NEW EXTRACTANTS FOR SEPARATION OF PLATINUM-GROUP METALS FROM CHLORIDE SOLUTIONS AND THEIR APPLICATION TO RECYCLING PROCESSES

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Abstract

In this paper some results on the application of four *N,N'*-tetrasubstituted malonamide derivatives for the extraction and separation of platinum-group metals (PGMs) are presented. The above mentioned extractants were specifically synthesized in order to evaluate their efficiency for the extraction of a specific metal, or group of metals, from aqueous chloride matrices. Different behaviours were obtained towards platinum(IV) and/or palladium(II) extraction, all the *N,N'*-tetrasubstituted malonamide derivatives allowing the mutual separation of the two metal ions, depending on the HCl concentration. Generally, extraction experiments were carried out involving initial aqueous phases containing 100 mg/L of each metal isolate, in varying 1M to 8M HCl concentration ranges, and 0.05M extractant in 1,2-dichloroethane solutions. From the preliminary results obtained, one can conclude that HCl concentrations and the structure of the malonamide derivative play a crucial role on the efficiency shown for Pt(IV) and/or Pd(II) extraction. The efficiency of the stripping stage of the loaded organic phases is variable, depending on the *N,N'*-tetrasubstituted malonamide derivative, as well as on the metal ion involved; for Pt(IV), distilled water and 1M HCl were generally successful, whereas for Pd(II), thiourea in HCl gave better results. The overall data already achieved suggest that these extractants may be good candidates for further evaluation in PGMs separations from real solutions resulting from recycling processes.

1- INTRODUCTION

Platinum and other related rare metals are used in several advanced technological applications such as electronics, fuel cells and catalysts (in automotive catalytic converters, oil refining and organic chemistry processing) [1]. Since they are rare and valuable, platinum-group metals (PGMs) are considered critical raw materials [2], and therefore their recycling is mandatory for economic, technical, environmental and resource conservation reasons.

In the recovery of PGMs, chloride hydrometallurgy is the most efficient approach [3], mainly in the refining steps. Solvent extraction technology is usually the operation used for separating PGMs, allowing high efficiency and selectivity performances. Due to the high adding value of the involved metals, these processes are very restricted to public knowledge. Moreover, the hydrometallurgical wastes containing PGMs are becoming more and more complex [4], requiring advanced research in order to improve existing technologies or to develop new ones.

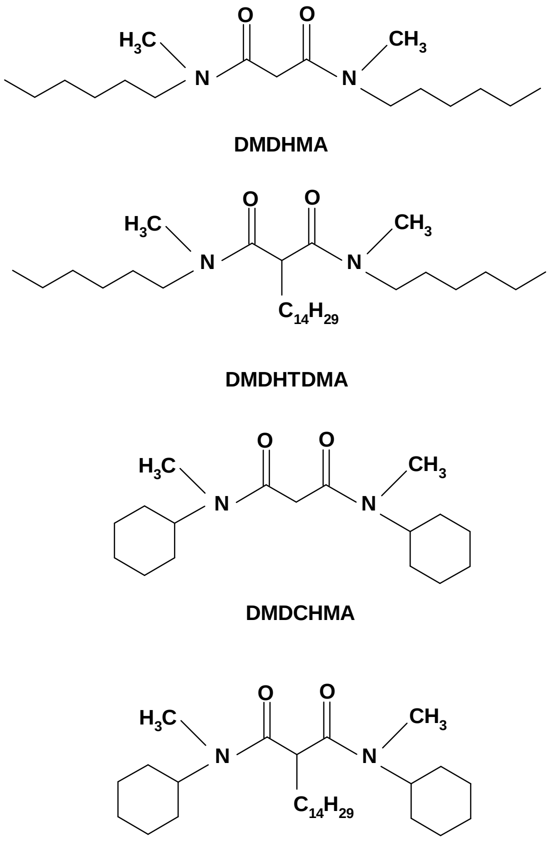
The application of solvent extraction to PGMs recovery is not new; accordingly, the mentioning of an important work, collecting some older but relevant information about the main extractants explored to date, and of the chemical behavior of PGMs chlorocomplexes as well, is worthwhile [5]. Concerning the increasing need of PGMs recovery from secondary sources such as the automotive catalysts, solvent extraction strategies have again been considered a promising alternative since the 1990s for this specific purpose [6], and thus several extractants for platinum, recovered from spent samples or included in standard chloride solutions, have been recently investigated. Those extractants fall mainly into two groups, amines and organophosphorous compounds, although others such as dialkylsulphoxides [7], diglycolamides and thiodiglycolamides [8], were also reported. The successful utilization of sulfide-containing monoamides for Pd(II) recovery from HCl concentrated aqueous media [9] has also been pointed out by Narita and co-workers.

A few amide derivatives have recently been proposed for the solvent extraction of PGMs from hydrochloric acid solutions, e.g., [8,9], and amongst them, *N*,*N'*-tetrasubstituted malonamides have been particularly investigated. In previous publications, the adequacy of *N*,*N'*-dimethyl-*N*,*N'*-diphenyltetradecylmalonamide (DMDPHTDMA) for the extraction of platinum [10], and later on its capacity to separate palladium, platinum, and rhodium [11] has been emphasized. The results of Pt(IV) extraction from hydrochloric acid media using DMDPHTDMA showed that the use of a labilizing agent, such as tin(II) chloride, is necessary to achieve an efficient metal extraction [10].

The present work describes some preliminary information about the use of four different *N*,*N'*-tetrasubstituted malonamide derivatives to recover platinum(IV) and / or palladium(II) from hydrochloric acid media, envisaging the finding of suitable PGMs extractants for the treatment of specific industrial leaching or effluent solutions containing these PGMs, namely those coming from the leaching of secondary sources.

2- MATERIALS AND METHODS

Four *N*,*N´*-tetrasubstituted malonamide derivatives, namely *N*,*N'*-dimethyl-*N*,*N'*-dihexylmalonamide (DMDHMA), *N*,*N'*-dimethyl-*N*,*N'*-dihexyltetradecylmalonamide (DMDHTDMA), *N*,*N'*-dimethyl-*N*,*N'*-dicyclohexylmalonamide (DMDCHMA), and *N*,*N'*-dimethyl-*N*,*N'*-dicyclohexyltetradecylmalonamide (DMDCHTDMA), whose structures are displayed in figure 1, were synthesized according to well-established procedures [10,12], their purification and characterization being accomplished through the use of adequate chromatographic and spectroscopic methods.



DMDHMA

DMDHTDMA

DMDCHMA

DMDCHTDMA

Figure 1: Structures of the N,N´-tetrasubstituted malonamide derivatives synthesized and investigated in this work.

The chemical yields achieved ranged from 50 to 97%. The characterization data obtained are fully in accordance with those expected, the chromatographic results indicating a purity range for all the compounds always higher than 90%.

All reagents and solvents were used without further purification. 100 mg/L Pt(IV) or Pd(II) solutions were prepared from the Pt(IV) and Pd(II) standard atomic absorption solutions, respectively (Fluka, 1001 mg/L Pt(IV), or Fluka, 997 mg/L Pd(II), both in 5% HCl), and dissolved in the required volumes of hydrochloric acid (Fisher Chemical, analytical reagent grade, ~37%).

The organic phases containing 0.05M of each extractant were generally prepared in 1,2-dichloroethane (1,2-DCE, Fluka, minimum 99.5%).

Distilled water, different HCl-concentrated solutions, thiourea (Sigma-Aldrich, >99%) in HCl, and salts such as potassium thiocyanate (Riedel-de Haën, 99%) in HCl, and penta-hydrated sodium thiosulfate (Riedel-de Haën, 99.5%) in water, were systematically tested as stripping agents either for Pt(IV) or Pd(II).

General extraction and stripping experiments were carried out at room temperature by contacting equal volumes of the organic and aqueous phases (A/O = 1) for 30 minutes, by mechanical shaking, adopting a rotation speed between 900 and 1000 rpm. This period of time has been found sufficient for the extraction systems to attain equilibrium. After separation of the two phases, the aqueous solutions were filtrated and the metal ion contents in the aqueous media were determined by UV/VIS spectroscopy (Hach Lange, DR 2800) using the tin(II) chloride method for platinum [10], or by atomic absorption spectrometry (AAS, Varian Spectra AA-20, or Solar 969 AA Spectrometer Thermo Elemental), whenever interferences or any difficulties arose with the spectrophotometric method for platinum determination. The metal ion concentrations in the organic phases were found by mass balance. The analysis of the solutions before and after extraction was performed in triplicate. The coefficient of variance estimated for the results achieved from the different extraction and stripping experiments is approximately ± 5%.

3- RESULTS AND DISCUSSION

Extraction of Pt(IV) and Pd(II)

Figure 2 shows the results obtained for the experiments performed using 1,2-DCE organic solutions containing 0.05M DMDHMA, DMDHTDMA, DMDCHMA, or DMDCHTDMA, and varying 1 and 8M hydrochloric acid concentrations in the aqueous media.

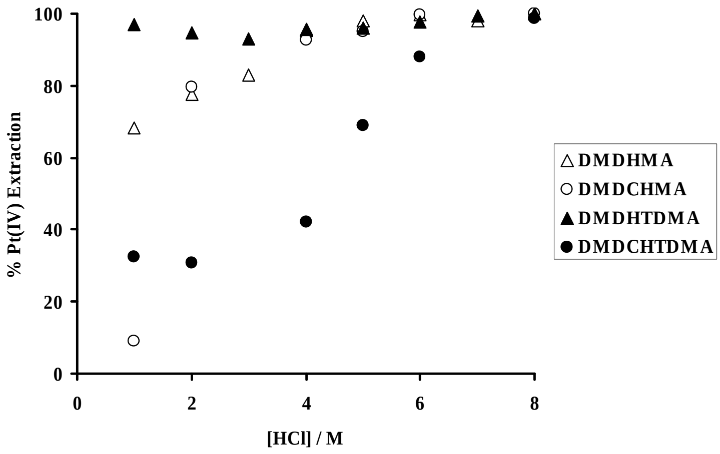


Figure 2: Effect of HCl concentration on Pt(IV) extraction by a 0.05M extractant solution in 1,2-DCE. [Pt(IV)] = 100 mg/L.

It can be observed that, in general, higher HCl concentrations favour Pt(IV) extraction for all malonamides tested. It should be pointed out that the results obtained for DMDCHMA are erroneous and do not correspond to a real solvent extraction of Pt(IV), as the removal of the metal ion from the aqueous solutions was due to the appearance of a precipitate containing platinum, systematically identified after the solvent extraction equilibration.

DMDHTDMA always extracted Pt(IV) above 93% for all the HCl solutions, whereas the non-central alkylated analogue, DMDHMA, only exhibited a similar behaviour for 4M and higher HCl concentrations. Regarding DMDCHTDMA, it is not adequate to extract Pt(IV) from more diluted HCl solutions, but a 88% Pt(IV) extraction for 6M HCl was observed, with an increasing tendency afterwards.

Concerning the behaviour of the same extractants for Pd(II) extraction, following a similar set of experimental conditions as for Pt(IV), the results obtained are now depicted in figure 3.

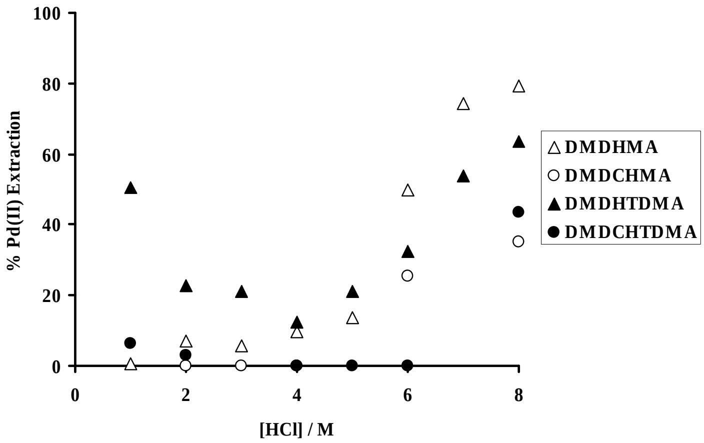


Figure 3: Effect of HCl concentration on Pd(II) extraction by a 0.05M extractant solution in 1,2-DCE. [Pd(II)] = 100 mg/L.

It can be said that the set of extractants tested is generally more adequate to extract Pt(IV) than Pd(II). DMDHMA exhibits a sinusoidal behaviour, showing a maximum 79% Pd(II) extraction for 8M HCl. Its central-alkylated analogue, DMDHTDMA, shows a parabolic profile instead, beginning by 50% Pd(II) extraction, reaching a minimum of 12% at 4M HCl, and then starting to increase until 63% at 8M HCl. DMDCHMA extracts some Pd(II) at 6M and 8M HCl, whereas DMDCHTDMA extracts a maximum of 43% Pd(II) at 8M HCl only.

Assuming that extractants may show a similar extractive behaviour when both Pt(IV) and Pd(II) coexist in the aqueous solutions, one may expect that: i) DMDHMA should be suitable to extract Pt(IV) efficiently at 4M HCl (%E = 95%), as the majority of Pd(II) should not be extracted (%E = 12%); ii) For similar reasons, DMDHTDMA is also adequate to extract Pt(IV) selectively over Pd(II) from 1M until 4M HCl; iii) DMDCHTDMA may extract Pt(IV) over Pd(II) selectively at 6M HCl.

Stripping of Pt(IV) and Pd(II)

In order to become viable solvent extraction systems, it is necessary that the loaded organic phases may be efficiently stripped, in order to recover the metals and recycle the solvent.

Several stripping agents have been tested to release Pt(IV) from DMDHMA and DMDHTDMA: distilled water, HCl solutions up to 5M, 0.1M and 0.5M thiourea in 1M or 2M HCl, 0.1M and 0.5M potassium thiocyanate in 1 or 2M HCl, 1M sodium thiosulfate in water. The maximum Pt(IV) stripping achieved from DMDHMA was with water and 1-3M HCl solutions, reaching about 36% for the loaded phases equilibrated with 4 to 7M HCl initial solutions. Regarding DMDHTDMA, the maximum Pt(IV) stripping achieved was 22% when thiourea in 3M HCl was used, the loaded organic phase obtained after contact with a 1M HCl feed aqueous solution. Therefore, one may conclude that the stripping of Pt(IV) from both compounds does not seem to be an easy task. The situation looks more promising with DMDCHTDMA, as loaded organic phases, after contact with 6M HCl solutions, released Pt(IV) efficiently when equilibrated with water or 1M HCl, with stripping percentages of 60% and 90%, respectively.

Regarding Pd(II) stripping, it has particularly been checked for the loaded DMDHMA and DMDHTDMA organic phases obtained after contact with 8M HCl solutions, as they are the most efficient extraction situations: the best results were 96% for DMDHMA and 74% for DMDHTDMA, obtained when a 0.1M thiourea in 1M HCl was employed.

4- CONCLUSIONS

The results obtained so far denote that DMDHMA, DMDHTDMA, and DMDCHTDMA may be good candidates to separate Pt(IV) from Pd(II), provided that more efficient stripping agents for Pt(IV) for the two former compounds may be found. This research will proceed through the utilization of mixed metal ion solutions and attempts to use more environmental-friendly diluents than 1,2-DCE. The final goal of this work is the development of efficient and selective processes to separate PGMs from real solutions resulting from recycling processes of spent automobile or industrial catalysts.

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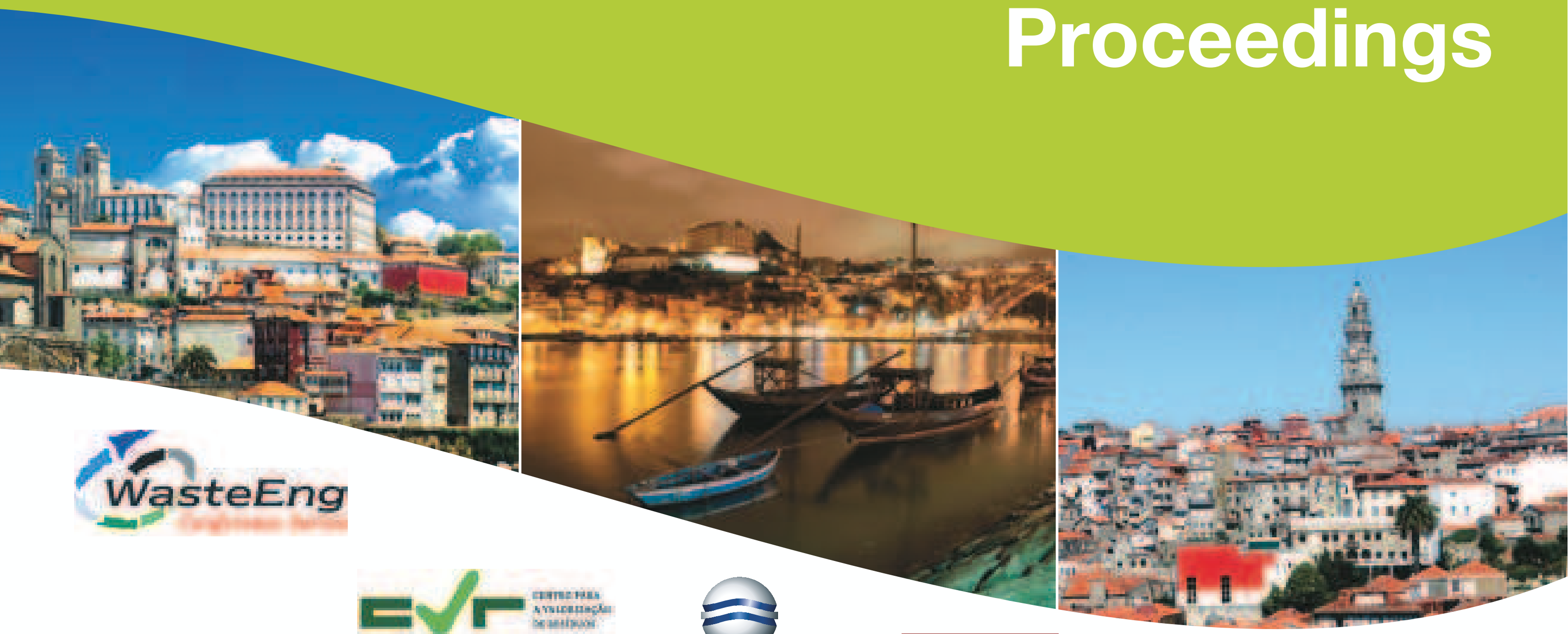

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