PLATINUM-PORPHYRIN INVOLVED IN THE UV-VIS SPECTROPHOTOMETRIC DETECTION OF RHODAMINE B AND OXYGEN PEROXIDE

Ion Fratilescu[1]*, Diana Anghel[1], Anca Lascu[1], Camelia Epuran[1], Eugenia Fagadar-Cosma[1]

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

Abstract

Based on the potential toxicity of rhodamine B, the purpose of this study was to realize a novel UV-vis spectrophotometric method for the rapid and not expensive detection of this dye from water, soft drinks and various foods, using as sensitive material Pt(II) 5,10,15,20-tetra(4-methoxy-phenyl)-porphyrin (Pt(II)-TMeOPP). The method was successful in the detection domain $2x10^{-8}$M up to $1.2x10^{-7}$M. The second achievement was the application of this complex formed between Pt(II)-TMeOPP and rhodamine B as potential sensitive agent for the sensing of hydrogen peroxide, and it proved to be efficient in the medical field relevance (5-14x10-8 M).

Introduction

Rhodamine B is an organic dye having as scaffold the xanthene structure (Figure 1a) and is often used for measuring absolute fluorescence quantum yields [1], as biomarker and tracer for wildlife studies [2,3]. The organic chloride salt rhodamine b with IUPAC name N-[9-(ortho-carboxyphenyl)-6-(diethylamino)-3H-xanthen-3-yli-dene] diethyl ammonium chloride is very soluble in water and gives a powerful reddish coloration. The xanthene dye is also used as a colorant in textiles, food industry and as water tracer [4]. Based on the knowledge that Rhodamine B inhibits the proliferation of human lip fibroblasts KD cells that are essential for the maintenance of the healthy lip tissue, so that the application of this compound as coloring agent in cosmetics such as: lipsticks and soaps, has to be strictly monitored. There are also studies that report the toxicity of rhodamine B which leads to liver damage, erythrocyte hemolysis, mutagenicity and carcinogenicity [5].
Based on the potential toxicity of rhodamine B, the purpose of this study is to realize a novel spectrophotometric method for the rapid and not expensive detection of this dye from water, using as sensitive material Pt(II)-5,10,15,20-tetra(4-methoxy-phenyl)-porphyrin (Pt(II)-TMeOPP), with the structure presented in Figure 1b.

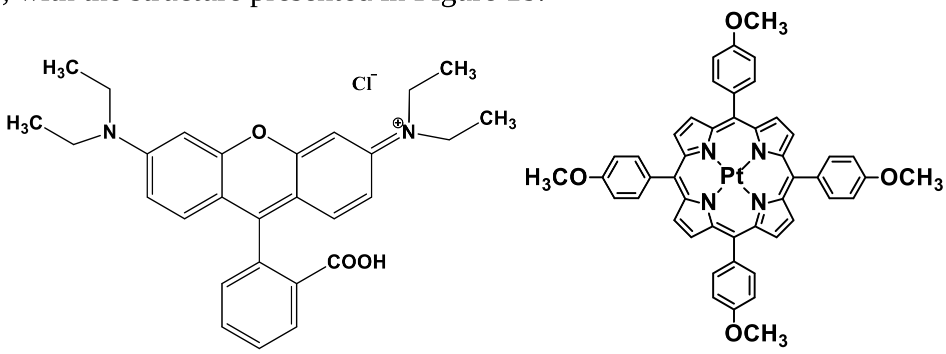

Figure 1. a) The xanthene-type structure of rhodamine B; b) the structure of Pt(II)-TMeOPP
The second aim was to use the complex formed between Pt(II)-TMeOPP and rhodamine B as potential sensitive agent containing two active fluorescent dyes, for the sensing of hydrogen peroxide.

Experimental

Apparatus. For the spectrophotometric determinations we used a UV-visible JASCO V-650 spectrophotometer with Perkin Elmer quartz cuvettes with 1 cm pitch.

Reagents. The Pt(II)-5,10,15,20-tetra(4-methoxy-phenyl)-porphyrin was synthesized and fully characterized, in our laboratory, as previously reported [6].

Tetrahydrofuran (THF) was acquisited from MerkK GaA (Darmstadt, Germany). The rhodamine B origin is from Polskie Odczynniki Chemiczne (Gliwice, Poland).

Spectrophotometric method for rhodamine B detection. The experiment is based on the UV-vis spectrophotometric titration of 5 mL Pt(II) 5,10,15,20-tetra(4-methoxy-phenyl)-porphyrin solution ($c=1.592x10^{-5}M$) in THF, with portions of 0.5 mL rhodamine B solution ($c=2.004x10^{-5}$ M). After each addition of rhodamine, the mixture was stirred with electromagnetic stirrer for 30 seconds and the UV-vis spectrum was performed.

The second experiment consisted in stepwise addition of 0.03 mL of H_2O_2 to the sample 7 from the previous experiment, under stirring.

Results and discussions

Figure 2 is showing the overlapped UV-vis spectra after adding rhodamine B to the solution of Pt(II)-5,10,15,20-tetra(4-methoxy-phenyl)-porphyrin. The metalloporphyrin displays the characteristic spectrum for a Pt-porphyrin with the Soret band located at 405 nm and the Q band placed at 511 nm. The rhodamine B has the main characteristic peak at 560 nm. The emergence of a new band blue shifted relative to the bare rhodamine B band at 550 nm, together with the appearance of two isosbestic points on the Soret band at 386 nm, respectively at 421 nm, associated with the decrease of the Soret band and the increase of the new band proves that a new complex was formed.

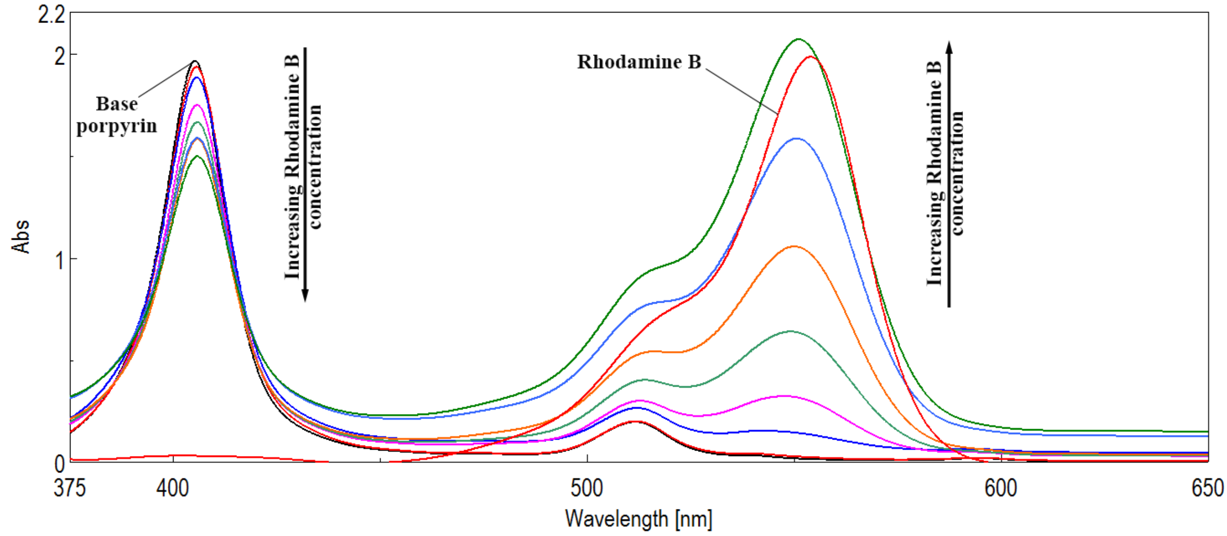

Figure 2. Superposed UV-vis spectra proving the obtaining of the complex between Pt(II)-TMeOPP and rhodamine B.

Besides, the graphical representation between the intensity of absorption measured at Soret band and the concentration of rhodamine B is linear with a fair correlation coefficient of 98.66% (Figure 3), in a domain from $2x10^{-8}$ M up to $1.2x10^{-7}$ M, a field that is relevant for the monitoring of soft drinks, red wine grape juice and chili oil [7]. As a conclusion, Pt(II)-TMeOPP can act as sensitive compound for the detection of rhodamine B in several drinks and foods. In order to achieve a real optical sensor, further studies will be performed regarding the effect of different analytes interference.

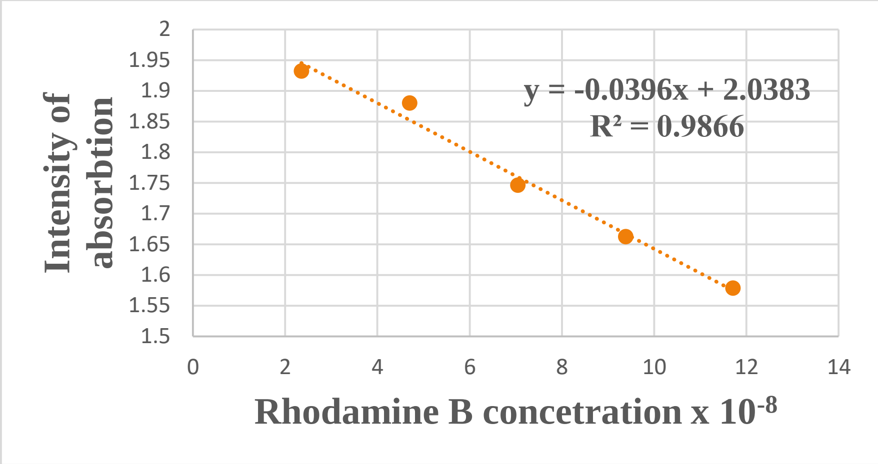

Figure 3. The linear dependence between the intensity of absorption measured at Soret band and the concentration of rhodamine B

The second part of this investigation, was focused on the capacity of the complex formed between the Pt(II)-TMeOPP and rhodamine B to detect hydrogen peroxide. As can be seen from Figure 4, by increasing H_2O_2 concentration, the intensity of the Soret band of the complex is continuously decreasing, while the main band of the complex, located at 550 nm is increasing.

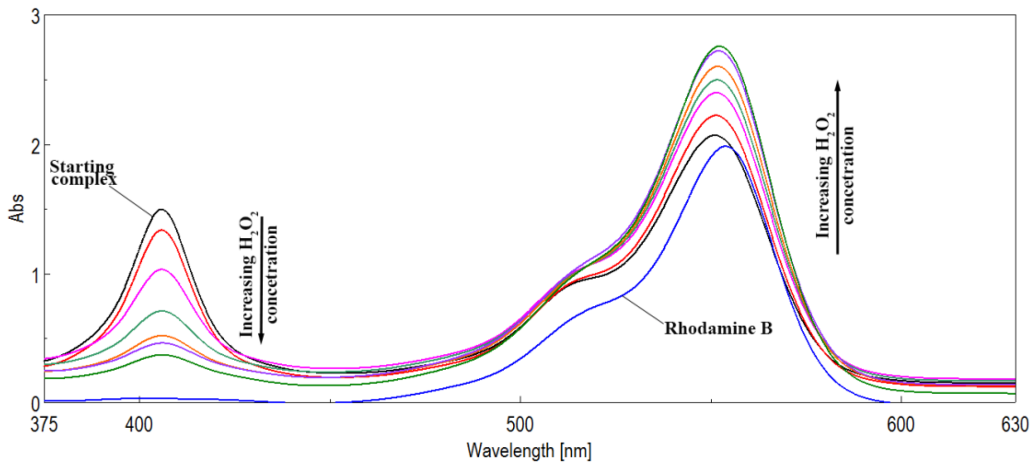

Figure 4. The overlapped UV-vis spectra of the complex Pt(II)-TMeOPP - rhodamine B showing the influence of adding H_2O_2

This phenomenon, going to the complete disappearance of the Soret band and the hyperchromic effect of the band at 551 nm, can be explained by the capacity of the rhodamine B partner to decompose the porphyrin ring in the presence of H_2O_2. Nevertheless, the dependence between the intensity of absorption measured at 551 nm and the H_2O_2 concentration (Figure 5) is linear in a field (5-14x10^{-8} M) that is of medical relevance for oxidative stress tests [8].

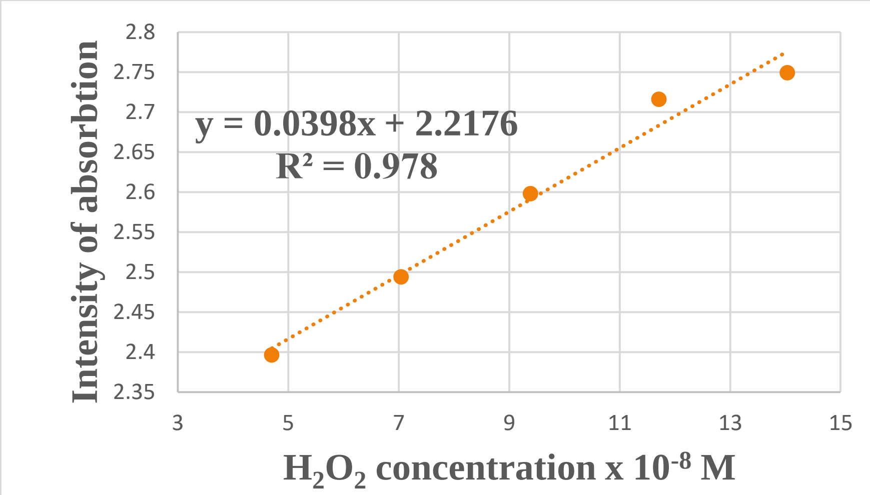

Figure 5. The dependence between the absorption intensity of the complex between Pt(II)-TMeOPP and rhodamine B and the concentration H_2O_2 read at 551 nm

Conclusion

This work comprised many steps: the obtaining of a new complex complex between rhodamine B and Pt(II)-TMeOPP; the potential application on the spectrophotometric detection of rhodamine B from foods and drinks in the field $2x10^{-8}$ M up to $1.2x10^{-7}$ M using the Pt-porphyrin as sensitive material; the application of the complex for the detection of minute amounts of hydrogen peroxide with relevance for medical tests. The work has to be continued with the study of different analytes interference in order to set up the real sensors.

Acknowledgements

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