

Selective extraction of palladium from acidic nitrate solutions with thiamacrocycles-synergized dinonylnaphtalenesulfonic acid systems

M. Draye, A. Favre Reguillon, G. Le Buzit, J. Foos, M. Lemaire, A. Guy

▶ To cite this version:

M. Draye, A. Favre Reguillon, G. Le Buzit, J. Foos, M. Lemaire, et al.. Selective extraction of palladium from acidic nitrate solutions with thiamacrocycles-synergized dinonylnaphtalenesulfonic acid systems. Journal of Radioanalytical and Nuclear Chemistry, 1997, 220, pp.105-107. 10.1007/BF02035358. hal-00006490

HAL Id: hal-00006490 https://hal.science/hal-00006490

Submitted on 16 Feb 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

Selective extraction of palladium from acidic nitrate solutions with thiamacrocycles-synergized dinonylnaphthalenesulfonic acid systems

M. Draye,* A. Favre-Réguillon,* G. Le Buzit,* J. Foos,* M. Lemaire,** A. Guy*

*Laboratoire des Sciences Nucléaires du CNAM, 2 rue Conté, 75003 Paris, France

**Institut de Recherche sur la Catalyse (CNRS), Laboratoire de Catalyse et Synthèse Organique, CPE, 43, boulevard du 11 Novembre 1918, 69622 Villeurbanne Cédex, France

09022 Villeurbanne Ceuex, Prance

Thiamacrocycles-synergized sulfonic acid extraction systems have been studied for removing traces of palladium from nitric acid solutions. The influence of the concentration of nitric acid, HDNNS, and thiamacrocycle were studied. Then different thiamacrocycles, with various cavity size and with or without substituent were evaluated. Influences on the extraction and stripping behavior is discussed.

Introduction

Spent nuclear fuels contain significant quantities of valuable metals among them palladium.¹ Hence, it is of utmost interest to design and develop an efficient process for the recovery of palladium from reprocessed HLW solutions originating from the PUREX process which is used almost universally for nuclear fuel reprocessing. Several methods for the selective recovery of palladium for acid solution, using liquid/liquid²⁻⁵ or solid/liquid extraction,⁶ have been studied. As a part of our investigation in this area, different thiamacrocycles have been evaluated as selective extractant for palladium.

It is well known that towards soft metal cations, i.e., Hg^{2+} , Ag^+ , Au^{3+} and Pd^{2+} , thiamacrocycles are excellent complexing agents⁷⁻⁹ and, in particular, the thiamacrocycle $10S3^8$ (Fig. 1). Therefore, the thiamacrocycles were found not to form lipophilic complexes to transfer palladium from an aqueous phase to a dodecane solution with an inorganic anion such as nitrate or chloride. However, the use of large organic soluble anions, dinonylnaphthalene sulfonic acid (HDNNS), which also functioned as liquid ion exchangers made it possible to extract palladium. This paper reports results for the extraction of palladium from aqueous nitric acid solutions using synergistic mixtures of various thiamacrocycles and HDNNS.

Experimental

The thiamacrocycles 2-octyl-1,4,7-trithiacyclononane (2-octyl-9S3), 2-octyl-1,4,7-trithiacyclodecane (2-octyl-10S3) were prepared according to the method previously described.⁸ The thiamacrocycles 1,4,7-trithiacyclononane (9S3), 1,4,7-trithiacyclodecane (10S3), 1,4,7,10,13-pentathiacyclopentadecane (15S5), 1,4,7,10,13,16-hexathiacyclooctadecane (18S6), 1,4,8,11,14,18-hexathiacyclotetraeicosane (20S6) and 1,4,7,10,13,16,19, 22-octathiacyclotetraeicosane (24S8) were purchased from Aldrich chemicals and used as received.

The dinonylnaphthalenesulfonic acid (HDNNS), obtained from Interchim (Montlucon France), was approximately 50% in kerosene. The HDNNS was titrated and used as received.

Mixed solutions of a thiamacrocycle and HDNNS in dodecane were prepared by addition of HDNNS and dodecane to weighted amounts of thiamacrocycle. Equilibration of these mixed HDNNS/thiamacrocycles solutions with the aqueous nitric acid solutions containing $0.1 \cdot 10^{-3}$ M of palladium were performed by shaking equal quantities (5 ml) of aqueous and organic phases for 1 minute. After phase separation, both phases were sampled (4 ml) and palladium was then stripped from the organic phase by back extraction to an aqueous receiving phase. Palladium in the aqueous phases was atomic absorption determined by spectroscopy (UNICAM type SP9: 1 = 246.7 nm, air-acetylene flame). Analyses were typically reproducible to the percentage of palladium extracted within 3%.

Results and discussion

The complexing behavior towards palladium of a commercially available thiamacrocycle, 10S3, was evaluated (Fig. 1). The influence of the nitric acid, thiamacrocycles and HDNNS concentrations on palladium extraction were determined. Then, different thiamacrocycles with various cavity size and substituent were tested in the conditions previously determined.

Influence of the nitric acid concentration on the palladium percentage of extraction with the thianacrocycle 10S3 is shown in Fig. 2, in which the experimental conditions were selected as [HDNNS] = 10 mM and [10S3] = 5 mM. It can be seen that the percentage of extraction decreased with an increasing nitric acid concentration.

Constraints are imposed by the presence of nitric acid which concentration in the high-level liquid wastes is typically 1M. Thus, the concentration of nitric acid for the



Fig. 1. Stucture of extractants



Fig. 2. Pd percentage of extractions as a functions of nitric acid concentration for palladium (0.1 mM) extraction into a dodecane 10 mM in HDNNS, 5 mM in 10S3, 8 mM in 15S5 and 0.1 mM in Pd



Fig. 3. Percentage of extraction of Pd as a function of thiamacrocycle,
Pd concentration 0.1 mM contained in a 1M nitric acid solution into a dodecane solution 8 mM in HDNNS

extraction step was 1M. A decreased in the percentage of extraction of palladium was observed when the molarity of HNO_3 raised, so 3M nitric acid concentration was used in order to enhance stripping during the back extraction.

Then, the influence of the concentration of the thiamacrocycle on the percentage of extraction of palladium was studied at a 1M constant concentration of nitric acid (Fig. 3).

Below a concentration of 0.25 mM in 10S3, the system leads to low palladium percentages of extraction. From this concentration, the extraction of palladium increases



Fig. 4. Percentage of extraction as a function of HDNNS concentration for palladium (0.1 mM) extraction from 1 M nitric acid solution into a dodecane solution 1 mM in 10 S3



Fig. 5. Structure of the extractants studied

significantly with increasing concentration of thiamacrocycle to reach a plateau for a concentration of 0.5 mM. In those case, the ratio HDNNS/thiamacrocycle was close to 5. Then, the variation of the palladium percentage of extraction as a function of the concentration of HDNNS was studied (Fig. 4) at constant nitric acid (1M) and thiamacrocycle (1 mM) concentrations.

An increase of the extraction of the palladium is observed with increasing HDNNS concentration. A maximum efficiency is obtained with a 5 mM HDNNS concentration and above this concentration, a plateau is reached. In those case the ratio HDNNS/thiamacrocycle was close to 5. These results are coherent with those obtained with the study of the variation of the percentage of extraction of palladium as a function of the concentration of thiamacrocycle.

We have studied the extraction of palladium with 10S3 and HDNNS. The influence of the concentration of the different components was investigated. Studies have shown a synergistic extraction between the naphthalene sulfonic acid and the macrocycle. This was explained by the complementary size matching of ionic radii of ions and ligand cavities. Then, new thiamacrocycles (Fig. 5), substituted or not, with different cavities size and different numbers of sulphur atoms were evaluated for the palladium extraction using synergistic effect with HDNNS in dodecane.

The extraction and stripping efficiencies for palladium into dodecane solution and recovery were done as determined previously (Table 1).

When the cavity size increased, the extraction of palladium raised (entries 1-5), If the cavity is too large, the efficiency of extraction drops (entry 6). The effect of size of the chelate rings on complex stability is shown in Table 1 (entry 1 vs. 2 and 4 vs. 5). Palladium seems to have better affinity for six-membered chelate rings rather than five-membered chelate rings. With the same number of complexing atoms (entries 4-5), palladium extraction is markedly enhanced when six-membered chelate rings is used. But when the complex formed is to strong, the efficiency of the back extraction is low (entry 5). The 20S6 possesses an optimal size of cavity for palladium extraction and Pd(II)-20S6 complex may be so strong that its stripping fails. When the size of the cavity is increased to the 24S8, the capacity of extraction drops. In any solvent extraction process it becomes almost imperative to back extract the metal from the loaded organic phase. Then, the choice of an appropriate extractant depends on an equilibrium between extraction efficiency and stripping efficiency to.

In a general manner, the thiamacrocycles used had a very limited solubility in dodecane. Thiamacrocycle 18S6, 20S6 and 24S6 were slightly soluble under those conditions. Functionalised thiamacrocycle were then synthesised. Substitution of thiamacrocycle by an octyl group produced thiamacrocycles with markedly enhanced solubility in dodecane and with higher extraction efficiencies. Octylthiamacrocycles showed higher extraction efficiencies but lower back-extraction efficiencies (entries 7-8).

Those result underlines further the great potential of thiamacrocycles for the recovery of palladium from aqueous acidic radioactive liquid wastes into dodecane solutions. The synergistic combination of a thiamacrocycle and the organophilic sulfonic acid, HDNNS, was found to

Table 1. Extraction and stripping efficiencies for palladium recovery
into a dodecane solution 4 mM in HDNNS containing one
of the thiamacrocycles, initial HNO ₂ 1M, Stripping HNO ₂ 3M

Entry	Thiamacrocycle	Extraction efficiency,%	Stripping efficiency,%
la	9\$3	46	85
2 ^a	10S3	60	87
3 ^b	1585	66	86
4 ^c	18S6	79	86
5°	2086	99	38
6 ^c	24S8	21	24
7 ^a	2-octyl-9S3	91	3
8 ^a	2-octyl-10S3	98	10

^a4 mMol $\cdot 1^{-1}$.

^b0.5 mMol $\cdot 1^{-1}$.

 $^{\circ}0.34 \text{ mMol} \cdot 1^{-1}$.

form an effective extraction system for extraction of palladium from acidic solutions. The size selective synergistic effect is most prominent in the 15S5 to 20S6 size range. And, more systematic investigations into competitive extraction need to be made to further characterised this system.

References

- 1. R. P. BUSH, Platinum Metals Rev., 35 (1991) 202.
- V. GUYON, A. GUY, J. FOOS, R. CHOMEL, T. MOUTARDE, G. LE BUZTT, M. LEMAIRE, J. Radioanal. Nucl. Chem., 187 (1994) 19.
- 3. S. FANG, L. FU, Y. WANG, J. Radioanal. Nucl. Chem., 186 (1994) 285.
- 4. R. G. SCHULER, C. B. BOWERS, J. E. SMITH, V. VAN BRUNT, M. W. DAVIS, Polyhedron, 6 (1987) 1125.
- 5. G. H. RIZVI, J. N. MATHUR, M. S. MURALI, R. H. IYER, Sep. Sci. Technol., 31 (1996) 1805.
- 6. A. WARSHAWSKY, Extraction of platinium group metal ions by ion exchange resins, in: Critical Reports on Applied Chemistry, Vol. 19, Ion Exchange and Sorption Processes in Hydrometallurgy, M. STREAT and D. NADEN (Eds), John Wiley & Sons, 1987.
- 7. O. HEITZSCH, K. GLOE, H. STEPHAN, E. WEBER, Solv. Extr. Ion Exch., 12 (1994) 475.
- 8. V. GUYON, A. GUY, J. FOOS, Tetrahedron, 51 (1995) 4065.
- 9. J. P. SHUKLA, S. R. SAWANT, A. KUMAR, R. K. SINGH, N. VARADARAJAN, NUCL. Sci. J., 33 (1996) 39