N,N′-dimethyl-N,N′-dicyclohexylsuccinamide: A novel molecule for the separation and recovery of Pd(II) by liquid-liquid extraction

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ABSTRACT

N,N′-dimethyl-N,N′-dicyclohexylsuccinamide (DMDCHSA) is investigated as a potential molecule for the liquid-liquid extraction of Pd(II) from chloride solutions for the first time. The effect of several parameters on Pd(II) extraction, such as the contact period between both phases, hydrochloric acid, extractant and hydrogen ion concentrations, is evaluated. Pd(II) extraction equilibrium is very fast (30 s) and the extraction percentage (%E) increases with the HCl concentration in the aqueous phases, being higher than 60% for [HCl] > 5 M. The loading capacity of DMDCHSA for Pd(II) is reasonable (molar ratio extractant/metal higher than 16). Several stripping agents (e.g. distilled water, 1 M HCl, seawater and 20 g/L chloride solution as NaCl) were successfully used to transfer Pd(II) to a new aqueous phase, and data obtained from five successive extraction-stripping cycles suggest a good DMDCHSA stability pattern. Attempts to replace 1,2-dichloroethane (1,2-DCE) by commercial and more environmentally friendly diluents showed much worse %E for Pd(II). Selectivity tests with binary, ternary and more complex metal ion solutions were carried out to evaluate the performance of DMDCHSA towards Pd(II) recovery from 6 M HCl, when in presence of Pt(IV), Fe(III), Zn(II), Al(III) and Ce(III), metal ions usually present in solutions that may result from the hydrometallurgical treatment of spent automobile catalytic converters. It was generally observed that the additional metal ions do not affect the recovery of Pd(II) by DMDCHSA, although Fe(III) and Pt(IV) were co-extracted in a great extent. A solvent extraction (SX) scheme is proposed, based on a previous separation of Fe(III) with tributylphosphate (TBP) and on the selective and sequential stripping of Pt(IV) and Pd(II) from the loaded DMDCHSA with 0.01 M thiourea in 0.5 M HCl and seawater, respectively. The dependence of the Pd(II) distribution ratios on DMDCHSA and acidity, complemented with UV–Visible spectroscopy data, points out to DMDCHSA:Pd(II) extracted species with a 2:1 molar ratio and suggests the occurrence of an outer-sphere ion pair reaction, in which both $[PdCl_4]^{2-}$ and HCl are extracted.

1. Introduction

Platinum group metals (PGMs) have a high economic value and have been considered critical raw materials [1]. These facts are associated to the PGMs scarcity in the Earth's crust, to the difficult replacement of PGMs in many applications (fuel cells, electronics and catalysis) and also to the high supply risks associated to them [2].

Palladium belongs to the PGMs group, representing only $1.5 \times 10^{-6}\%$ of the Earth's crust; its demand and production led to an increase of its market price in the last few years [3–6]. Palladium has

been used for several purposes, including automobile catalysts, electronics, industrial catalysts, electronic circuitry, dental alloys, jewellery, and lately in the treatment of cancer [7–9]. Hence, the recovery and reuse of PGMs, namely palladium, from industrial wastes is crucial, for technical and economical reasons [10].

Industries have been using different methods to recover PGMs from aqueous solutions in the past few years: solvent extraction (SX) (also known as liquid-liquid extraction), ion exchange, evaporation, cementation, chemical precipitation, electrochemical and sorption methods [11–14]. PGMs recovery by hydrometallurgical processes

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usually involves aqueous chloride phases, the best to dissolve PGMs, allowing high recovery performances [15]. Accordingly, SX has been used as one of the most successful methods for the separation of PGMs from chloride leach solutions, since it can present excellent efficiency and selectivity patterns [16]. In order to plan a SX experiment, the knowledge about PGMs species in concentrated chloride media is extremely important; for instance, $[PdCl_4]^{2-}$ is the predominating Pd(II) species at 1 M and higher HCl concentrations [17–20].

Several extractants have been proposed for the recovery of palladium from chloride solutions of different origin. In industrial SX, the most used extractants to recover Pd(II) and Pt(IV) can directly extract the respective chlorocomplexes through ion pairs, implicating the protonation of the organic compound. Two types of extractants are typically involved: amines and ammonium salts [18]. The extraction of Pd(II) can also be achieved using neutral organophosphorus compounds [21], hydroxyoximes (Cleare, 1979) [22], ketoximes [23], 8-hydroxyquinoline derivatives [24], phosphonium salts [25] and even thiol and dithioether derivatives [26,27].

The use of a wide range of amide derivatives, both monoamides and diamides, as well as sulphur-containing amides (thioamides and thiodiglycolamides) has been largely explored in the last few years for PGMs extraction.

Several sulphur-containing monoamides [28,29] including *N*-methyl-*N*-phenyl-octanthioamide (MPHTA) and *N*-methyl-*N*-cyclohexyl-octanthioamide (MCHTA) were recently successfully tested for Pd(II) extraction from concentrated chloride medium [30]. Sulphur-containing diamides, such as thiodiglycolamide derivatives, namely *N*,*N*′-dimethyl-*N*,*N*′-diphenylthiodiglycolamide (DMDPHTDGA) [31,32] and *N*,*N*′-dimethyl-*N*,*N*′-dicyclohexylthiodiglycolamide, (DMDCHTDGA) [16,33–35] demonstrated potential to extract Pd(II) and Pt(IV), and the separation of both PGMs from the loaded DMDCHTDGA was achieved using a selective stripping approach [16,35]. According to Narita and co-workers [36], *N*,*N*,*N*′*N*′-tetra-*n*-octylthiodiglycolamide also exhibited good affinity towards Pd(II) extraction from HCl solutions.

Beyond these extractants, several *N*,*N*′-tetrasubstituted malonamide derivatives, namely *N*,*N*′-dimethyl-*N*,*N*′-dihexylmalonamide (DMDHMA) [37], *N*,*N*′-dimethyl-*N*,*N*′-dicyclohexylmalonamide (DMDCHMA) [37], *N*,*N*′-dimethyl-*N*,*N*′-diphenylmalonamide (DMDPHMA) (Data not published), *N*,*N*′-dimethyl-*N*,*N*′-dibutylmalonamide (DMDBMA) [38], *N*,*N*′-dimethyl-*N*,*N*′-dihexyltetradecylmalonamide (DMDHTDMA) [37], *N*,*N*′-dimethyl-*N*,*N*′-dicyclohexyltetradecylmalonamide (DMDCHTDMA) [39] and *N*,*N*′-dimethyl-*N*,*N*′-diphenyltetradecylmalonamide (DMDPHTDMA) [40] have been tested for the extraction and separation of Pd(II) and Pt(IV) [41], or even for other PGMs such as Rh(III) [42] and Ru(III) [43] from HCl media. In general, good results were obtained for Pd(II) recovery and for other PGMs separations, although the extraction behaviour and efficiency usually depend on the chemical structure of the malonamide tested.

The presence of an additional carbon atom between the carbonyl groups results in *N*,*N*,*N*′,*N*′-tetrasubstituted succinamides, which are bigger molecules than the respective malonamides, thus theoretically more suitable to "accommodate" large sized PGM extracted species.

The present paper is part of a broader research to find out SX extractants able to recover PGMs from industrial leaching processing or effluents. It describes, for the first time, the effect of several extraction parameters on the performance of *N*,*N*′-dimethyl-*N*,*N*′-dicyclohexylsuccinamide (DMDCHSA) for the recovery of Pd(II) from hydrochloric acid media, a succinamide derivative that showed previously a good extraction ability for Pt(IV) in similar conditions [44]. Thus, in addition, the separation of Pd(II) from Pt(IV) and Fe(III), both extracted by DMDCHSA, was investigated using different extraction and stripping stages and conditions. A process scheme based on the use of DMDCHSA is proposed herein, aiming to obtain purified Pd(II) and Pt(IV) solutions by employing several extraction and stripping steps. Comparison of the Pd(II) extraction behaviour of DMDCHSA with other diamides, namely DMDPHSA as a different succinamide, malonamides and thiodiglycolamides, is also done.

2. Experimental

2.1. Synthesis and characterization of DMDCHSA

The synthesis and characterization of DMDCHSA was previously reported [44].

2.2. Solvent extraction experiments

All reagents and solvents were used without further purification. Hydrochloric acid (37%, AnalaR NORMAPUR) solutions containing 9×10^{-4} M Pd(II) were prepared from the Pd(II) chloride salt (99%, Aldrich). The HCl concentration of the metal solutions ranged from 1 to 8 M. Solutions with 2.5×10^{-3} and 5×10^{-3} M of Pd(II) in 6 M HCl were prepared to be used in the extraction isotherm tests, adopting the successive loading of the same portion of organic phase and varying the aqueous/organic (A/O) ratios.

The organic phases containing 0.05 M DMDCHSA, or other desired concentrations, were generally prepared in 1,2-dichloroethane (1,2-DCE, Fluka, minimum 99.5%). In the experiments performed to investigate the effect of different diluents on Pd(II) extraction, other diluents were also used, such as dichloromethane (Riedel-de Haën, analytical reagent, minimum 99.8%), toluene (Panreac, minimum 99.5%), kerosene (Sigma-Aldrich, boiling point 175–325 °C), xylene (analytical reagent, Lab-Scan, minimum 99%, mixture of isomers), 1-octanol (Acros Organics, 99%), Escaid 100® (Exxon Mobil, boiling point 195–245 °C, 18–24% aromatic content), Varsol 80® (Exxon Mobil, boiling point 206–238 °C, 24% aromatic content), Exxsol D80® (Exxon Mobil, boiling point 208–236 °C, 0.2 wt% aromatic hydrocarbon content), and Shellsol D70® (Shell Chemicals, boiling point 198–242 °C, low aromatic content).

Distilled water, 1 M HCl, seawater, 20 g/L chloride solution (as NaCl) and a "nutrient medium" composed by sodium lactate (6 g/L), yeast extract (1 g/L), trisodium citrate dihydrate (0.3 g/L), ascorbic acid (0.1 g/L) and thioglycolic acid (85.3 mg/L) dissolved in seawater were used as agents to strip palladium from the loaded organic phases.

The extraction and stripping experiments were performed at room temperature by contacting equal volumes of the organic and aqueous phases (A/O = 1) for 30 min, using mechanical stirring, with a rotation speed between 900 and 1000 rpm. After separation of the two phases, the aqueous solutions were filtered and their palladium concentration was determined by flame-Atomic Absorption Spectrometry (AAS, Analytikjena NovAA 350 model spectrometer). The aqueous solutions were analysed before and after the extraction or stripping experiments.

The extractant reutilization experiments consisted of five successive cycles of extraction and stripping. A solution containing 9.4×10^{-4} M Pd(II) in 6 M HCl was contacted with an organic phase of 0.05 M DMDCHSA in 1,2-DCE under the usual set of experimental conditions and, after each stripping stage with seawater, the same organic extract was again equilibrated with a fresh portion of aqueous solution.

For the selectivity experiments, a 6 M HCl solution containing 9×10^{-4} M Pd(II), 5×10^{-4} M Pt(IV), 1×10^{-3} M Zr(IV), 1.8×10^{-2} M Al(III), 9×10^{-3} M Fe(III) and 7×10^{-4} M Ce(III) – from the corresponding chloride salts: PtCl$_4$ (Aldrich), ZrCl$_4$ (Merck), AlCl$_3$ (Panreac), FeCl$_3$·6H$_2$O (Aldrich) and CeCl$_3$ (Aldrich) – was equilibrated with 0.05 M DMDCHSA in 1,2-DCE. Tributyl phosphate (TBP, 97%, Aldrich) was used without further purification. Kerosene (Aldrich) was employed as diluent and 2-decanol as modifier (98%, Aldrich). Distilled water, 1 M HCl, seawater and 0.01 M thiourea (99%, Aldrich) in 0.5 M HCl were used as stripping agents. After separation of the two phases, as performed for the Pd analysis, the aqueous solutions were filtered and the metal concentrations were determined by flame-AAS and/or by Microwave Plasma Atomic Emission Spectroscopy (MP-AES).

The experiments were carried out in duplicate for each condition. The analysis of the solutions before and after extraction was performed

in triplicate. The metal ion concentration values obtained from the extraction and stripping experiments always present a coefficient of variance lower than ± 5%.

3. Results and discussion

3.1. Effect of equilibration time on the extraction of palladium(II)

After preliminary tests where the ability of DMDCHSA for Pd(II) extraction was confirmed, the present study started by the evaluation of the effect of contact time on Pd(II) extraction. For that purpose, a set of experiments was performed using 6 M HCl solutions, maintaining the Pd(II) concentration at 5×10^{-4} M, and using a 0.05 M DMDCHSA in 1,2-DCE as organic phase. The time of contact between the two phases varied from 0.5 to 60 min, all the other parameters being those indicated in the experimental section. The obtained results indicated that the kinetics for this system is extremely fast, since about 70% of Pd(II) extraction (%E) was achieved just after 30 s of contact between the two phases; accordingly, the metal %E after 1, 2, 3, 5, 10, 15, 30 and 60 min were also very similar. The fast kinetics exhibited by DMDCHSA for Pd(II) extraction seems to be a characteristic also demonstrated by other diamide derivatives, being in general agreement with the ones previously reported: *e.g.*, less than 5 min for DMDPHTDGA [45], 10 min for *N,N′*-dimethyl-*N,N′*-didecylthiodiglycolamide, MDTDGA [46], and 15 min for both *N,N,N′,N′*-tetraoctylthiodiglycolamide, TOTDGA [36] and DMDCHTDGA [33].

The Pt(IV) extraction rate of DMDCHSA, and also the one presented by *N,N′*-dimethyl-*N,N′*-diphenylsuccinamide (DMDPHSA) under the same experimental conditions was similarly extremely fast, since 100% and 81% were extracted, respectively, just after 30 s of contact between the two phases [44].

The results obtained for the Pd(II) extraction kinetics are relevant aiming an eventual industrial application, because long contact times to reach equilibrium could be a limiting factor for the viability of the metal recovery process.

Although much lower contact times could be used, a contact time of 30 min was adopted for all the subsequent essays, to assure that there is enough time to reach the thermodynamic equilibrium of each system in all the extraction conditions utilized.

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

Extraction experiments were carried out using 5×10^{-4} M of Pd(II) in 1 M to 8 M HCl solutions, and 0.05 M DMDCHSA in 1,2-DCE as organic phase. The extraction results obtained are displayed in Fig. 1. It can be seen that Pd(II) is progressively more extracted as the HCl concentration increases in the aqueous solutions. About 80% of Pd(II) extraction was achieved from 8 M HCl.

Table 1 summarizes the Pd(II) extraction behavior of several *N,N,N′,N′*-tetrasubstituted diamides with similar structures (succinamides, malonamides and thiodiglycolamides) in order to compare the extraction profile of DMDCHSA with others already investigated for the same purpose.

From Table 1 it is clear that the change of the succinamide structure by replacing the cyclohexyl by phenyl groups has a negative effect on Pd(II) extraction, since values of %E lower than 10% are obtained for HCl solutions ranging from 1 M to 8 M, regardless of the acid concentration. A similar situation (no extraction of Pd(II) on the same HCl concentration range) is observed for the corresponding malonamide (DMDPHMA).

As expected, DMDCHSA presents a significantly higher Pd(II) extraction than the corresponding malonamide (DMDCHMA) from HCl concentrations ranging from 3 M to 8 M, thus confirming, as hypothesized, that the presence of an additional carbon atom between the amide groups turns the extractant more suitable to accommodate the high sized Pd(II) extracted species.
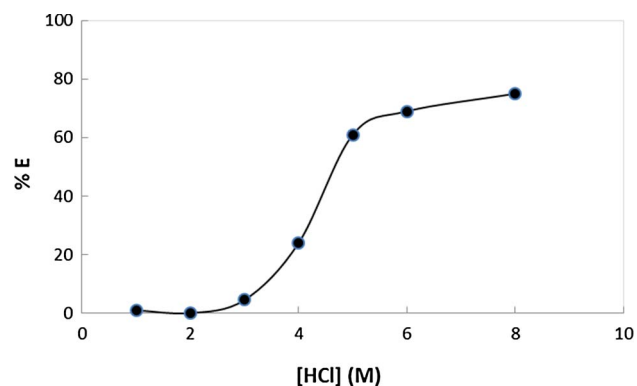

Fig. 1. Effect of HCl concentration on Pd(II) extraction by 0.05 M DMDCHSA in 1,2-DCE. [Pd(II)] = 5×10^{-4} M.

For the malonamides, the increase of the extractant hydrophobicity, obtained by the introduction of an alkyl chain (a tetradecyl group) in the central carbon atom of the molecule, did not bring any benefits to Pd(II) extraction. Therefore, the alkylation of the succinamides, that would turn the extractant more expensive, was not performed. As it was previously observed for the extraction of Fe(III) with malonamide derivatives [47,48], the extraction of Pd(II) from HCl solutions ranging from 1 M to 8 M is affected by the type of *N,N′*-substituents.

The presence of an additional sulphur atom on the diamide structures originating thiodiglycolamide derivatives has a positive effect on Pd(II) extraction, as DMDCHTDGA is able to extract Pd(II) from HCl solutions independently of their concentration (from 1 M to 8 M), which is in accordance with the behavior previously described for TOTDGA, despite the use of a different diluent (a mixture of 80% *n*-dodecane and 20% 2-ethylhexanol). A similar Pd(II) extraction profile is also presented by DMDPHTDGA in chloroform, proving that, in this case, the replacement of the cyclohexyls by the phenyl substituents does not affect the metal extraction. Contrarily, the replacement by butyl groups resulting in DMDBTDGA appears to have had an adverse effect, since Pd(II) is only quantitatively extracted from 1.5 M to 4.5 M HCl solutions, decreasing gradually for higher acid concentrations, although the use of a different diluent should also be considered.

In short, the Pd(II) extraction behavior as a function of HCl concentration varies considerably, showing that the length and/or combination of substituent groups, the introduction of a sulphur atom and also the use of different diluents are responsible for diverse Pd(II) recovery profiles when different diamide derivatives are used.

3.3. Effect of different diluents on the extraction of palladium(II)

The toxicity of chlorinated diluents is well known, thus their use for industrial applications is not desirable. In view of that, several alternative diluents to 1,2-DCE were tested, in order to determine their influence on the extraction performance of DMDCHSA for Pd(II). Aromatic diluents (toluene and a mixture of xylene isomers), commercial diluents such as kerosene, Escaid 100®, Varsol 80®, Exxsol D80® and Shellsol D70®, mainly selected having in view an industrial application, and an alternative polar diluent, 1-octanol, more environmentally-friendly than chlorinated diluents, were tested. The Pd(II) extraction experiments were performed from 6 M HCl and DMDCHSA concentration was kept constant at 0.05 M. The extractant was completely soluble in all the mentioned diluents. The overall results obtained are displayed in Table 2.

The results shown in Table 2 point out that polar diluents like 1-octanol and particularly dichloromethane and 1,2-DCE allow a higher %E for Pd(II) comparing with non-polar diluents (aromatic and commercial) which are not efficient for Pd(II) extraction by DMDCHSA. The best diluent tested was 1,2-DCE, followed by dichloromethane, which indicates that the use of polar diluents can be determinant to obtain

Table 1
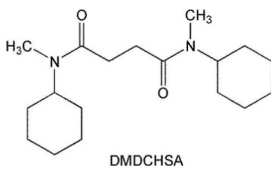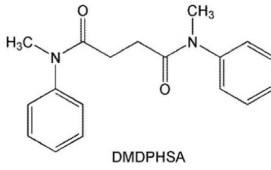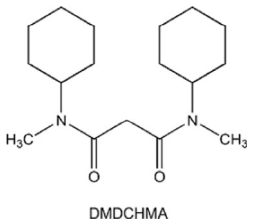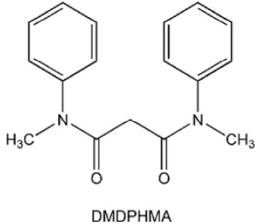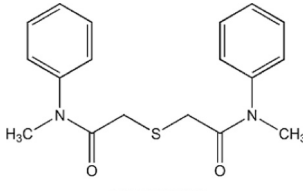Summary of Pd(II) extraction behavior of several *N,N,N′,N′*-tetrasubstituted diamides.
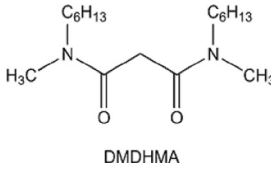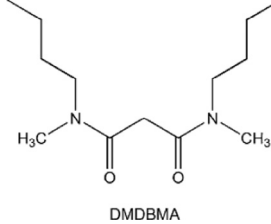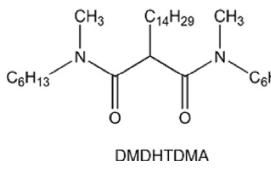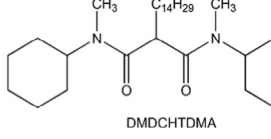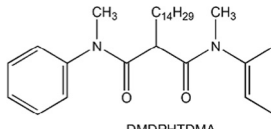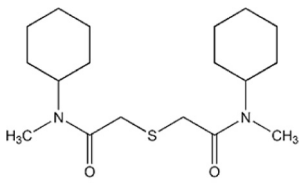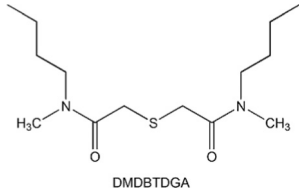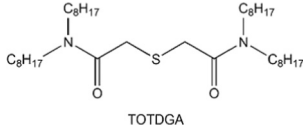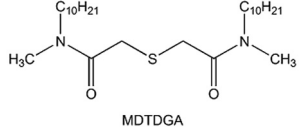
Type of diamide	Chemical structure and respective acronym	Pd(II) Extraction behaviour	Reference
Succinamide	DMDCHSA	Pd(II) is progressively more extracted as the HCl concentration increases. About 80% extraction from 8 M HCl, using 1,2-DCE as diluent	This paper
	DMDPHSA	Below 10% extraction independently of HCl concentration, using 1,2-DCE as diluent	This paper
Malonamide	DMDCHMA	No extraction was detected from 1 to 5 M HCl, ~25% extraction from 6 M HCl and ~35% extraction from 8 M HCl with 1,2-DCE as diluent	[37]
	DMDPHMA	No extraction was detected from 1 to 8 M HCl using 1,2-DCE as diluent	Not published
	DMDHMA	Extraction increases with the increase in HCl concentration (sinusoidal behaviour), showing no extraction from 1 M HCl and a maximum extraction (79%) at 8 M HCl, with 1,2-DCE as diluent	[37]
	DMDBMA	Extraction decreases from 65% at 1 M HCl to 22% at 8 M HCl for the extractant dissolved in 1,2-DCE	[38]
	DMDHTDMA	Extraction follows a parabolic profile: 50% at 1 M HCl, reaching a minimum of 12% at 4 M HCl, and then starting to increase until 63% at 8 M HCl, with 1,2-DCE as diluent	[37]
	DMDCHTDMA	Extraction from 1 and 2 M HCl is below 10%, from 4 M to 6 M HCl is null and at 8 M HCl is around 40%, using 1,2-DCE as diluent	[39]
	DMDPHTDMA	Maximum %E towards the Pd(II), Pt(IV) and Rh(III) reaches 20–30%, being lower than 15% for Pd(II) for all HCl concentrations (1–9 M). When SnCl$_2$ is present, the %E for Pd(II) is significantly enhanced, being higher than 80% for all HCl concentrations. All data were obtained with 1,2-DCE as diluent	[40]

Table 1 (*continued*)

Type of diamide	Chemical structure and respective acronym	Pd(II) Extraction behaviour	Reference
Thiodiglycolamide	DMDCHTDGA	Quantitatively extracted from 1 to 8 M HCl using 1,2-DCE as diluent. When the diluent is replaced by toluene the %E is > 97%, but it started to decrease for HCl concentrations of 5–6 M and higher	[16,29,33,35]
	DMDPHTDGA	Extraction is quantitative for all HCl concentrations tested in chloroform	[32,45]
	DMDBTDGA	Efficient extraction from 1.5 M until 4.5 M HCl, with a gradual decrease afterwards (no extraction at 7.5 M HCl), using toluene as diluent	[56]
	TOTDGA	Quantitatively extracted from HCl solutions until 8 M in a mixture of 80% *n*-dodecane and 20% 2-ethylhexanol	[36]
	MDTDGA	The %E is between 50% and 67% for 1.0–2.0 M HCl, of about 83% for 4.0 M HCl, 98% for 5.0 M, and > 99% for 6.0 M and 7.0 M HCl in 80% dodecane-20% 2-ethylhexanol	[46]

good Pd(II) extraction. Similar results were previously obtained for Pt(IV) removal by succinamide derivatives (DMDCHSA, DMDPHSA) and also by malonamide derivatives (DMDBMA and DMDCHTDMA) [38,39]. The justification that has been pointed out for those results is that the hydrocarbon diluents usually promote aggregation of the extractants, consequently inhibiting the metal ion withdrawal. Polar diluents seem to avoid aggregation [44]. 1,2-DCE alone does not extract Pd(II), confirming the determinant role of DMDCHSA in the extraction of the metal ion.

3.4. Extraction isotherm of palladium(II) by DMDCHSA

In order to determine the loading capacity of DMDCHSA in 1,2-DCE for Pd(II), appropriate tests were performed using 2.5×10^{-3} M Pd(II) in 6 M HCl. The organic phase was contacted with fresh aqueous solutions using different A/O volume ratios, from 1 to 15, between the two phases. The obtained results are shown in Fig. 2.

The information collected from Fig. 2 shows that the maximum loading of DMDCHSA for Pd(II) is near 3×10^{-3} M Pd(II), which corresponds to an extractant:Pd(II) molar ratio higher than 16. This

Table 2
Effect of different diluents on the extraction percentage of 5×10^{-4} M Pd(II) in 6 M HCl by 0.05 M DMDCHSA.

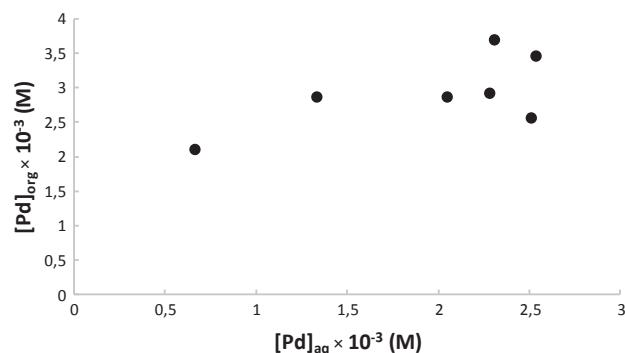| Diluent	% E Pd (II)
1,2-DCE (without DMDCHSA)	0
1,2-DCE	69
Dichloromethane	59
1-Octanol	27
Toluene	16
Kerosene	16
Xylene (mixture of isomers)	14
Escaid 100®	3
Varsol 80®	4
Exxsol 80®	4
Shellsol D70®	2

Fig. 2. Extraction equilibrium isotherm for Pd(II) by 0.05 M DMDCHSA in 1,2-DCE. [Pd(II)] = 2.5×10^{-3} M.

result reveals that the loading capacity of this extractant for Pd(II) is merely reasonable. The experimental methodology adopted to construct the extraction equilibrium isotherm is probably responsible for some degree of uncertainty near the saturation point, but the collected overall information denotes that DMDCHSA is not able to saturate as would be expected taking into account the composition of the extracted species determined from the slope analysis experiments (DMDCHSA/ Pd = 2, see Section 3.7.1). Possible reasons for this behaviour are the incomplete Pd(II) extraction (at the adopted conditions ≈ 70%) and the likely HCl co-extraction, which should hamper Pd(II) extraction itself. Under similar conditions, the loading capacity of DMDCHSA for Pt(IV) was much higher [44].

3.5. Stripping of palladium(II) from the loaded organic phases and extractant reutilization

Taking into account the good results obtained for the extraction of Pd(II) by DMDCHSA, the search for adequate aqueous solutions to strip the metal ion to a new purified aqueous phase is a relevant issue for the success of the process. For that purpose, 1 M HCl and distilled water were used as stripping agents for Pd(II). The organic phase, 0.05 M DMDCHSA in 1,2-DCE, was previously equilibrated with 5×10^{-4} M Pd(II) in 6 M HCl at A/O = 1. After Pd(II) extraction (%E = 70%), the organic phase containing about 3.5×10^{-4} M Pd(II) was therefore contacted with the stripping agents during 30 min, with an A/O = 1. When these two stripping agents were involved, the phase separation was fast and no third phase was observed.

The stripping percentages (%S) achieved with 1 M HCl and distilled water were 100% and 80%, respectively. These results show that Pd(II) can be easily and quantitatively stripped from the loaded DMDCHSA organic phases using 1 M HCl. Considering these results, which indicate that chloride ions seem to be efficient Pd(II) stripping agents, low-cost and easily available solutions rich in chloride ions (seawater and NaCl solution of 20 g/L in chloride ion) were tested. An additional and more complex solution, called "nutrient medium", containing lactate and other salts also dissolved in seawater, was also tested. The "nutrient medium", usually used for bacterial growth, was chosen based on the possibility of combining SX with a subsequent biological process allowing the bioreduction of Pd(II) and thus the consequent recovery of metallic Pd [49]. Also the choice of testing a 20 g/L chloride solution as stripping agent (a concentration similar to that found in seawater) intended to compare its stripping performance with the one shown by seawater.

The %S results obtained for Pd(II) recovery from the loaded organic phase of DMDCHSA in 1,2-DCE using the five stripping agents tested are summarized in Table 3.

All solutions containing dissolved chloride ions were efficient for Pd stripping, although Pd(II) was only quantitatively stripped by 1 M HCl, seawater and the 20 g/L Cl⁻ (as NaCl) solution. Good %S were also obtained using distilled water and even the "nutrient medium". The efficient use of seawater or NaCl solution as stripping agents, both economic and largely available sources of chloride ions in coastal areas, can contribute for the cost-effective viability of the overall SX process.

Table 3
Percentage of Pd(II) stripping from loaded organic phases of DMDCHSA in 1,2-DCE (obtained from the extraction of 5×10^{-4} M Pd(II) in 6 M HCl solutions) through the use of different stripping agents.

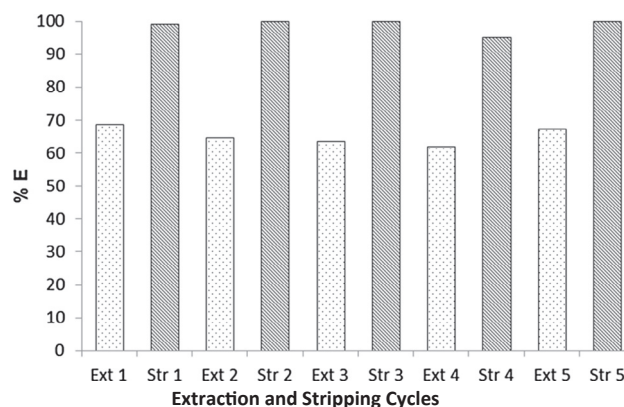| Stripping Agent	%S
1 M HCl	100
Distilled water	80
Seawater	100
"Nutrient medium"	73
20 g/L Cl⁻ solution (as NaCl)	100

Fig. 3. Evaluation of the performance of 0.05 M DMDCHSA in 1,2-DCE in successive extraction-stripping cycles. Seawater as stripping agent. [Pd(II)] = 9×10^{-4} M in 6 M HCl.

It should be mentioned that these three chloride solutions were previously tested for Pt(IV) stripping from 0.05 M DMDCHSA and DMDPHSA, both in 1.2-DCE, with poor results. The percentage of Pt(IV) stripping from DMDCHSA with 1 M HCl and with 20 g/L of chloride ion as NaCl were quite different from those obtained for Pd(II), since values of %S of 26% and 40% were obtained, respectively. The %S results for Pt(IV) stripping using DMDPHSA and 1 M HCl, "Nutrient medium" or 20 g/L of chloride solution (as NaCl) were less than 20% in all cases [44]. These results can be promising in view of a selective recovery of Pt(IV) and Pd(II), since employing 1 M HCl would theoretically remove Pd(II) from the organic phase, while Pt(IV) would mainly remain. Regarding the use of seawater as stripping agent for both Pd(II) and Pt(IV) from DMDCHSA, the results were very similar, and values around 100% were attained. However, the results achieved for the stripping of Pd(II) from DMDPHSA using seawater did not exceed %S of 58%.

The stability of DMDCHSA when reused was also investigated. For that purpose, five successive extraction-stripping stages using feed aqueous phases containing 9×10^{-4} M Pd(II) in 6 M HCl and seawater as stripping solution were performed, always involving the same organic phase fraction (0.05 M DMDCHSA in 1,2-DCE).

The results obtained in each extraction and stripping cycle are represented in Fig. 3. They clearly demonstrate that the reutilization of DMDCHSA is feasible, since in all the stripping stages the values of Pd (II) %S were near 100%, while the %E of Pd(II) varied between 62% and 69%. It should be noted that the reutilization of DMDCHSA aiming the extraction of Pt(IV) has been previously assessed in five successive extraction-stripping cycles, for the same extraction conditions and using seawater as stripping agent, with values near 100% in both extraction and stripping stages being reached [44].

The results achieved with DMDCHSA for Pd(II) in terms of reutilization after several extraction and stripping cycles are very encouraging in view of an eventual industrial application.

3.6. Selectivity studies

The selectivity experiments were carried out using several 6 M HCl solutions: binary solutions containing Pt(IV) and Pd(II); ternary solutions with Pt(IV), Pd(II) and one of the following metal ions: Fe(III), Al (III), Ce(III) or Zr(IV); and a complex solution containing simultaneously Pt(IV), Pd(II) and the four metals previously indicated. It should be mentioned that the selection of those metal ions was based on literature data concerning the composition of the pregnant solutions resulting from the leaching of automotive catalysts [50]. It was decided to use about 100 mg/L for each metal ion in the aqueous phase, which corresponds to 9×10^{-4} M Pd(II), 5×10^{-4} M Pt(IV), 1×10^{-3} M Zr (IV), 4×10^{-3} M Al(III), 2×10^{-3} M Fe(III) and 7×10^{-4} M Ce(III). A three-metal ion solution containing a higher concentration of Fe(III) of
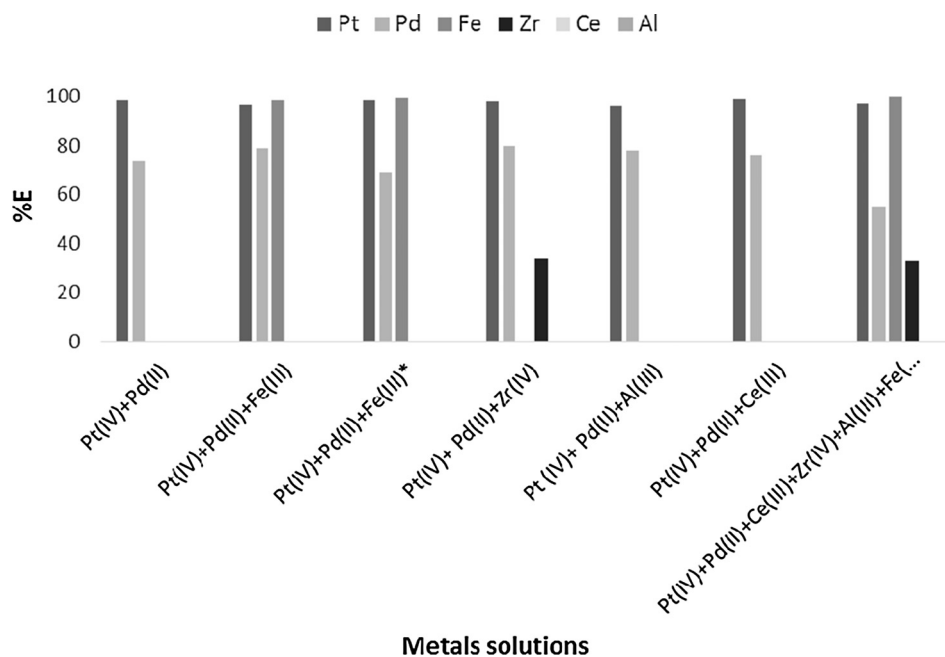
about 500 mg/L, corresponding to 9×10^{-3} M, denoted as Fe(III)*, was also tested. Those solutions were equilibrated with 0.05 M DMDCHSA in 1,2-DCE, adopting the usual set of experimental conditions. No third phase was observed in any of the experiments performed. The extraction profiles obtained are displayed in Fig. 4.

The obtained results show that the presence of both metals Pd(II) and Pt(IV) in the same solution almost does not interfere in their extraction by DMDCHSA, since their %E was 68% and 100%, respectively. The %E of these metals from the ternary solutions is very similar. However, in the experiment involving all the metals, the %E of Pd(II) decreased to 55%. Regarding Pt(IV), any of the other metals did not affect its %E, since values near 100% were obtained in all the essays.

Fe(III) was completely removed from the ternary and multiple metals solutions, independently of its concentration. No extraction of Al (III) and Ce(III) was detected neither from the ternary nor from the multiple solutions. The selectivity results obtained also denote that Zr (IV) was partially extracted (~30%) from both solutions.

Taking into account the lack of selectivity of DMDCHSA for Pd(II) extraction, and based on information from the literature [51], additional selectivity studies were designed (scheme presented in Fig. 5) aiming the selective separation of Pd(II) and Pt(IV) from ternary solutions containing Fe(III).

Nguyen et al. [51] reported that 0.3 M TBP in kerosene is efficient for the separation of Fe(III) from chloride leaching solutions. Thus, the potential of 0.3 M TBP in kerosene in the presence of 5% (v/v) 2-decanol as modifier [51] for the selective extraction of Fe(III) from a ternary aqueous solution composed by 9×10^{-4} M of Pd(II), 5×10^{-4} M of Pt(IV) and 2×10^{-3} M of Fe(III) in 6 M HCl was tested. Subsequently, the resulting aqueous phase (almost without Fe(III)), was contacted with 0.05 M of DMDCHSA in 1.2-DCE for the extraction of both Pd(II) and Pt(IV). Finally, different stripping agents were contacted with the PGMs loaded organic phase aiming the separation of Pd (II) and Pt(IV). The selectivity results from this study are presented in Fig. 6.

The 1st extraction using 0.3 M of TBP in kerosene + 5% (v/v) 2-decanol as organic phase allowed to extract 99% of Fe(III), while the extraction of Pd(II) and Pt(IV) can be considered negligible (7% and 6%, respectively). The stripping of Fe(III) from the loaded organic phase was achieved simply by using distilled water: a %S of 91% was attained. The aqueous phase resulting from the 1st extraction

containing Pd(II) and Pt(IV) was subjected to a second extraction with 0.05 M of DMDCHSA in 1,2-DCE. The percentage of Pd(II) and Pt(IV) extraction did not exceed 60% (60% and 49%, respectively), as shown in Fig. 6 - 2nd Ext. Nevertheless, good stripping results for Pd(II) and Pt (IV) were obtained using seawater and 0.01 M thiourea in 0.5 M HCl, respectively. It was possible to strip Pt(IV) from the loaded organic phase with an efficiency of 94%, while the percentage of Pd(II) stripped was lower than 19% (Fig. 6 - 2nd Str_HCl + thiourea). The Pd(II) remaining in the loaded organic phase can then be stripped with seawater, considering that a %S of 100% was obtained with that solution (Fig. 6 - 2nd Str_seawater). 1 M HCl was not efficient to selectively strip Pd(II) or Pt(IV), since a simultaneous removal of both metals occurred (Fig. 6 - 2nd Str_HCl 1 M). It should be noted that the extraction scheme suggested in Fig. 6 can possibly be optimized in order to enhance the results of the 2nd extraction and stripping stages. For instance, the results of the 2nd extraction with DMDCHSA can be improved by using more than one extraction step. In fact, according to [52], systematic studies of SX schemes already proposed in the literature are still necessary, since they are always crucial to better determine the actual potential of the extractants prior to their application to real secondary leaches.

3.7. Slope analysis

The following studies were performed aiming to acquire some knowledge about the Pd(II) extraction reactions.

3.7.1. Effect of DMCHSA concentration

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) in the extracted species. Hence, the influence of DMDCHSA concentration on the extraction of 9×10^{-4} M Pd(II) from 6 M HCl was investigated. For that purpose, organic phases with DMDCHSA concentrations in the range of 0.01 M to 0.1 M were contacted for 30 min with the aqueous phase. The plot of log D versus log [DMDCHSA], displayed in Fig. 7, shows a straight line ($R^2 = 0.998$) with slope near 2, which indicates that probably an average of two DMDCHSA molecules may surround each of the Pd(II) extracted species.
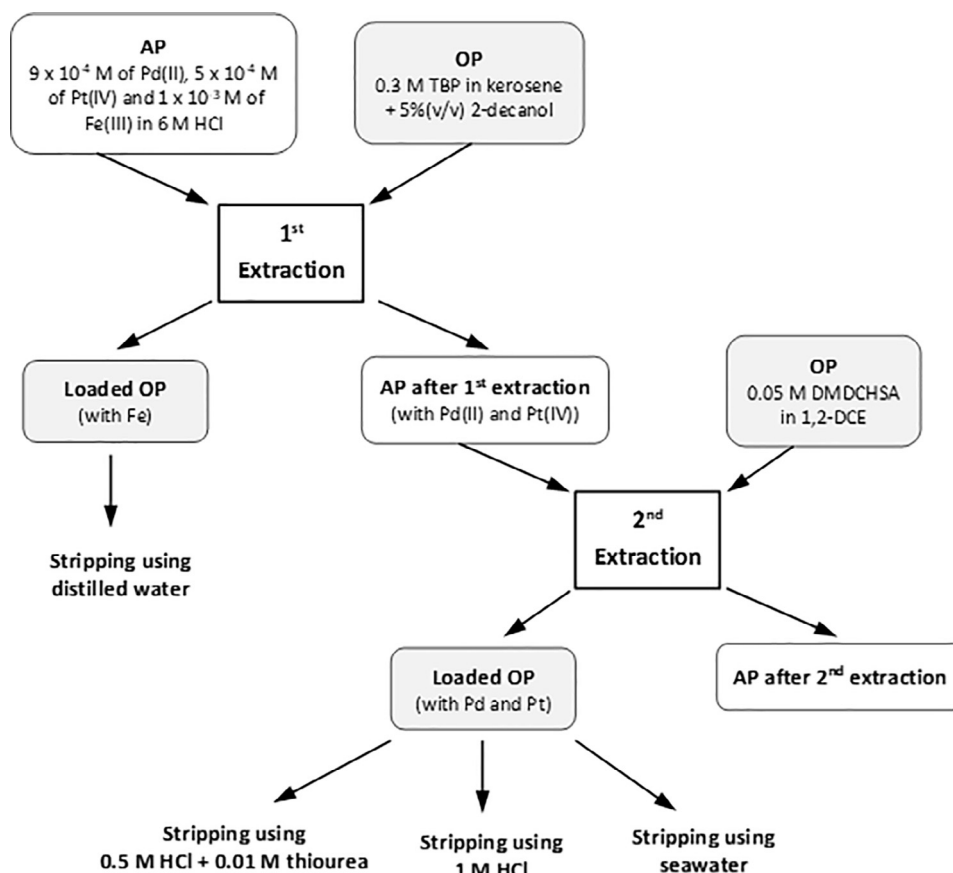
Fig. 5. Design of the selectivity experiments. AP: Aqueous phase; OP: Organic phase.
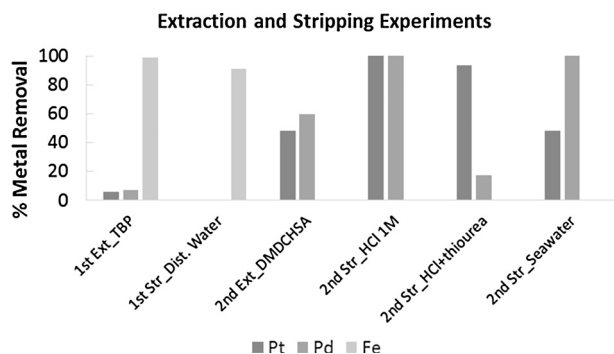

Fig. 6. %E and %S values for the selectivity experiments based on an initial ternary solution containing 9×10^{-4} M of Pd(II), 5×10^{-4} M of Pt(IV) and 2×10^{-3} M of Fe(III) in 6 M HCl, firstly equilibrated with 0.3 M TBP in kerosene, and subsequently with 0.05 M DMDCHSA in 1,2-DCE. Extraction and stripping conditions: A/O = 1, room temperature, 900–1000 rpm, 30 min equilibration.
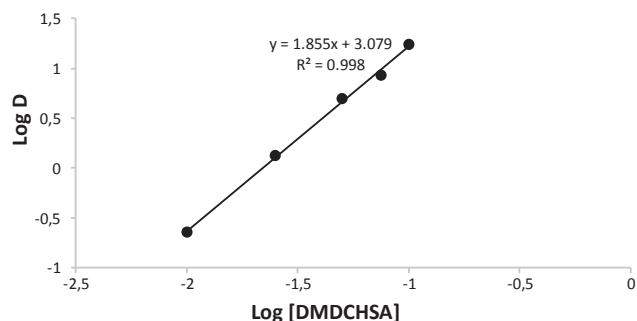
3.7.2. Effect of hydrogen ion concentration

It should be mentioned that the concentration ranges used in the slope analysis studies (effect of acidity and chloride ions) were limited by the solubility of NaCl in the HCl solutions used.

The effect of hydrogen ion concentration on the extraction of 9×10^{-4} M Pd(II) by 0.05 M DMDCHSA in 1,2-DCE, in the range of 1 M to 5 M, keeping the total chloride ion concentration constant at 5 M through the addition of sodium chloride, was studied.

Pd(II) extraction was performed from a solution with high electrolyte concentration, thus the activities of hydrogen ions were considered instead of their concentrations.

The log-log plot between the Pd(II) distribution ratios and hydrogen-ion activities is displayed in Fig. 8.

The obtained results fit well in a straight line ($R^2 \approx 0.991$) and the slope is 2.8, which suggests that possibly an average of about three

Fig. 7. Effect of DMDCHSA concentration in 1,2-DCE on Pd(II) extraction from 6 M HCl. [Pd(II)] = 9×10^{-4} M.
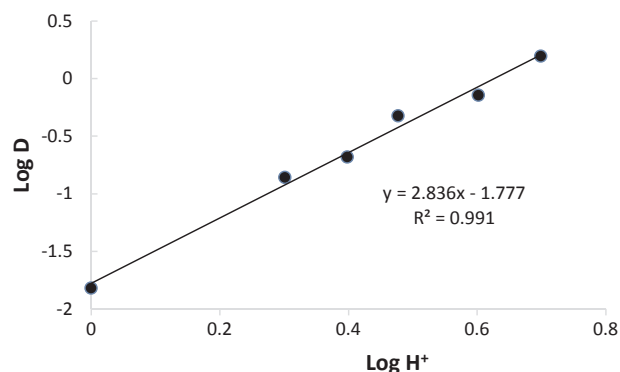

Fig. 8. Effect of hydrogen ion concentration on Pd(II) extraction for a constant 5 M chloride concentration. [Pd(II)] = 9×10^{-4} M, [DMDCHSA] = 0.05 M in 1,2-DCE.

hydrogen ions may be consumed in Pd(II) extraction, at least for a 5 M total chloride concentration, which explains the fact that the increase of HCl concentration in the aqueous phase also increases the efficiency of Pd(II) extraction.

3.8. UV–Visible data

Taking into account that $[PdCl_4]^{2-}$ is the predominating Pd(II) species at 1 M and higher HCl concentrations [17–20], the UV–Visible spectra of the metal ion aqueous phase containing 6 M HCl and the resulting Pd-loaded organic phases were recorded. In both cases the spectra exhibit a similar band with a maximum located at 471–480 nm, which is consistent with the presence of $[PdCl_4]^{2-}$ that, according to the literature (*e.g.* [53,54]), absorbs at $\lambda = 476$ nm in toluene.

Hence, the equilibrium and spectroscopic data suggest the extraction of Pd(II) as $[PdCl_4]^{2-}$ by a positively charged extractant (protonated), resulting in an outer-sphere electrostatic attraction as a result of an ion pair reaction. However, taking into account that three protons seem to be consumed, the co-extraction of one HCl molecule should be admitted. The direct extraction of $[PdCl_4]^{2-}$, the predominant Pd(II) species in the HCl concentration range of 1–8 M [55], is consistent with the fast Pd(II) extraction rate exhibited by this system [20,45].

The occurrence of several amides protonation in acidic media (*e.g.* DMDCHTDGA) leading to ion pair extraction reactions is largely reported in the literature for Pt(IV) extraction [16,32,35,38]. On the other hand, evidences concerning Pd(II) extraction reactions involving different amide derivatives suggest the occurrence of two different mechanisms: the direct extraction of $[PdCl_4]^{2-}$ through an ion pair reaction resulting from the extractant protonation, as seems to happen with DMDCHSA, and/or the replacement of chloride anions from the complexation sphere of $[PdCl_4]^{2-}$ by ligand molecules, due to the lability nature of this chlorocomplex, giving rise to inner-sphere complexes in the organic phase [30,34]. Actually, Paiva et al. [56] and additional studies with other thiodiglycolamide derivatives, *e.g.*, MDTDGA [46] and TOTDGA [36], point out 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 for DMDPHTDGA [45].

4. Conclusions

This paper reports for the first time the potentialities of a succinamide derivative, *N,N′*-dimethyl-*N,N′*-dicyclohexylsuccinamide (DMDCHSA) in 1,2-dichloroethane (1,2-DCE) for the liquid-liquid extraction of Pd(II) from HCl media. It was found that Pd(II) extraction increases with HCl concentration, and values higher than 60% were obtained from 5 M or higher HCl concentrations. In addition, the extraction process is fast and the extractant presents a reasonable loading capacity, although the use of commercial and more environmentally friendly diluents than 1,2-DCE negatively affect the extraction efficiency. Pd(II) can be efficiently stripped to a new aqueous phase by a simple contact with seawater, and DMDCHSA can be reutilized several times without losing its extraction ability.

Selectivity studies showed that Fe(III) and Pt(IV) are co-extracted with Pd(II), but a SX scheme based on the previous extraction of Fe(III) with TBP is proposed herein, followed by the simultaneous extraction of Pd(II) and Pt(IV) by DMDCHSA and a sequential stripping of Pt(IV) by thiourea in HCl, and Pd(II) by seawater. Slope analysis and spectroscopic data point out to an extractant: Pd(II) ratio of 2:1 and are consistent with the occurrence of an outer-sphere ion pair mechanism, in which Pd(II) is extracted as $[PdCl_4]^{2-}$, most likely together with an HCl molecule.

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