RECOVERY OF PLATINUM FROM LEACHING SOLUTIONS BY INTERACTION WITH PORPHYRINS

Anca Lascu[1*]

[1]*Institute of Chemistry "Coriolan Dragulescu", M. Viteazul Ave. 24, 300223-Timisoara, Romania,* Tel: +40256/491818; Fax: +40256/491824
[*]*email: ancalascu@yahoo.com*

Abstract
Two differently substituted base porphyrins, one containing aliphatic unsaturated groups and one functionalized with basic effect at the periphery: 5,10,15,20-tetrakis-(4-allyloxyphenyl)-porphyrin and 5,10,15,20-tetrakis-(4-aminophenyl)-porphyrin, were investigated for their capacity to complex with hexachloroplatinic acid from leaching solutions. Their different nature makes them interact differently with the hexachloroplatinic acid in solution, as aminophenylporphyrin is more capable to form more stable complexes, therefore it is suitable for the recovery of platinum from diluted solutions (removal capacity is large 86.6 %) whereas the amount of platinum that can be recovered by allyloxyphenylporphyrin is lower, only 74.07 %.

Introduction
The automotive industry uses large amounts of platinum salts as catalysts. As platinum is a rare metal and the natural resources are scarce, the recovery of platinum from leaching solutions has to be taken into serious consideration. This can be achieved based on the capacity of some materials to generate complexes with hexachloroplatinic acid. Some of the compounds capable to perform this task are base porphyrins, properly substituted at the periphery with functional basic groups, or metalloporphyrins, due to their capacity to coordinate ligands at the metal centers [1]. The following step is to obtain platinum colloid, by reducing the already coordinated systems.
A couple of aliphatic- and amino-substituted porphyrin bases were investigated for their capacity of platinum absorption.
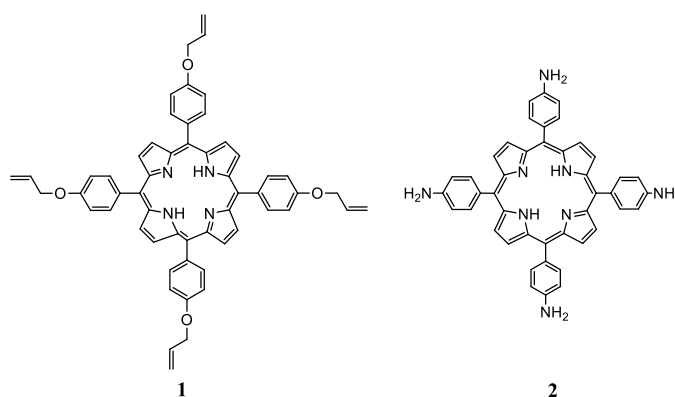

Figure 1. Structure of the investigated compounds: 5,10,15,20-tetrakis-(4-allyloxyphenyl)-porphyrin (1); 5,10,15,20-tetrakis-(4-aminophenyl)-porphyrin (2)

Experimental
Materials and methods. N,N-Dimethylformamide was purchased from Merck (Darmstadt, Germany), chloroplatinic acid hexahydrate was acquired from Sigma-Aldrich (St. Louis, USA). The porphyrins 5,10,15,20-tetrakis-(4-allyloxyphenyl)-porphyrin (1); 5,10,15,20-

tetrakis-(4-aminophenyl)-porphyrin (2) were synthetized and characterized as published in previous papers [2].

The experiments were performed in 5 mL porphyrin solutions in DMF, to which increasing amounts of hexachloroplatinic acid solution in water (c = 1.03 x 10^{-3} M) were added. The mixtures were stirred for 30 seconds and then the UV-vis spectrum was recorded for each step.

Apparatus. For recording UV-visible spectra, standard 1 cm pass quartz cells were used on a JASCO UV- V-650 spectrometer (Japan).

Results and Discussions

In order to have a precise measurement, without the effect of volatile solvents, the porphyrins were solved in DMF, a polar, nonvolatile solvent compatible with water. The platinum-containing agent of use in the experiment was hexachloroplatinic acid solution in water (c=1.03 x 10^{-3} M).

The absorption domain of the chloroplatinic acid solution does not interfere with the absorption wavelengths of the investigated porphyrins, as can be observed in Figure 2.
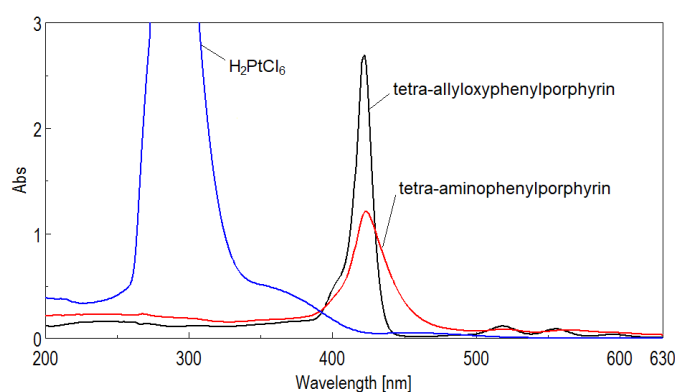

Figure 2. Comparative UV-vis spectra of the investigated compounds

The overlapped spectra for the successive adding of chloroplatinic acid to the solutions of the two porphyrin-base compounds of interest are presented in Figure 3.
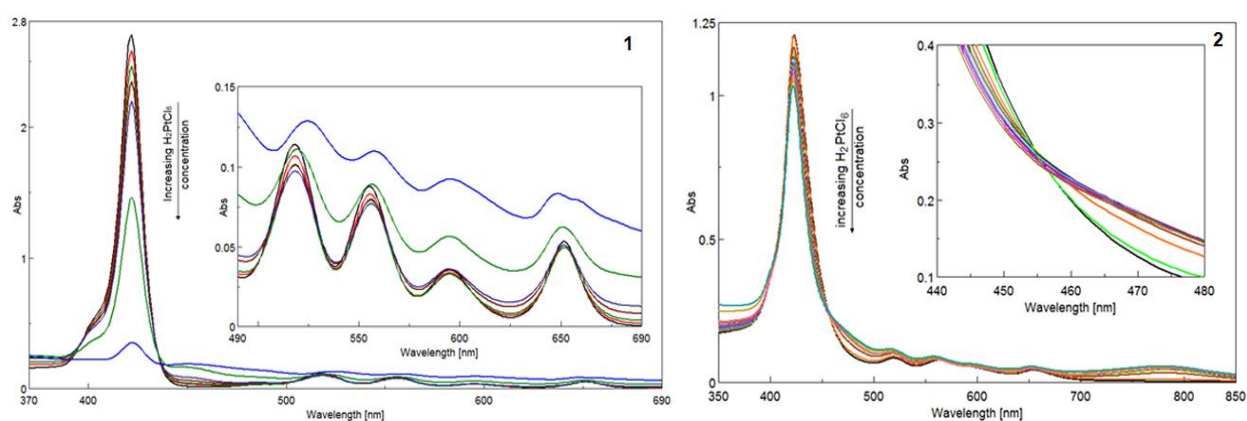

Figure 3. Comparison of the UV-vis spectra after adding chloroplatinic acid to 5,10,15,20-tetrakis-(4-allyloxyphenyl)-porphyrin (1) and 5,10,15,20-tetrakis-(4-aminophenyl)-porphyrin (2). Details present magnification of Q bands and of isosbestic points.

It can be noticed that the allyloxyphenyl porphyrin can only interact with small amounts of platinum from the solution, the intensity of the Soret band decreases drastically after adding 2.2 mL chloroplatinic solution (Figure 3(1)). Nevertheless, some interaction between the

porphyrin molecule and the platinum ions takes place, as isosbestic points show: one on the descending branch of the Soret band, at 435 nm and one at 564 nm, on the Q3 band.

The aminophenylporphyrin is able to better interact with platinum ions in solution, many intermediate species are present, as proven by the presence of numerous isosbestic points: one at 458 nm, on the Soret band, then on the Q bands, in increasing wavelength: 528 nm, 570 nm and 665 nm respectively (Figure 3(2)). The isosbestic point at 570 nm corresponds to the H_2PtCl_6 concentration interval of 2.023 x 10^{-5} M to 7.644 x 10^{-5} M. Also, a new peak appears at 784 nm, probably due to self- aggregation phenomena [3]. Besides, these isosbestic points, together with the appearance of the new peak, indicate a possible acid-base complexation between the weak hexachloroplatinic acid and the four amino groups at the periphery of the porphyrin molecule, that can be protonated. The presumed final complex can have the structure presented in Figure 4.
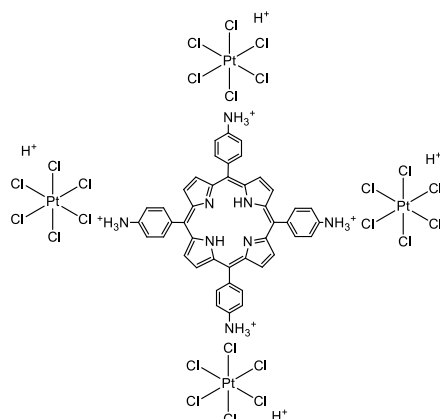

Figure 4. The presumed structure for the complex formed between the tetra-aminophenylporphyrin and the hexachloroplatinic acid

The linear dependence between the intensity of absorption read at the Soret wavelength maxima and the H_2PtCl_6 concentration for the two porphyrins under investigation are presented in Figure 5.

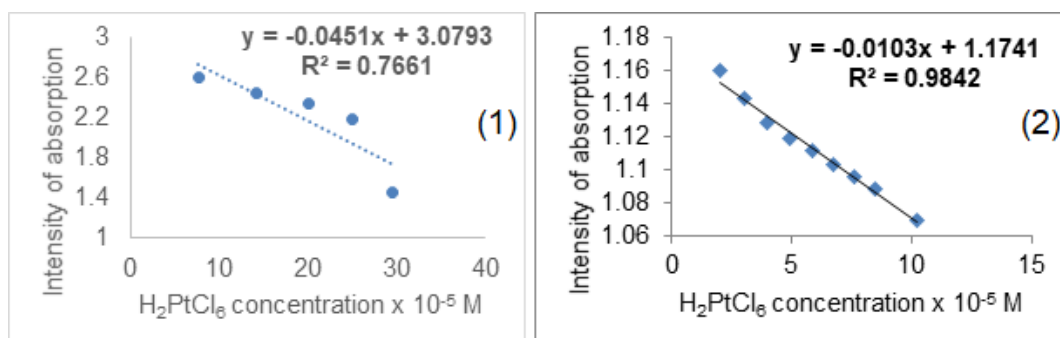Figure 5. Linear dependence between the intensity of absorption read at Soret maximum wavelength and the H_2PtCl_6 concentration for allyloxyphenylporpyrin (1) and for aminophenylporphyrin (2)

It can be observed that the capacity to recognize platinum ions is very poor in the case of allyloxyphenylporphyrin, as the intensity of absorption read at 422 nm is linear with the concentration of chloroplatinic acid only in the concentration domain of 7.6 x 10^{-5}M to 29.5 x 10^{-5} M, with a poor correlation coefficient of 76.61% and with low sensitivity. In comparison, the chloroplatinic acid concentration interval (2.023 x 10^{-5} M to 10.227 x 10^{-5} M) for which

the dependence between the intensity of absorption of aminophenylporphyrin and platinic acid concentration is linear, is represented by a high correlation coefficient of 98.42%.

The capacity to remove platinum ions from a solution, with the aid of porphyrin molecules, was the purpose of this study. Therefore, according to [1] the quantity of platinum that can be retrieved by the porphyrins can be evaluated according to the equation:

$$Qe = \frac{(C_0 - C_e)\,V}{m}\ (mg/g)$$

Where, adapting the formula for our specific case and taking into consideration the variation of platinic acid:

C_0 is the concentration of Pt in the porphyrin solution at the end of the experiment expressed in ppm

C_e is the concentration of the Pt in the porphyrin solution at the beginning of the experiment expressed in ppm

V is the volume of the solution in L

m is the quantity of porphyrin in the solution expressed in g

The distribution coefficient (K_D) shows the affinity of the porphyrin solution toward Pt colloidal particles and can be calculated according to the equation:

$$K_D = \frac{Q_e}{C_e}\ (L/g)$$

The removal capacity of Pt colloidal particles from solution can be calculated according to the formula:

$$Removal\ capacity\ (\%) = \frac{(C_0 - C_e)}{C_0}\ x\ 100$$

Table 1 presents the results obtained for the two porphyrins investigated.

Porphyrin	Q_e [mg Pt/g porphyrin]	K_D [L/g]	R_c [%]
5,10,15,20-tetrakis-(4-allyloxyphenyl)-porphyrin	1175.208	78.809	74.07
5,10,15,20-tetrakis-(4-aminophenyl)-porphyrin	581.75	293.8	86.6

If the capacity to remove platinum from dilute solutions is the desired target, then the 5,10,15,20-tetrakis-(4-aminophenyl)-porphyrin is the better material as given in Table 1, each NH$_2$ base unit being capable to interact with the hexachloroplatinic acid.

The platinum can be recovered as colloid or as platinum particles by reducing the novel generated complexes either with sodium citrate or with excess NaBH$_4$, a more potent reducing agent and subsequent centrifugation of the solution.

Conclusion

Two differently substituted porphyrin-base compounds, one containing aliphatic unsaturated groups and one containing basic groups at the periphery: 5,10,15,20-tetrakis-(4-allyloxyphenyl)-porphyrin and 5,10,15,20-tetrakis-(4-aminophenyl)-porphyrin, were investigated for their capacity to complex hexachloroplatinic acid from leaching solutions. Their different nature makes them interact differently with the platinum ions in solution. So, aminophenylporphyrin is more capable to bind hexachloroplatinic acid, therefore it is suitable for the recovery of platinum from diluted solutions.

Acknowledgements

References
[1] D. Vlascici, I. Popa, V.A. Chiriac, G. Fagadar-Cosma, H. Popovici, E. Fagadar-Cosma, Chem. Cent. J.7 (2013) 111-118.
[2] B.O. Taranu, I. Popa Sebarchievici, I. Taranu, M.I. Birdeanu, E. Fagadar-Cosma, Rev. Chim. -Bucharest 67(5) (2016) 892-896.
[3] E. Tarabukina, E. Fagadar-Cosma, C. Enache, N. Zakharova, M. Birdeanu, J. Macromol. Sci. B 52(8) (2013) 1092–1106.