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Palladium(II) Recovery from Hydrochloric Acid Solutions by *N,N'*-Dimethyl-*N,N'*-Dibutylthiodiglycolamide

Ana Paula Paiva ^{1,*}, Mário E. Martins ^{1,†} and Osvaldo Ortet ^{1,2,†}

¹ Centro de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Lisboa 1749-016, Portugal; E-Mails: mario.mem@live.com.pt (M.E.M.); oaortet@fc.ul.pt (O.O.)

² Departamento de Ciência e Tecnologia, Universidade de Cabo Verde, 379C, Praia 279, Santiago Island, Cape Verde

† These authors contributed equally to this work.

* Author to whom correspondence should be addressed; E-Mail: appaiva@fc.ul.pt; Tel.: +351-217-500-953; Fax: +351-217-500-088.

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Abstract: *N,N'*-dimethyl-*N,N'*-dibutylthiodiglycolamide (DMDBTDGA) has been synthesized, characterized, and is investigated in this work as a potential liquid-liquid extractant for palladium(II), platinum(IV), and rhodium(III) from hydrochloric acid solutions. Pd(II) is the only ion which is efficiently removed by DMDBTDGA in toluene from 1.5 M to 4.5 M HCl, but it is not extracted from 7.5 M HCl. Pd(II) stripping is quantitatively achieved by an acidic thiourea solution. Pd(II) extraction kinetics are highly favored (2–5 min). Distribution data points to a DMDBTDGA: Pd(II) species with a 1:1 molar ratio. Pd(II) can selectively be recovered by DMDBTDGA from 4.0 M HCl complex mixtures containing equivalent concentrations of Pt(IV) and Rh(III). When five-fold Fe(III) and Al(III) concentrations are present, only Pt(IV) in the presence of Fe(III), and Fe(III) itself, are extensively co-extracted together with Pd(II). However, Fe(III) can easily be eliminated through an intermediate scrubbing step with water.

Keywords: Palladium(II); hydrochloric acid; liquid-liquid extraction; thiodiglycolamide derivative

1. Introduction

Platinum, palladium, and rhodium, three elements included in the class of the platinum-group metals (PGMs), are rather scarce in the earth, with their core mineral resources concentrated in South Africa and Russia [1]. The preservation of day-to-day life in the Western world would be threatened if the supply of PGMs was to rely on their mines only, since PGMs are currently used in several technological applications, and with a tendency for further development. The exclusive catalytic properties of PGMs place these elements in the forefront of the fabrication of automobile catalysts (to drop the harmful emissions of the motor engines) and also in the chemical industry [2]. Therefore, recycling practices are nowadays determinant for balancing the overall supply of PGMs worldwide [3].

Spent automobile catalytic converters are the main secondary source of PGMs recycled by the metallurgical industry, through the use of pyro and/or hydrometallurgical methods [4]. The direct hydrometallurgical leaching of PGMs from spent catalysts involves hydrochloric acid alone, or with different oxidizing agents [5], with the liquid-liquid extraction (solvent extraction, SX) [6] and the ion exchange [7] techniques being the most common approaches to separate, concentrate, and purify solutions containing PGMs. The composition of the leaching media coming from the treatment of secondary sources is rather different from the original leaching solutions of the PGMs mines [6]; therefore, SX research for improving the performance of well-known and/or commercial extractants [8,9] or for developing new molecules [10,11] to process the typical leaching media of secondary raw materials is currently very active.

Within the novel molecules created to improve the selective and efficient recovery of PGMs from chloride solutions, various sorts of amide derivatives deserve a special mention. For the recovery of platinum(IV), several malonamides, e.g., [11,12], and thiodiglycolamides [10,13] have proven their adequacy; sulfide-containing monoamides [14], thiodiglycolamides [15,16], thioamides [17], and a dithiodiglycolamide [18] have also been proposed for palladium(II) extraction. Recently, amide-containing tertiary amine compounds have been reported as suitable for rhodium(III) recovery [19].

Following the promising results found for *N,N'*-dimethyl-*N,N'*-dicyclohexylthiodiglycolamide (DMDCHTDGA) toward Pd(II) extraction [13,20,21], this article reports some preliminary research regarding the synthesis and use of another member of the same family, *N,N'*-dimethyl-*N,N'*-dibutylthiodiglycolamide (DMDBTDGA), as a SX agent for Pd(II) (Figure 1). This work is an attempt to better understand the role played by different alkyl substituents (butyl vs. cyclohexyl) when *N,N'*-thiodiglycolamide derivatives are used as Pd(II) extractants, in addition to the methyl groups placed at the nitrogen atoms. Accordingly, a step-by-step comparison of the performances of DMDBTDGA and DMDCHTDGA is carried out, highlighting the similarities and main differences observed. Generally, it can be considered that the replacement of the cyclohexyl groups of DMDCHTDGA by the butyl substituents in DMDBTDGA worsens the ability of this latter compound to efficiently and selectively recover Pd(II) when compared with the performance shown by DMDCHTDGA [13,20]. Accordingly, a tentative rationalization of the potential main factors contributing to the differences found between DMDBTDGA and DMDCHTDGA in Pd(II) extraction is presented and discussed.

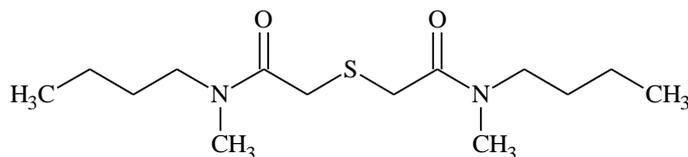


Figure 1. Structure of *N,N'*-dimethyl-*N,N'*-dibutylthiodiglycolamide (DMDBTDGA).

2. Experimental Section

2.1. Synthesis and Characterization

The FTIR spectrum was recorded in a Satellite Mattson spectrophotometer (Thermo Mattson, Madison, WI, USA) using NaCl cells. The ^1H and ^{13}C NMR spectra (400 MHz for ^1H and 100 MHz for ^{13}C nuclei) were acquired on a Bruker Avance 400 (Bruker Corporation, Billerica, MA, USA) using deuterated chloroform (Sigma-Aldrich, St Louis, MO, USA, 99.8%) as solvent. For the GC-MS analysis an Agilent 6890 gas chromatograph (Agilent Technologies, Santa Clara, CA, USA), equipped with a non-polar capillary column Hewlett-Packard HP5-MS (Hewlett-Packard, Palo Alto, CA, USA) and coupled to a mass spectrometer Agilent 5973 (electronic impact of 70 eV, Agilent Technologies), was used. The temperature program consisted of an initial heating at 50 °C for 1 min, a raise of 15 °C/min until 180 °C, and another sequential increase of 25 °C/min until 280 °C, remaining at this latter temperature for 3 min. The temperature of the injector was fixed at 280 °C. The preparation of the samples was accomplished by dilution of a small portion of the compound in 200 μL of dichloromethane, and encapsulating the solution in a small vial prior to its analysis.

The synthesis of *N,N'*-dimethyl-*N,N'*-dibutylthiodiglycolamide (DMDBTDGA) was carried out similarly to the one previously reported for *N,N'*-dimethyl-*N,N'*-dicyclohexylthiodiglycolamide (DMDCHTDGA) [13]. A yellowish viscous residue was obtained, with a global yield of 41%.

FTIR (NaCl cells, cm^{-1}): 1643 (C=O).

^1H NMR (CDCl_3 , δ in ppm): 3.47–3.50 (4H, multiplet, $\text{CH}_2\text{-S}$), 3.28–3.38 (4H, multiplet, N-CH_2), 3.03 (3H, singlet, N-CH_3), 2.92 (3H, singlet, N-CH_3), 1.47–1.61 (4H, multiplet, $\text{N-CH}_2\text{-CH}_2$), 1.26–1.36 (4H, sextuplet, $\text{CH}_3\text{-CH}_2$), 0.90–0.96 (6H, multiplet, $\text{CH}_3\text{-CH}_2$).

^{13}C NMR (CDCl_3 , δ in ppm): 13.83 ($\text{CH}_3\text{-CH}_2$), 19.94, 19.97 ($\text{CH}_3\text{-CH}_2$), 29.27, 30.60 ($\text{CH}_3\text{-CH}_2\text{-CH}_2$), 33.53, 33.64, 34.09, 34.25 ($\text{CH}_2\text{-S}$), 33.65, 35.71 (N-CH_3), 47.87, 50.33 (N-CH_2), 168.42 (C=O).

GC-MS: retention time = 13.70 min, 91% abundance; m/z = 288 (molecular ion, $[\text{M}]^+$), 114 (base peak, $[\text{CH}_3(\text{CH}_2)_3\text{NCH}_3\text{CO}]^+$), 87 $[\text{CH}_3(\text{CH}_2)_3\text{NCH}_3 + \text{H}]^+$ and 57 $[\text{CH}_3(\text{CH}_2)_3]^+$.

2.2. Solvent Extraction Experiments

Feed aqueous phases containing about 9.4×10^{-4} M Pd(II), 5.1×10^{-4} M Pt(IV), or 9.7×10^{-4} M Rh(III) (about 100 mg L^{-1} each) were prepared from atomic absorption spectroscopy standards (1003 ± 4 mg L^{-1} Pd(II) in 5% HCl, 1000 ± 4 mg L^{-1} Pt(IV) in 5% HCl, 1001 ± 6 mg L^{-1} Rh(III) in 5% HCl, all provided by Fluka, a subsidiary company of Sigma-Aldrich), in the required volumes of hydrochloric acid (~37%, p.a., Fisher Chemicals, Fisher Scientific Unipessoal, Lisboa, Portugal). Organic phases with 0.02 M DMDBTDGA were settled in toluene (Sigma-Aldrich, $\geq 99.3\%$). For the

determination of the stoichiometry of the DMDBTDGA: Pd(II) species, organic phases with DMDBTDGA concentrations varying between 1.6×10^{-3} to 2.0×10^{-2} M were considered. A 0.1 M thiourea solution (99%, Sigma-Aldrich) in 1.0 M HCl (~37%, p.a., Fisher Chemicals) was systematically used as Pd(II) stripping media [13,17].

For the selectivity experiments, 4.0 M HCl solutions containing 9.4×10^{-4} M Pd(II) and 5.1×10^{-4} M Pt(IV) were prepared, as well as similar ones with the additional presence of 9.7×10^{-4} M Rh(III) (about 100 mg L⁻¹ of each metal ion). Quaternary and five-metal ion solutions were further arranged, containing the three PGMs with 9.0×10^{-3} M Fe(III) (prepared from iron(III) chloride hexahydrate, 99%, Riedel-de Haën, a subsidiary company of Sigma-Aldrich) and/or 1.9×10^{-2} M Al(III) (prepared from aluminum(III) chloride, >98%, Merck, Merck & Co., Inc., Kenilworth, NJ, USA). The Fe(III) and Al(III) contents in the aqueous solutions were of about 500 mg L⁻¹.

Extraction and stripping experiments were generally performed by stirring equal volumes of aqueous and organic phases (A/O = 1) at room temperature (25 ± 2 °C) and adopting a rotation speed between 900 and 1000 rpm. The preliminary experiments carried out to evaluate the extraction affinity of DMDBTDGA toward Pd(II), Pt(IV) and Rh(III) in different HCl concentrations were performed considering a contact time of 30 min. After the investigation of the kinetics associated with Pd(II) extraction, the adopted agitation time for the subsequent experiments was 5 min. The period of shaking time considered for the stripping assays was always 30 min.

After separation of the two phases, the aqueous and organic extracts were always filtrated to minimize mutual entrainments. In the selectivity experiments, the assays including the presence of Fe(III) involved an additional scrubbing step of the loaded organic phase with distilled water.

The determination of the metal contents in single ion aqueous phases, before and after extraction, was performed by flame atomic absorption spectrophotometry (AAS, novAA 350, Analytik Jena, Jena, Germany). For the analysis of the multi-metallic aqueous solutions, inductively coupled plasma-atomic emission spectrometry (ICP-AES, model Ultima from Horiba Jobin-Yvon S.A.S., Longjumeau, France) was used instead. Metal ion concentrations in organic phases were calculated by mass balance. At least two replicates were considered for all the experiments, and the analysis of the aqueous solutions before and after extraction was systematically made in triplicate. The uncertainties determined for the extraction and stripping results are in the range of $\pm 5\%$ to $\pm 8\%$.

3. Results and Discussion

3.1. Palladium(II), Platinum(IV) and Rhodium(III) Extraction, and Palladium(II) Stripping

In order to appraise the extraction characteristics of DMDBTDGA toward Pd(II), Pt(IV), and Rh(III), several experiments were programmed to screen the effect of hydrochloric acid concentration on their distribution ratios (*D*). Accordingly, equal volumes of aqueous solutions containing about 9.4×10^{-4} M Pd(II), 5.1×10^{-4} M Pt(IV), or 9.7×10^{-4} M Rh(III) (in varying HCl concentrations between 1.0 M and 8.0 M) and organic phases with 0.02 M DMDBTDGA in toluene were put in contact for 30 min. The extraction results obtained are displayed in Figure 2, in which a plot showing the dependence of the log *D* values of Pd(II), Pt(IV), and Rh(III) on HCl concentrations can be observed.

Figure 2 illustrates that DMDBTDGA does not exhibit any appreciable capacity to extract Pt(IV) and Rh(III). In fact, the maximum $\log D$ values found for Pt(IV) and Rh(III) were -0.12 and -0.75 , respectively, both at 7.0 M HCl. Inversely, Pd(II) extraction is rather efficient between 1.5 M ($\log D = 1.17$) and 4.5 M HCl ($\log D = 1.01$), but a decreasing tendency is clearly visible for higher HCl concentrations. At 7.5 M HCl there is no Pd(II) extraction.

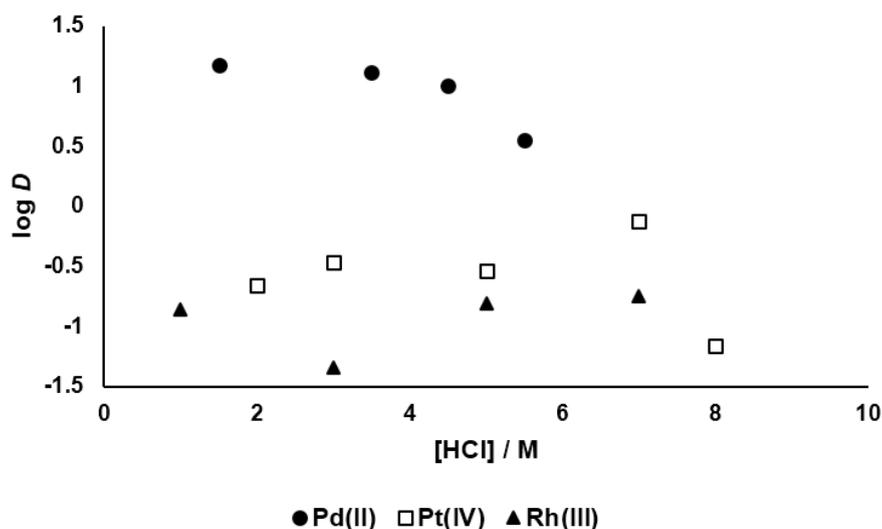


Figure 2. Variation of the $\log D$ values of Pd(II), Pt(IV), and Rh(III) with the HCl concentration (9.4×10^{-4} M Pd(II), 5.1×10^{-4} M Pt(IV), or 9.7×10^{-4} M Rh(III) in 1.0 M to 8.0 M HCl; 0.02 M DMDBTDGA in toluene; A/O = 1, room temperature, 900–1000 rpm, 30 min). Standard deviations: $\pm 5\%$.

A direct comparison of the Pd(II) extraction behavior shown by DMDBTDGA can be established with DMDCHTDGA [20], since the adopted experimental conditions are similar. The two extraction profiles are depicted in Figure 3. It is rather visible that both extractants reduce their extraction ability of Pd(II) as the HCl concentration in the aqueous phases increases, but DMDCHTDGA is much more efficient than DMDBTDGA. It is likely that the diluent (toluene) may play a determinant role in what concerns the dependence on the HCl concentration of both extraction systems [20], since Pd(II) was quantitatively extracted regardless of the HCl content (until 8.0 M HCl) by 0.05 M DMDCHTDGA in 1,2-dichloroethane [13].

Furthermore, the more HCl-concentrated equilibrium aqueous phases (from 5.5 M HCl onwards) resulting from contact with the DMDBTDGA toluene solutions showed a very visible stronger yellow tonality than the initial feeds, which could denote the loss of the organic compound to the aqueous phases. This assumption was confirmed after extraction of those aqueous solutions with toluene, the analysis of the residues showing the presence of DMDBTDGA. Hence, at least when toluene is used as the diluent, it is likely that the decrease of Pd(II) extraction efficiency on the enhancement of HCl concentration may partially be explained by the dissolution of DMDBTDGA in the more acidic HCl solutions, in addition to other phenomena of interfacial nature [20]. The DMDCHTDGA system involves a more hydrophobic extractant, having four extra carbon atoms when compared with DMDBTDGA; hence, a stronger yellowish tone in the equilibrium aqueous phase after contact with DMDCHTDGA was only visible for the 8.0 M HCl aqueous solution.

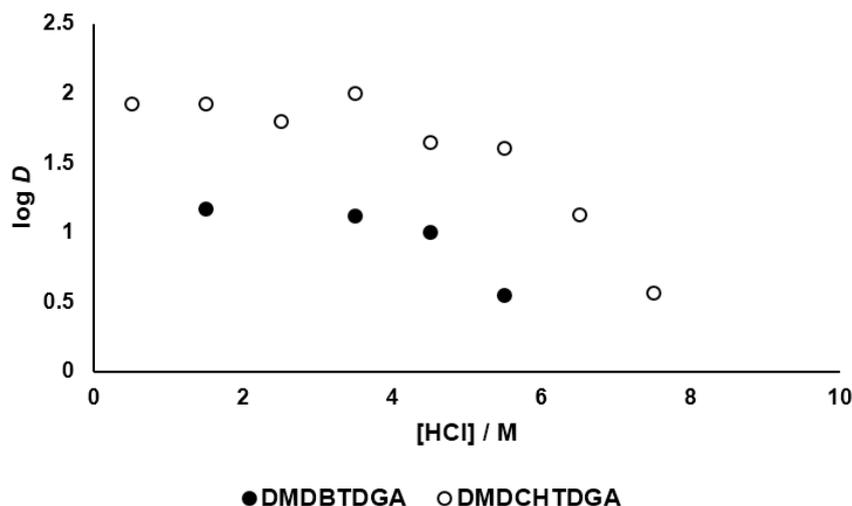


Figure 3. Variation of the $\log D$ values of Pd(II) with the HCl concentration by DMDBTDGA and DMDCHTDGA (9.4×10^{-4} M Pd(II) in 0.5 M to 7.5 M HCl; 0.02 M DMDBTDGA or DMDCHTDGA* in toluene; A/O = 1, room temperature, 900–1000 rpm, 30 min). Standard deviations: $\pm 5\%$ (*: data collected from [20]).

A few other thiodiglycolamide derivatives have been previously investigated to extract Pd(II), for instance *N,N'*-dimethyl-*N,N'*-diphenylthiodiglycolamide (DMDPHTDGA) in chloroform [22], and *N,N,N',N'*-tetraoctylthiodiglycolamide (TODTDGA), in 80 vol. % *n*-dodecane-20 vol. % 2-ethylhexanol [15], with Pd(II) being totally extracted from HCl solutions until 8.0 M HCl. A completely different behavior has been found for *N,N'*-dimethyl-*N,N'*-didecylthiodiglycolamide (MDTDGA), dissolved in 80 vol. % *n*-dodecane-20 vol. % 2-ethylhexanol, as D values of about 1–2 were achieved for 1.0–2.0 M HCl, of about 5 for 4.0 M HCl, 60 for 5.0 M, and >100 for 6.0 M and 7.0 M HCl [16]. Therefore, features such as the length and/or combination of substituent groups, and diluents as well, cause diverse Pd(II) extraction profiles when HCl concentration in the aqueous chloride media vary.

Nonetheless, the adequacy of DMDBTDGA in toluene to extract Pd(II) from HCl solutions until 4.5 M HCl is unquestionable, and therefore, further research on this extractive system is rather justifiable.

In order to confirm that Pd(II) stripping from DMDBTDGA is similarly efficient as when DMDCHTDGA is used [13,20], the Pd(II) loaded organic phases coming from the contact with the HCl solutions until 4.5 M HCl were equilibrated with equal volumes of 0.1 M thiourea in 1.0 M HCl. Pd(II) was always quantitatively stripped to the thiourea aqueous phases, with these results opening good perspectives for the utilization of this solvent system for selective Pd(II) recovery from complex metallic solutions.

3.2. Kinetics of Palladium(II) Extraction

This set of experiments was carried out using a feed aqueous solution containing 9.4×10^{-4} M Pd(II) in 4.5 M HCl, and involving a 0.02 M DMDBTDGA in toluene as the organic phase. The time of contact for both phases varied between 2 and 60 min, and all the other parameters were kept constant.

It was found that the extraction kinetics for these systems is very favorable, as can be seen in Figure 4a 2 min contact results in the highest log D value obtained, with an apparent tendency to decrease for longer contact periods. A higher uncertainty of the results ($\pm 8\%$) may partially justify this unexpected trend. However, the pattern achieved also suggests the possible occurrence of a more complex phenomenon: if the direct kinetic constant is larger than the one corresponding to the forward extraction reaction, this means that Pd(II) would be extensively extracted at very short times, and after a few minutes, when the forward reaction takes place, D values would decrease until equilibrium is reached. Further investigation is obviously needed to support such an assumption.

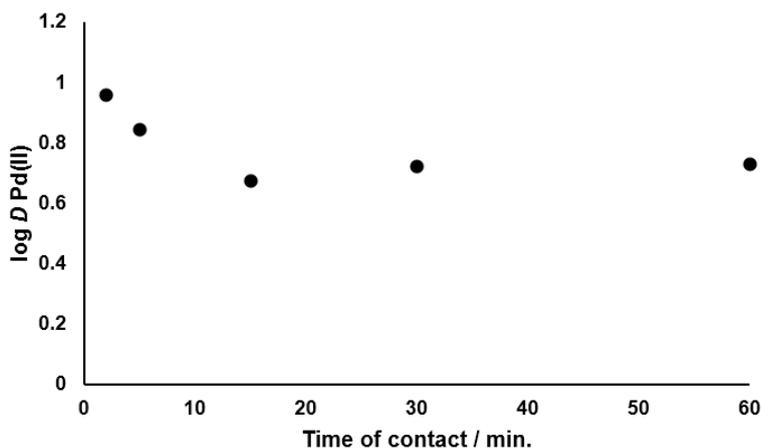


Figure 4. Variation of the log D values of Pd(II) with the contact time (9.4×10^{-4} M Pd(II) in 4.5 M HCl; 0.02 M DMDBTDGA in toluene; A/O = 1, room temperature, 900–1000 rpm). Standard deviations: $\pm 8\%$.

Nevertheless, the period of time necessary for DMDBTDGA to efficiently extract Pd(II) is quite short, being in general agreement with the ones previously reported for other thiodiglycolamide derivatives, e.g., less than 5 min for DMDPHTDGA [22], 10 min for MDTDGA [16], and 15 min for both TODTDGA [15] and DMDCHTDGA [20].

Accordingly, a contact time of 5 min was adopted for all the subsequent experiments with DMDBTDGA.

3.3. Effect of DMDBTDGA Concentration on Palladium(II) Extraction

The evaluation of the effect of the extractant concentration on the D values of Pd(II) provides information about the stoichiometry of the extractant: Pd(II) species, contributing to the establishment of the Pd(II) extraction reactions. These sets of experiments were carried out under the usual extraction conditions and involved a 9.4×10^{-4} M Pd(II) in 4.5 M HCl aqueous solution, which was contacted with DMDBTDGA organic phases with concentrations varying between 1.6×10^{-3} to 2.0×10^{-2} M.

The log-log plot between the Pd(II) D values and the initial DMDBTDGA concentrations indicates a slope value of about 1.2, as shown in Figure 5. However, as the DMDBTDGA concentrations are not in a sufficiently large excess when compared with that of Pd(II), the DMDBTDGA-Pd(II) species concentrations cannot be neglected or, in other words, the initial DMDBTDGA concentration should not

be considered as similar to the DMDBTDGA concentrations at equilibrium. Accordingly, an iterative method previously developed in our group to overcome these situations was applied [23].

In this method, calculations for the free extractant concentrations are carried out upon consideration of different stoichiometric molar ratios between the extractant and the metal ion. When plotting the log-log plots involving the equilibrium ligand concentrations, the coincidence between the slope value obtained and the estimated one is sought [23]. For the DMDBTDGA system, slopes were coincident for a 1.10 value (Figure 5). Hence, this result suggests that species having a 1:1 DMDBTDGA: Pd(II) stoichiometry should exist in the organic solutions.

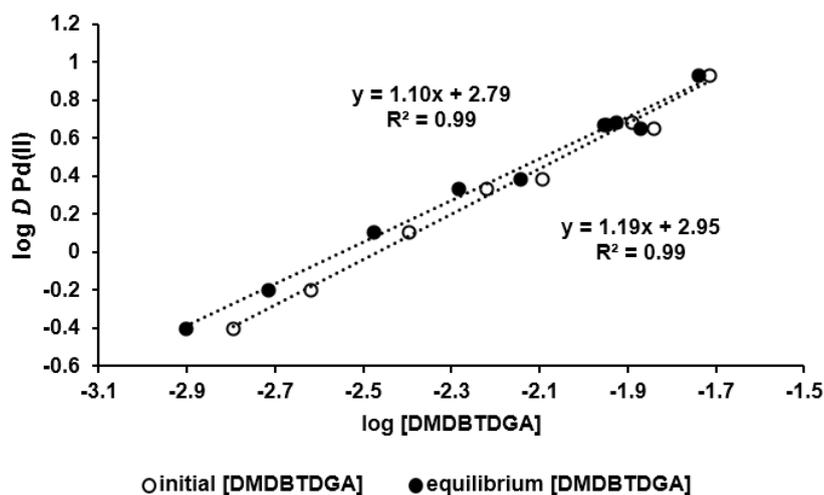


Figure 5. Dependence of the Pd(II) log D values on the log of the initial and equilibrium DMDBTDGA concentrations (9.4×10^{-4} M Pd(II) in 4.5 M HCl; 1.6×10^{-3} to 2.0×10^{-2} M DMDBTDGA in toluene; A/O = 1, room temperature, 900–1000 rpm). Standard deviations: $\pm 5\%$.

Knowing that the predominant Pd(II) species for 1 M and higher HCl concentrations is $[\text{PdCl}_4]^{2-}$ [24–26], the general data on the Pd(II) extraction reactions involving different amine and amide derivatives indicates the occurrence of two different mechanisms: the direct extraction of $[\text{PdCl}_4]^{2-}$ by a positively charged extractant, resulting in an outer-sphere electrostatic attraction, and/or the replacement of chloride anions from the complexation sphere of $[\text{PdCl}_4]^{2-}$ by ligand molecules, due to the liability nature of this chlorocomplex, giving rise to inner-sphere complexes in the organic phase [24]. Previous studies with other thiodiglycolamide derivatives, e.g., MDTDGA [16] and TODTDGA [15], point to inner-sphere complexation reactions when Pd(II) is extracted from 3.0 M HCl (in spite of their completely different profile when the influence of HCl in the feed aqueous solution is taken into account) whereas the metal ion seems to be extracted by a mixing of outer-sphere ion pairs and inner-sphere complexation by DMDPHTDGA [22].

Further research is needed to determine how is Pd(II) extracted by DMDBTDGA from 4.5 M HCl, although the fast extraction rate of the metal ion in this system may eventually suggest the existence of ion-pair extraction reactions [22,27]. Assuming this is the case, a proposal for the Pd(II) species extracted by DMDBTDGA would be the outer-sphere electrostatic attraction between the $[\text{PdCl}_4]^{2-}$ species and

the protonated extractant on its two amide sites, in a similar scheme as the one suggested for the DMDCHTDGA-Pt(IV) species [13].

3.4. Selectivity for Palladium(II) Extraction

The selectivity shown for Pd(II) extraction by DMDBTDGA is a relevant key point whose evaluation is rather pertinent. On one hand, the separation of Pd(II) from the other two PGMs can be envisaged; subsequently, its isolation from base metals such as Al(III) and Fe(III), often appearing in the leaching solutions of end-of-life anthropogenic sources, is again interesting. Therefore, focusing on the use of HCl media with a more practical interest, 4.0 M HCl solutions with two—Pd(II) and Pt(IV)—and three PGMs—Pd(II), Pt(IV) and Rh(III)—were considered, all with concentrations of about 100 mg L⁻¹.

The overall data obtained for the DMDBTDGA extractive performance toward the three PGMs are illustrated in Table 1, shown by the separation factors (SF) of Pd(II) in relation to each of the other metal ions (calculated as $SF = D_{Pd}/D_{metal}$). Hence, the higher the SF, the more selective for Pd(II) recovery DMDBTDGA is. As similar tests were previously carried out with DMDCHTDGA [20], the results obtained with this compound are also included in Table 1 for a direct comparison.

Table 1. Selectivity of DMDBTDGA for extraction of two and three PGM solutions (solutions 1 and 2, respectively), evaluated through the correspondent separation factor values (SF). Standard deviations: $\pm 5\%$.

[HCl] = 4 M	Solution 1		Solution 2
	Pt(IV)	Pt(IV)	Rh(III)
DMDBTDGA	261	356	~2880
DMDCHTDGA *	354	289	~2000

* Data collected from [20].

For the binary aqueous media—solution 1—it can be observed that the $SF_{Pd/Pt}$ achieved for DMDBTDGA is good, and a similar situation is extended for the three PGMs solution. Rh(III) is practically not extracted. The selective performance shown by DMDBTDGA for Pd(II) recovery when Pt(IV), and Pt(IV) and Rh(III), are present in the 4.0 M HCl solution is comparable to the data previously found for DMDCHTDGA [20]. Pd(II) was efficiently stripped by 0.1 M thiourea in 1.0 M HCl from the DMDBTDGA loaded organic phases—84 to 86 mg L⁻¹—with a maximum Pt(IV) contamination of 7 mg L⁻¹.

Other experiments were subsequently carried out involving four metals in the feed aqueous phases, namely the three PGMs with either 500 mg L⁻¹ Al(III) (solution 3) or Fe(III) (solution 4), and finally five-metal aqueous solutions were also considered, containing the three PGMs, Al(III) and Fe(III) (solution 5), all with similar concentrations as described above. The overall results are depicted in Table 2.

Table 2. Selectivity of DMDBTDGA for extraction of three PGMs with Al(III) or Fe(III) (solutions 3 and 4, respectively) and three PGMs with Al(III) and Fe(III) (solution 5), evaluated through the correspondent SF values. Standard deviations: $\pm 5\%$.

[HCl] = 4 M	Solution 3			Solution 4			Solution 5			
	Pt(IV)	Rh(III)	Al(III)	Pt(IV)	Rh(III)	Fe(III)	Pt(IV)	Rh(III)	Al(III)	Fe(III)
DMDBTDGA	271	759	673	5	66	26	5	126	169	26
DMDCHTDGA *	314	~2180	~7300	20	996	30	32	~1650	~2260	38

* Data collected from [20].

In the presence of Al(III), the $SF_{Pd/Pt}$ by DMDBTDGA is comparable to the ones previously achieved, whereas Rh(III) is more extracted than before. Al(III) is not extracted extensively. As expected, due to what previously occurred with DMDCHTDGA [20], Fe(III) is widely extracted by DMDBTDGA, and Pt(IV) withdrawal markedly increases as well. In spite of that, the Pd(II) distribution ratio is high ($D = 20$). The general selective behavior toward Pd(II) found earlier for DMDCHTDGA [20] is better than that determined for DMDBTDGA.

The results displayed in Table 2 for the extraction of the five-metal aqueous phase (solution 5) show that Rh(III) and Al(III) are now generally more extracted by DMDBTDGA, whereas the SF values for the pairs Pd/Pt and Pd/Fe are the same as those obtained for solution 4. The D value for Pd(II) was about 11. These overall results are worse than the ones achieved for DMDCHTDGA [20], also included in Table 2.

Although extensively extracted, Fe(III) can efficiently be scrubbed from the loaded organic media with water [20]. Hence, focusing on the treatment of solution 5, 90% of Fe(III) from the loaded organic phase transferred to water, accompanied by a maximum of 2 mg L^{-1} Pd(II). Pd(II) was efficiently stripped by 0.1 M thiourea in 1.0 M HCl from the loaded organic phase— 86 mg L^{-1} —with residual contaminations of Pt(IV) and Fe(III) less than 1 mg L^{-1} . Neither water nor the thiourea solution were able to remove the Pt(IV) content from the loaded DMDBTDGA solution. An efficient stripping agent to recover Pt(IV) has not still been found to date, but its discovery would be crucial to take profit of the extensive co-extraction of Pt(IV) with Pd(II), as the two PGMs could be further separated by selective stripping [13]. The extraction of Pt(IV) together with Pd(II) was not so effective when DMDCHTDGA was used, as can be seen in Table 2 [20].

In summary, the selectivity patterns observed for DMDBTDGA toward Pd(II) are relatively good; among the metal ions tested, only Pt(IV) in the presence of Fe(III), and Fe(III) itself, are extensively extracted together with Pd(II). Fe(III) is easily removed through an intermediate scrubbing step with water. Nevertheless, the selective behavior for Pd(II) recovery shown by the other thiodiglycolamide derivative previously investigated—DMDCHTDGA [20]—is generally much better than that of DMDBTDGA, particularly if Al(III) and Fe(III), and not only Pt(IV) and Rh(III), are present in the feed 4.0 M HCl aqueous phase. These selectivity differences can be rationalized by resorting to the role the substituent groups in the thiodiglycolamide skeleton are likely to play; the butyl groups are apparently too short to favor a more specific selectivity trend, and probably to avoid significant losses of the extractant to the more acidic HCl phases as well. The cyclohexyl substituents, on the other hand, proved to be more adequate to achieve better extraction efficiency and selectivity profiles for Pd(II) recovery by DMDCHTDGA [20].

The evaluation of the performance shown by MDTDGA toward Pd(II) extraction has already been carried out [16], but under quite different experimental conditions than those adopted in this work. A direct comparison between the extraction systems involving DMDBTDGA and DMDCHTDGA with MDTDGA is not possible at present, but the screening of the extraction behavior for Pd(II) depicted by a similar thiodiglycolamide derivative with octyl or decyl groups, in addition to the two methyl substituents, would surely be worthwhile.

4. Conclusions

N,N'-dimethyl-*N,N'*-dibutylthiodiglycolamide (DMDBTDGA) has been synthesized to test its practical usefulness as a SX reagent to recover PGMs from concentrated HCl media. DMDBTDGA in toluene is efficient for Pd(II) extraction until 4.5 M HCl, with a gradual decrease afterwards. Pd(II) in the loaded organic phases is quantitatively stripped by a 0.1 M thiourea in 1 M HCl solution. The extraction kinetics are very favorable (5 min maximum), and the distribution data points out to an extractant: Pd(II) ratio of 1:1.

Pd(II) is selectively recovered from 4.0 M HCl solutions containing the three PGMs under study. However, the selectivity patterns become worse when excess concentrations of Al(III) and Fe(III) co-exist in the HCl solution: Pd(II) distribution ratios are not critically affected, but Pt(IV) is much more extracted than before, together with Fe(III). The Fe(III) interference can nonetheless be eliminated by an intermediate scrubbing step of the loaded organic phases with water. Al(III), one of the main contaminants in real leaching solutions of the hydrometallurgical treatment of secondary raw materials, is not extensively extracted.

The selectivity figures obtained for DMDBTDGA, although reasonable, are poorer than those achieved for DMDCHTDGA [20], another thiodiglycolamide derivative tested under similar conditions.

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Author Contributions

Mário E. Martins and Osvaldo Ortet carried out the synthesis and characterization of DMDBTDGA, as well as the SX experiments. Ana Paula Paiva supervised all the research and wrote the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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