

## Recovery of Platinum(IV) and Palladium(II) from Complex Hydrochloric Acid Matrices by a Thiodiglycolamide Derivative

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### Summary

The solvent extraction performance of *N,N'*-dimethyl-*N,N'*-dicyclohexylthiodiglycolamide (DMDCHTDGA) towards Pt(IV) and Pd(II) in HCl solutions has recently been published. It was shown that these two platinum-group metals (PGMs) are efficiently extracted from 8 M HCl aqueous phases, being subsequently separated by sequential strippings: 1 M HCl allows Pt(IV) recovery, whereas Pd(II) is only back-extracted by thiourea in HCl. In this work, selectivity tests were carried out to evaluate the performance of DMDCHTDGA towards the recovery of both PGMs, from 8 M HCl aqueous phases, when in presence of Rh(III), Fe(III), Ni(II), Zn(II), Al(III), Ce(III) and Zr(IV), simulating the leaching 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) and Pt(IV) by DMDCHTDGA. Fe(III), Zn(II) and Zr(IV) are co-extracted with Pt(IV) and Pd(II); Fe(III) and Zn(II) were efficiently scrubbed with water, whereas Zr(IV) was removed by an acidified aqueous solution. Inversely, Ni(II) is not extracted, and Rh(III) and Ce(III) appear only traceably in the loaded organic phase. Al(III) is a concern, as it is appreciably extracted, and none of the tested back-extraction solutions was able to strip it.

### Introduction

Platinum, palladium and related rare metals are nowadays considered critical raw materials. In fact, platinum-group metals (PGMs) are not abundant in the Earth's crust, and the maintainance of their supply is a concern, mainly because PGMs technological applications have been progressively increasing in last years and are hardly replaceable – in electronics, fuel cells, and in automobile and industrial catalysts, to mention only a few [1]. Furthermore, PGMs large utilization in areas such as jewelry and health should not be forgotten as well. All these reasons justify an extensive investigation on new and modified hydrometallurgical processes to attain PGMs separation and / or concentration from complex industrial leaches or effluents [2], and the versatility of solvent extraction to contribute for such objectives is widely recognized [3].

The solvent extraction systems that are industrially used to recover Pt(IV) and Pd(II) from chloride leaching solutions of primary sources usually involve tertiary amines, ammonium salts and neutral organophosphorus compounds, as well as alkyl sulfides, hydroxyoximes and 8-hydroxyquinolines for Pd(II) [3]. These extractants are generally not so adequate to treat leaching solutions coming from the recycling of secondary sources, as these latter traditionally have more complex and specific compositions. Therefore, the investment on the finding of new types of extractant

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molecules, which may show a more versatile behavior in terms of selectivity and kinetics, for instance, is presently rather active.

Considering the novel extractant molecules that have recently been proposed for Pt(IV) and Pd(II) recovery from chloride aqueous phases, extractants bearing nitrogen and / or sulfur atoms are the most popular. Compounds of the amide-type, e.g., malonamide for Pt(IV) [4-6], diglycolamide and thiodiglycolamide for Pt(IV) and Pd(II) [7,8], and sulfide-containing monoamides [9], a dithioether [10], pyridinecarboxamides [11] and fatty imidazolines [12] for Pd(II) have been reported.

In sequence of the investigation revealing the adequacy of *N,N'*-dimethyl-*N,N'*-dicyclohexylthiodiglycolamide (DMDCHTDGA) to simultaneously recover Pt(IV) and Pd(II) from 8 M HCl solutions [8], this work describes and discusses the behavior of DMDCHTDGA towards the two PGMs when Rh(III) and other rare and contaminating metals coexist in the aqueous solutions. The chosen metals were Fe(III), Al(III), Ni(II), Zn(II), Ce(III) and Zr(IV), and the objective was to roughly simulate the composition of a leaching solution obtained from the hydrometallurgical treatment of a spent automobile catalytic converter.

## Experimental

The synthesis of DMDCHTDGA was carried out as previously reported [8]. Its overall purity, determined by liquid chromatography coupled with mass spectroscopy (LC-MS), is above 85%. 0.05M DMDCHTDGA solutions in 1,2-dichloroethane (1,2-DCE) were used as organic phase.

For the preparation of the feed aqueous phases, atomic absorption spectroscopy standards of Pt(IV), Pd(II), Rh(III), Ce(III) and Zr(IV), and chloride salts of Fe(III), Al(III), Ni(II) and Zn(II) were arranged. Several 8 M HCl aqueous media were prepared, always containing Pt(IV) and Pd(II), and bearing different combinations of the other metals, with a maximum of five. All metal ion concentrations were of about 100 mg/L, with the exception of Fe(III) and Al(III), both with 500 mg/L. Distilled water, 1 M HCl, and 0.1 M thiourea in 1 M HCl were used as stripping agents.

General extraction and stripping experiments were performed at room temperature through contact of 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 contact time is enough to reach equilibrium conditions [8]. After separation of the two phases, the aqueous and organic extracts were always filtrated, to minimize mutual entrainments.

All the metal ion contents in the aqueous solutions, before and after extraction, were determined by inductively coupled plasma–atomic emission spectrometry (ICP-AES, Horiba Jobin-Yvon, Ultima). Metal concentrations in organic phases were found by mass balance. The coefficient of variance calculated for the extraction and stripping results presented in this article is about  $\pm 5\%$ .

For some of the experiments described in sequence, the involved DMDCHTDGA samples were not fresh, they had already been used for Pt(IV) extraction. This recycling procedure has been systematically adopted throughout the study, as it was found that DMDCHTDGA is robust and stable, its loading capacity is rather elevated [8], and its general extraction performance is not affected by incomplete Pt(IV) stripping. That is the reason why some of the determined Pt(IV) concentrations are untypically high, but those occurrences do not invalidate the information picked up from the extraction profiles obtained.

## Results and Discussion

### *Pt(IV) and Pd(II) binary mixture*

A 8 M HCl solution containing 100 mg/L Pt(IV) and Pd(II) was equilibrated with a 0.05 M DMDCHTDGA solution in 1,2-DCE, and the loaded organic phase was then sequentially contacted with 1 M HCl and 0.1 M thiourea in 1 M HCl, under the adopted general experimental conditions. The results obtained are displayed in Figure 1.

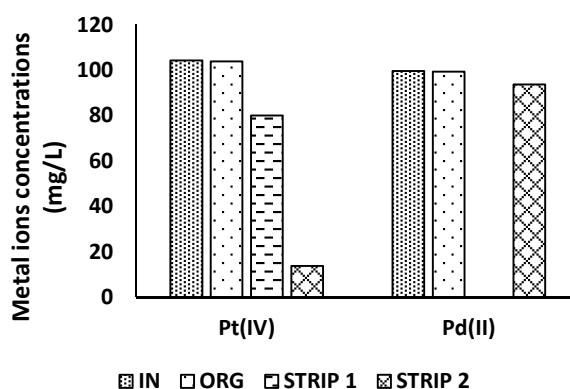


Figure 1 - Pt(IV) and Pd(II) concentrations (mg/L) in the initial 8 M HCl feed solution (IN), loaded 0.05 M DMDCHTDGA in 1,2-DCE organic extract (ORG), and stripping aqueous solutions (1 M HCl - STRIP 1, and 0.1 M thiourea in 1 M HCl - STRIP 2). Standard deviations:  $\pm 5\%$ .

It can be observed that DMDCHTDGA extracts Pt(IV) and Pd(II) almost quantitatively. The 1 M HCl solution strips 80 mg/L (77%) of Pt(IV), and Pd(II) stays in the organic phase. The thiourea solution efficiently re-extracts Pd(II) (94%), but about 14 mg/L of Pt(IV) are also co-stripped. A second contact of the organic phase with a new portion of thiourea solution did not release the Pt(IV) and Pd(II) contents still remaining in the organic medium after the first contact.

### *Ternary mixtures*

The solvent extraction performance of DMDCHTDGA was evaluated for four aqueous solutions containing one more metal - Rh(III), Ce(III), Al(III) or Zr(IV) - in addition to Pt(IV) and Pd(II), under the usual set of experimental conditions. Neither Rh(III) nor Ce(III) were appreciably extracted by DMDCHTDGA - only about 7 mg/L of both metals were extracted. None of these metals was detected in any stripping solution. The solvent extraction behavior towards Pt(IV) and Pd(II) was not affected.

Regarding the influence of Zr(IV), it was found that this metal ion is also efficiently extracted by DMDCHTDGA, but completely stripped by 1 M HCl – Figure 2. Hence, Pt(IV) and Zr(IV) co-exist in the 1 M HCl stripping solution.

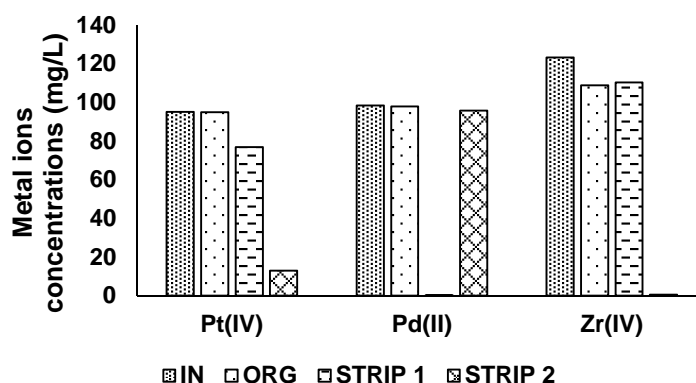


Figure 2 - Pt(IV), Pd(II) and Zr(IV) concentrations (mg/L) in the initial 8 M HCl feed solution (IN), loaded 0.05 M DMDCHTDGA in 1,2-DCE organic extract (ORG), and stripping aqueous solutions (1 M HCl - STRIP 1, and 0.1 M thiourea in 1 M HCl – STRIP 2). Standard deviations:  $\pm 5\%$ .

When in presence of 500 mg/L Al(III), DMDCHTDGA was able to transfer approximately 90 mg/L of this metal to the organic phase, about the same concentration as those of the PGMs – Figure 3. Al(III) was not detected in any of the stripping solutions. As the performance towards Pt(IV) and Pd(II) remains the same, it can be anticipated that the problem caused by the co-extraction of Al(III) may be solved if a suitable stripping agent, to be applied at the end of the solvent extraction scheme, is found.

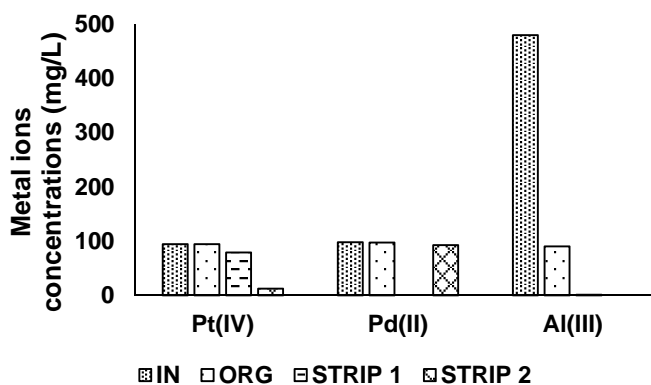


Figure 3 - Pt(IV), Pd(II) and Al(III) concentrations (mg/L) in the initial 8 M HCl feed solution (IN), loaded 0.05 M DMDCHTDGA in 1,2-DCE organic extract (ORG), and stripping aqueous solutions (1 M HCl - STRIP 1, and 0.1 M thiourea in 1 M HCl – STRIP 2). Standard deviations:  $\pm 5\%$ .

#### Complex mixtures with four and five metals

The solvent extraction performance of DMDCHTDGA was checked with a few complex mixtures containing four and five metals simultaneously. For instance, the results obtained for a mixture containing Pt(IV), Pd(II), Rh(III) and Fe(III) can be observed in Figure 4. For this case, and in the expectation that Fe(III), if extracted, could be scrubbed with water, the loaded organic phase was firstly contacted with

water, before the stripping stages. The DMDCHTDGA sample used was recycled, which explains why more Pt(IV) than expected appears in water and in stripping solutions.

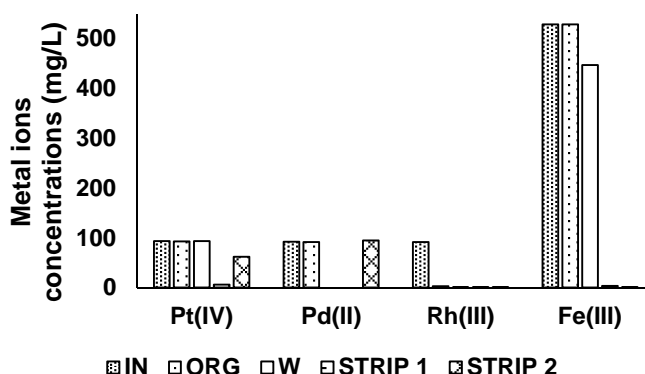


Figure 4 - Pt(IV), Pd(II), Rh(III) and Fe(III) concentrations (mg/L) in the initial 8 M HCl feed solution (IN), loaded 0.05 M DMDCHTDGA in 1,2-DCE organic extract (ORG), scrubbing water (W) and stripping aqueous solutions (1 M HCl - STRIP 1, and 0.1 M thiourea in 1 M HCl - STRIP 2). Standard deviations:  $\pm 5\%$ .

It can be observed that the majority of Fe(III) is effectively scrubbed with water. The solvent extraction behavior of DMDCHTDGA for the PGMs remains unchanged. Water is also a good releasing agent for Pt(IV).

A final example of the DMDCHTDGA solvent extraction performance towards complex metal ion mixtures can be observed in Figure 5, where Pt(IV), Pd(II), Rh(III), Ni(II) and Zn(II) coexist in the 8 M HCl solution. The scrubbing step with water was also carried out, and again the DMDCHTDGA sample was overloaded with Pt(IV).

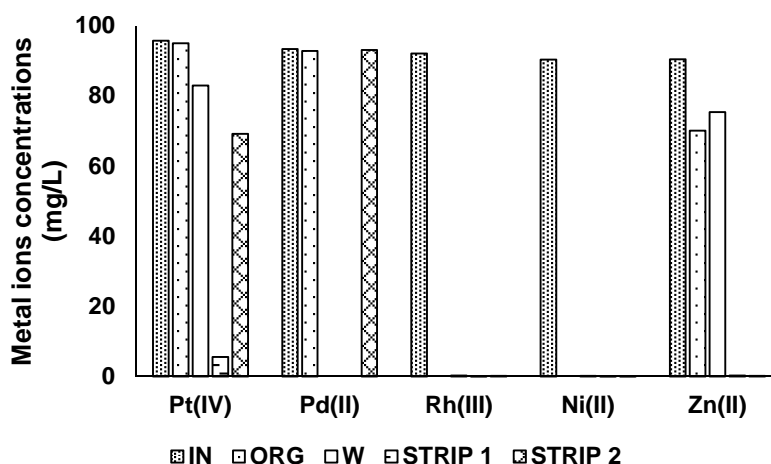


Figure 5 - Pt(IV), Pd(II), Rh(III), Ni(II) and Zn(II) concentrations (mg/L) in the initial 8 M HCl feed solution (IN), loaded 0.05 M DMDCHTDGA in 1,2-DCE organic extract (ORG), scrubbing water (W) and stripping aqueous solutions (1 M HCl - STRIP 1, and 0.1 M thiourea in 1 M HCl - STRIP 2). Standard deviations:  $\pm 5\%$ .

It can be seen that the performance towards Pt(IV) and Pd(II) is similar as before, Rh(III) and Ni(II) are not extracted, and Zn(II) is completely removed in the water scrubbing stage.

## Conclusions

*N,N'*-dimethyl-*N,N'*-dicyclohexylthiodiglycolamide (DMDCHTDGA), dissolved in 1,2-dichloroethane, proved to be a skilful extractant to recover Pt(IV) and Pd(II) from complex 8 M HCl solutions, somehow simulating the composition of leaches obtained from the hydrometallurgical recycling of spent automobile catalytic converters. Zn(II), Fe(III) and Zr(IV) were co-extracted with Pt(IV) and Pd(II); the former two were easily removed by a water scrubbing, and Zr(IV) was released by 1 M HCl (water was not tested for Zr(IV) removal). Ni(II), Rh(III) and Ce(III) were practically not extracted. Al(III) was extracted in an amount similar to Pt(IV) and Pd(II), and its stripping by any of the agents tested was unsuccessful. The finding of a suitable Al(III) stripping agent, to be applied after Pt(IV) and Pd(II) recovery, may solve this poisoning problem of DMDCHTDGA. The solvent extraction performance shown by DMDCHTDGA for Pt(IV) and Pd(II), always unchanged for all the conditions tested, is remarkable.

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## References

1. Saurat, M., Bringezu, S. *J. Ind. Ecol.* **2008**, *12*, 754–767.
2. Hagelüken, C. *Chim. Oggi* **2006**, *24(2)* suppl., 14–17.
3. Cox, M., in *Principles and Applications of Solvent Extraction*, 2<sup>nd</sup> Ed.; Rydberg, J., Musikas, C., Choppin, G.R., Eds.; Marcel Dekker Inc.: New York, 2004.
4. Malik P., Paiva, A.P. *Solv. Extr. Ion Exch.* **2009**, *27*, 36–49.
5. Malik P., Paiva, A.P. *Solv. Extr. Ion Exch.* **2010**, *28*, 49–72.
6. Costa, M.C., Assunção, A., Costa, A. M. R., Nogueira, C., Paiva, A.P. *Solv. Extr. Ion Exch.* **2013**, *31*, 12–23.
7. Narita, H., Tanaka, M., Morisaku, K. *Proc. ISEC 2005*, Beijing, China, Conf. Proc. Ed. Dep., ed.; 2005, pp. 227–232.
8. Paiva A.P., Carvalho, G.I., Costa, M.C., Costa, A.M.R., Nogueira C. *Solv. Extr. Ion Exch.* **2014**, *32*, 78-94.
9. Narita, H., Tamura, K., Tanaka, M. *US Patent 2009178513-A1*, July 2009.
10. Traeger, J., König, J., Städtke, A., Holdt, H.-J. *Hydromet.* **2012**, *127-128*, 30–38.
11. Szczepanska, I., Borowiak-Resterna, A., Wisniewski, M. *Hydromet.* **2003**, *68*, 159-170.
12. Anpilogova, G.R.; Bondareva, S.O.; Khisamutdinov, R.A.; Murinov, Yu.I. *Solv. Extr. Ion Exch.* **2014**, *32*, 206-220.