nitric acid for the adopted experimental conditions. Table 4 shows five successive extraction–stripping cycles done with 0.002 M TODTDGA or TEHDTDGA in n-dodecane followed by striping with 0.01 M thiourea in 0.1 M HNO_3, using fresh 5 M HNO_3 aqueous solutions of 0.001 M Pd(II) extraction in each stage.

As shown in Table 4, the extraction percentage of Pd(II) for five cyclic of extraction and stripping remained almost constant at the original value for TEHDTDGA or TODTDGA. These results clearly demonstrate the stability of TODTDGA or TEHDTDGA and that re-utilization is feasible, considering the recoveries higher than 99% were obtained even after a fifth successive contact with the aqueous feed solution. However, these results indicate that no degradation of the extractants in the used experimental conditions seems to occur in all cases. In this context, the results obtained in this work and that reported by others [18,20,21] reinforces the possibility of successive reutilization of TODTDGA or TEHDTDGA, which can probably be extended to other dithiodiglycolamide derivatives, in view of their industrial application.

4. Conclusions

- Four new multidentate ligands (dithiodiglycolamides, DTDGA) namely, TODTDGA, TEHDTDGA, THDTDGA, and TIBDTDGA were synthesized and used for the selective extraction of palladium(II) from other metal ions such as Zr(II), Nd(III), Fe(III), Mn(II), Sr(II), Ni(II), Cr(II), Pt(IV) and Cs(I) from nitrate solution. The equilibrium time for Pd(II) in the presence of above mentioned metal ions is much shorter (<5 min).

- The extraction of Pd(II) from 2 M HNO_3 is slightly affected by the branching of the alkyl group (isobutyl or 2-ethylhexyl) compared with the corresponding linear symmetrical alkyl chain dithiodiglycolamides (THDTDGA and TODTDGA). In general, the sequence of the studied systems (HNO_3, HCl or H_2SO_4) for the extraction of pd(II) from 2 M from each is the following: $HNO_3 \geq$ HCl >> H_2SO_4.
- The different aromatic and aliphatic diluents used have slightly effect on the extraction percentage (%E) of Pd(II) with the synthesized dithiodiglycolamides (DTDGA). The extraction of Pd(II) becomes nearly quantitative for both TODTDGA and TEHDTDGA from ~ 4 M HNO_3. The obtained results indicated that nitric acid molecule itself does not participate in the species formation. The stoichiometry of the palladium(II) extracted species (Pd: DTDGA) is 1:1.
- The quantitative extraction of palladium from various metal ions (binary mixture) in nitric acid solution may be obtained in a single contact. The investigated DTDGA showed great extractability and selectivity for palladium than the other investigated metal ions, which showed negligible extraction values under the same extraction conditions.
- The extraction percentage of Pd(II) for five cyclic of extraction and stripping remained almost constant at the original value for TEHDTDGA or TODTDGA, which can probably be extended to other dithiodiglycolamide derivatives, indicating excellent stability and re-utilization of these extractants in view of their industrial application.

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