

NANOSYSTEMS BASED ON MICELLE METALLO-PORPHYRINS

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Abstract. The nanosystems based on metallo-porphyrins have an increasing interest in fields extending from chemistry and biology. The investigations of metallo-porphyrins in micelles in non-aqueous solvents can provide significant informations relevant to enzymatic and cell membrane interactions, organic and inorganic reaction mechanisms. Triton X-100 has been widely used as a non-ionic surfactant for porphyrin-drugs solubilizing and stabilizing in solution. The non-polar environment of Triton X-100 micellar may be used to incorporate hydrophobic porphyrin molecules, due to ability of metallo-porphyrins to penetrate into micelles yielding to strong polar cavity of these micelles, and to decreasing of the photodegradation rate reaction in micellar medium, attributed to deep penetration of metallo-porphyrins into the micelles with the polar group OH oriented toward to the micelle surface. The present paper is deals with the absorption UV-Vis and fluorescence variation spectra of some porphyrins from TPP and TNP free bases and their metallic complexes with Mg, Zn, Cd during the photodegradation process.

Keywords: micelles, nanosystems, metallo-porphyrins

1. INTRODUCTION

Micelles are nanometer scale aggregates formed as a dynamic unilaminar phase in aqueous solutions of surfactants. In order to overcome the disadvantages of different drugs formulations and to increase their therapeutic action, various colloidal drug carriers, such as emulsions, liposomes, nanoparticles, and micelles, are currently being studied [1]. Their structure, dynamics and other properties of the micellar phase are subjects of extensive investigations in recent years, Figure 1.

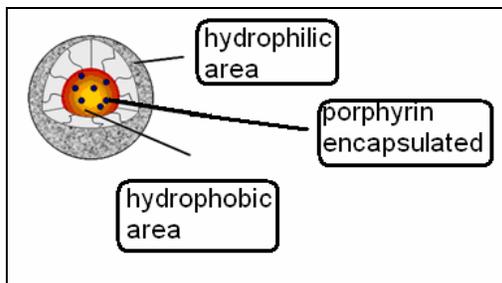


Fig.1. The micelle structure

Aqueous micelles are widely used to solubilize substances which are sparingly soluble in water. Interaction of various solutes with the micellar phase and encapsulation of molecules inside micelles are studied as models for the biomembranes [2], or a protein-molecule complex formation [3]. Triton X-100 is usually used as a template is the most effective in the production of the particles and the formation of their agglomerates in controlled size and morphology [4].

The porphyrins and their analogs play a diverse role in biological systems. Porphyrins and the four-coordinated

metallo-porphyrins have been show to have a strong tendency to get encapsulated inside micelles in monomeric forms [5,6].

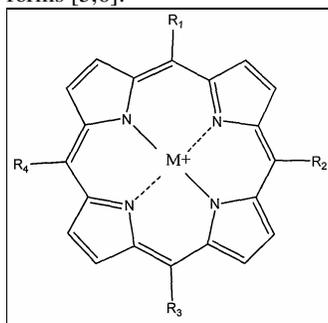


Fig.2. The molecular structure of TPP-Me (R=phenyl) and TNP-Me (R=naphthyl); (M⁺: Mg,Zn,Cd);

Triton X is a nonionic polydisperse p-(1,1,3,3-tetramethylbutyl) phenoxy poly (oxyethylene glycol). The encapsulation of different porphyrins into non-ionic micelles (as Triton X-100) could be a good model for studying different heme proteins and other porphyrin-containing biomolecules [7]. Micelles with an approximate spherical or spheroidal shape possess significant flexibility being recognized a very simplified model of the membranes. The presence of polar head groups and hydrophobic chains in micellar structures allows [8].

This paper is deals with some aspects about the photodegradation reaction of some metallo-porphyrins in benzene and micellar solutions. The studied porphyrins (metal complexes with Mg, Zn and Cd of 5,10,15,20-tetraphenylporphyrin, TPP and 5,10,15,20-tetranaphthylporphyrin, TNP), Figure 2, due to the molecular dimensions allow their enclosure inside of the micelle, yielding to their photostabilization.

2. EXPERIMENTAL PART

2.1. Synthesis method

5,10,15,20-tetraphenylporphyrin(TPP) and 5,10, 15,20-tetranaphthyl porphyrins (TNP), have been synthesized and purified in the laboratory after literature data [9-13]. The preparation method for the metallo-porphyrins is identical with Adler method [14].

The micelles containing porphyrins were prepared using 0.002 g TPP-Me (TNP-Me), 2 g Triton X 100 (LOBA) and 0.6 ml NH₃OH. TPP-Me (TNP-Me) was dissolved in Triton X 100 and then all quantity of NH₄OH was added. Water was added up to 100 ml.

2.1 Sample characterization

The UV-Vis spectra were recorded with a SPECORD M400, Carl Zeiss Jena spectrophotometer. The irradiations were achieved using a medium pressure mercury vapour lamp - 125 W, Romlux-Targoviste.

All measurements were done at room temperature and the probes were placed at a distance of 25 cm in front of the UV lamp.

For all prepared porphyrins UV-Vis spectra were measured in organic solvent and also in micellar solution. Spectra of irradiated solutions at irradiation times of 0-60 minutes were measured.

3. RESULTS AND DISCUSSION

The aim of this study was to observe the spectral changes which can occur at the metallo-porphyrins molecules solubilized in non-ionic micelle and in organic solvent like benzene. The irradiation of TPP-Me and TNP-Me solutions (figures 3-5) revealed that the evolution of the spectra show important differences in organic solvent from those in micellar solutions, even the absorption spectra of the initial solutions of porphyrins are not very similar in micellar systems and in other simple solvents, in good agreement with the literature [15]. The metallo-porphyrins in benzene, as organic solvent, shown a slight photodegradation upon irradiation while in micellar solution this observation was not valuable. The photodegradation rate of the porphyrins increased with the irradiation time in organic solvent, while in micellar solution no significant modifications were observed even at irradiation lasting hours. Although high concentrations of porphyrins were used, were obtained the same results, which argue a possible existence of an inner "free space" inside of the micelle. The spectral characteristics of the studied metallo-porphyrins are presented in table 1.

The micellar Triton X solution is formed of different entities with well defined properties. These solubilized species can have several ways of connecting and of orientation in the micelle. The position doesn't have to be fixed. Generally, a widely used model for hindered rotational dynamics of a probe in micelles is the wobbling-in-cone model [16]. This model has been used

to describe the rotational dynamics of some xanthen probes in micelles. The model requires that a part of the molecule remains near the surface and the rest of the molecule is free to wobble in a cone. The porphyrins nmolecules that we used in this study conform to this requirement; due to their planar-elliptic structure have the tendency to remain inside of the micellar medium. The wobbling motion inside the micelle is, likely to be confined in an elliptical cone because of the shape and the geometry of the porphyrins, this observation being more pronounced at TNP class than to the TPP class.

This structure permits a spontanous encapsulation of the guest molecule, in our case the porphyrin, through the hydrocarbon chains of the micelle [17].

The diameter of the porphyrin ring is (~13 Å) much smaller than the dimensions of micelles, and the solubilization site of the porphyrin inside micelles is ~6Å from the surface of the micelle²³. Also, this diameter of the porphyrin ring is much less than that of Triton X-100 and the porphyrin molecule could be physically accommodated inside the micelle and could be solubilized as monomers.

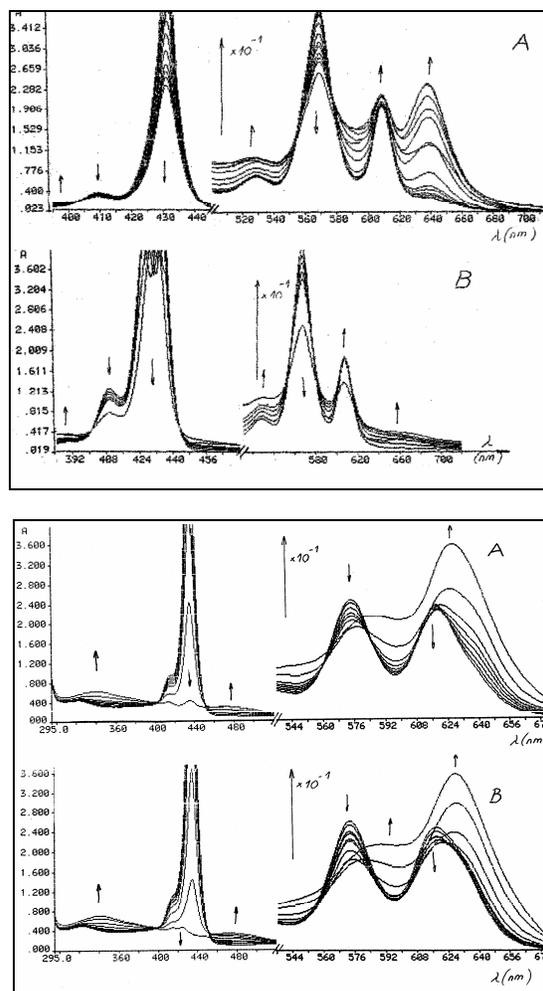


Figure 3. The spectral changes of TPP-Cd (A) and TNP-Cd (B) in benzene (A) and Triton X-100 (B)

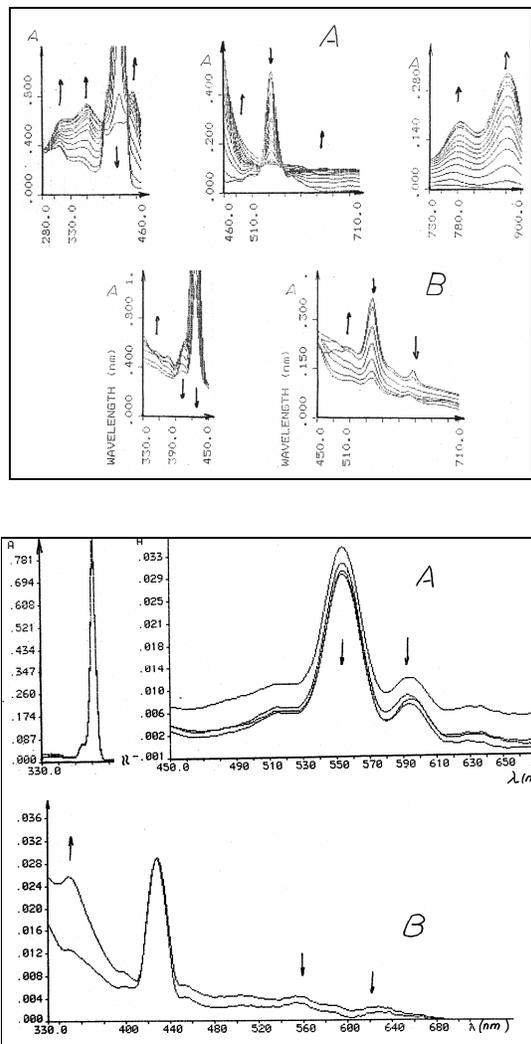


Figure 4. The spectral changes of TPP-Zn and TNP-Zn in benzene and Triton X-100

From the absorption spectra we could appreciate the decreasing of the studied porphyrin concentration, like in figures 3-5: in organic solvents, at the porphyrins free-bases, the reaction rate of TNP is higher than of TPP, while in micellar medium of Triton X the ratio is reverse. So, the non-ionic micelle could act as a very efficient photostabilizer. Because the fluorescence property of some molecules could be used to probe the micellar environment near the region where it's solubilized [18], it was used such property to identify the aggregation form of the enclosed porphyrins, and to explain the decreasing of the photodegradation dynamics. The fluorescence spectra of the studied porphyrins are presented in figure 6. The fluorescence lifetimes of porphyrins are in the range 13-17 ns in micelles and 9-12 ns in organic solvents [20]. The lifetimes of all the porphyrins in Triton X-100 micelles could be attributed to the monomeric forms and are larger than the values obtained in pure solvents.

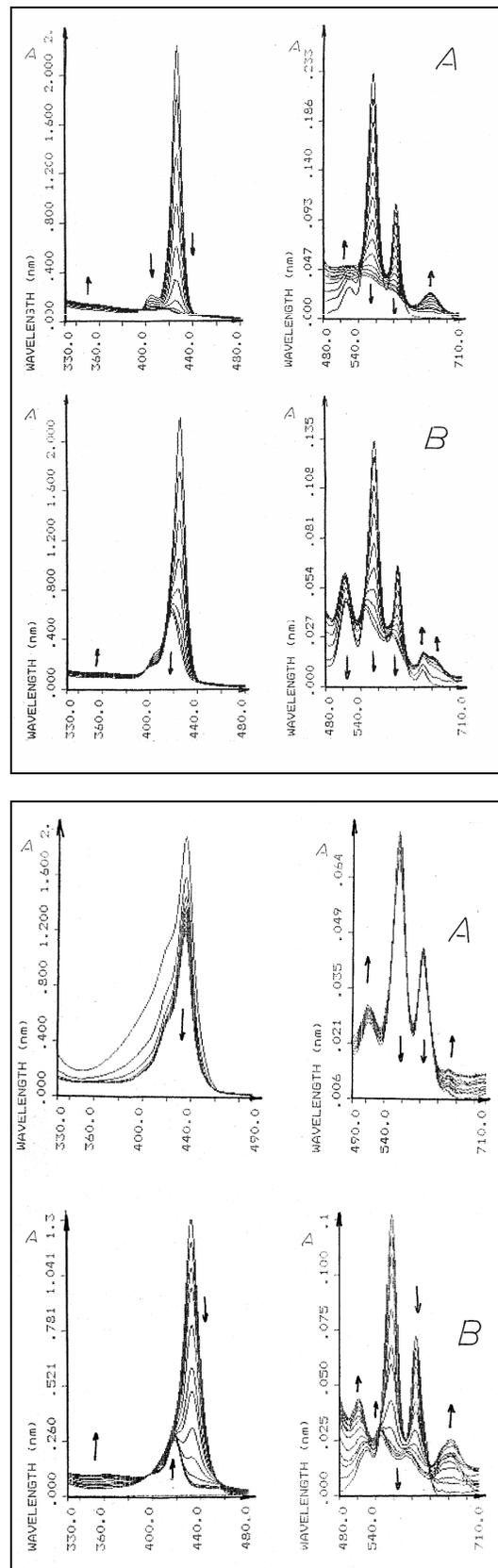


Figure 5. The spectral changes of TPP-Mg and TNP-Mg in benzene and Triton X-100

The increasing of the porphyrins lifetime in micelles can be ascribed to the reduction in the diffusion-limited fluorescence quenching by oxygen in micellar samples. This could be an explanation for the low rate photodegradation of all these porphyrins.

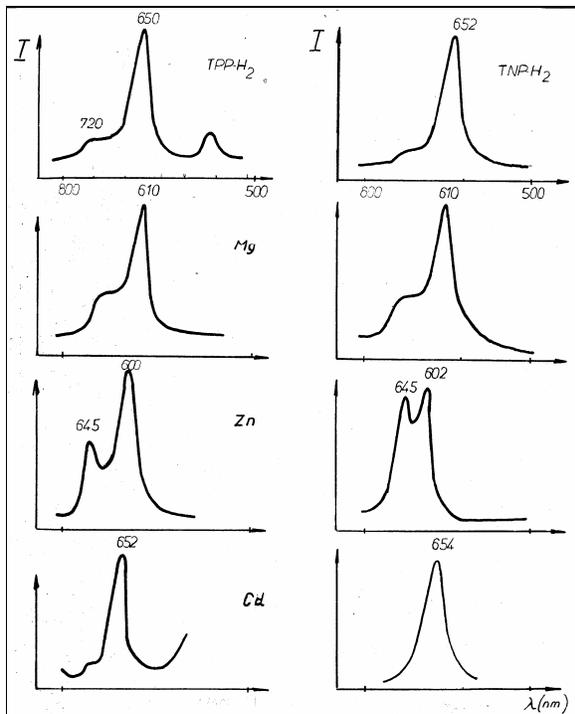


Figure 6. The fluorescence spectra of TPP, TNP and their metallic complexes with Cd, Zn and Mg

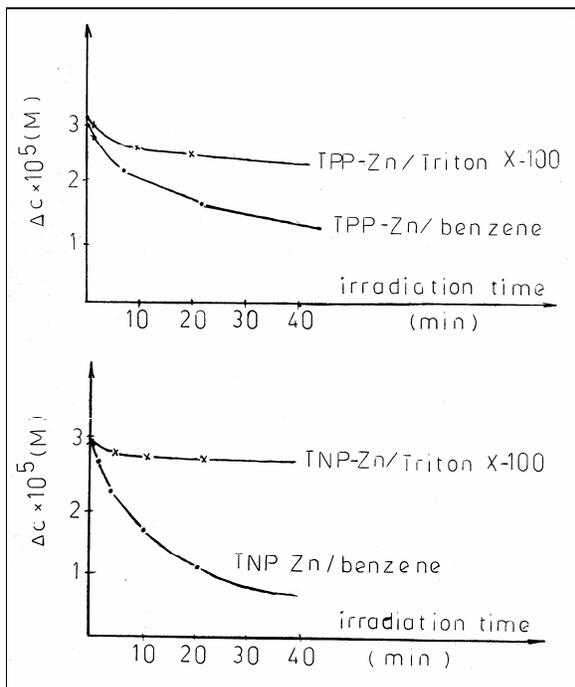


Figure 7. The photodegradation kinetic of TPP-Mg and TNP-Mg in benzene and Triton X-100

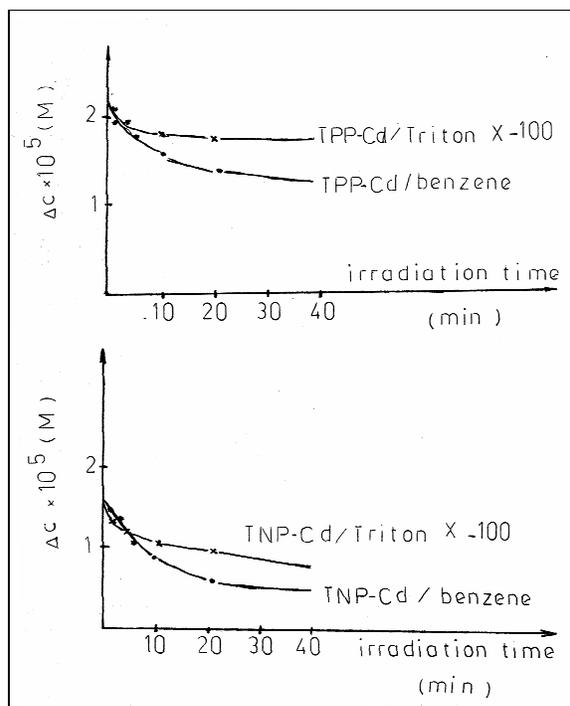


Figure 8. The photodegradation kinetic of TPP-Cd and TNP-Cd in benzene and Triton X-100

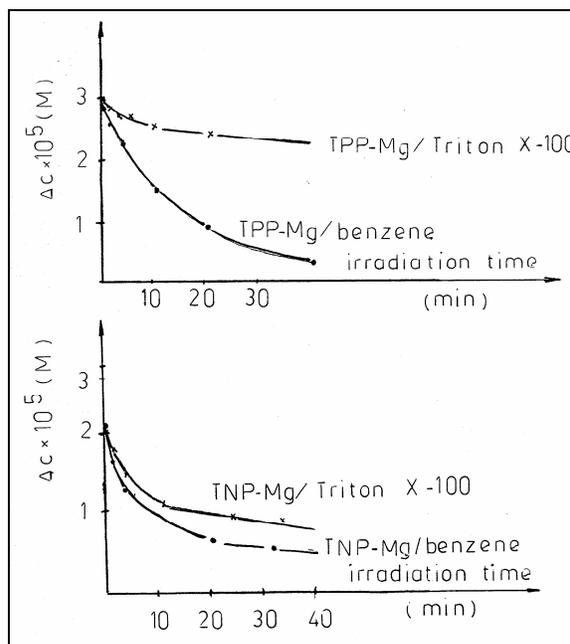


Figure 9. The fluorescence decay curve of TPP-Mg and TNP-Mg in benzene and Triton X-100.

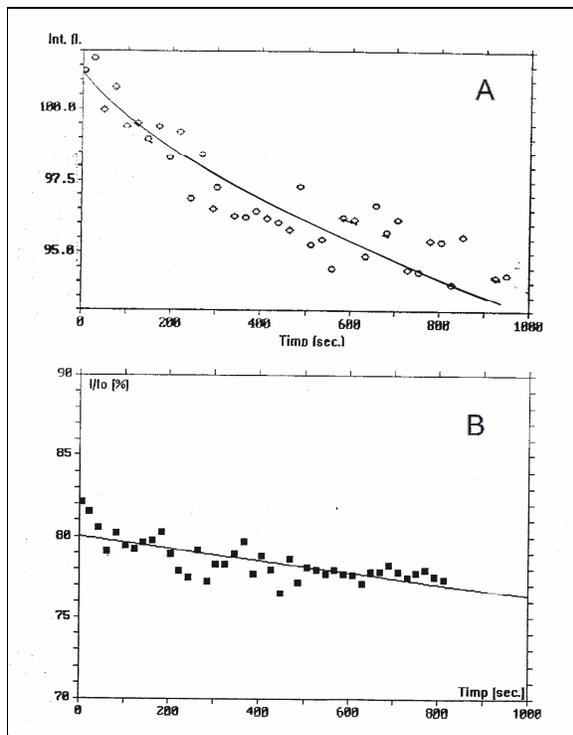


Figure 10. The fluorescence quenching of TPP-Mg in benzene (A) and Triton X-100 (B)

The dimension of the neutral micelle is limited by the equilibrium of the attraction forces between the polar parts and those of repulsion of the terminal groups. These forces are of course modified by the entering porphyrin so that one of our purposes was to determine to what extent these forces are modified and also what implications it has for the geometry of the whole aggregate. While the ionic micelles have an aggregation of 10-100 parent molecules due to the strong electrostatic repulsion between the ionic terminal groups, in case of a neutral micelle this number is far larger due to the weak repulsion between the ionic terminal groups. For Triton X 100 the critical concentration is 2.7×10^{-4} M. Above this concentration the porphyrins and micelles are coexisting in dynamic equilibrium. Also this characteristic parameter of the micelle, which is the critical concentration, could be modified by the presence of the porphyrin and its concentration [19].

Although older studies sustain the theory of spherical micelles in which the hydrocarbon chain is oriented to the center of the micelle and the OH groups to the exterior in a radial structure, recent studies predict for the micelle a structure of an ellipsoid of revolution. Also, from geometrical considerations, two possibilities can occur, i.e. the case of an oblate ellipsoid or that of a prolate ellipsoid. The model of an oblate ellipsoid is supported by energetically considerations, although the second model can't be neglected as being that of a host molecule for the porphyrin [20].

Concerning to the changes which could occur at the spectra of metallo-porphyrins in organic solvents

compared to that in micellar solution, upon irradiation the micelle act as a protecting shield around the porphyrin.

In the metallo-porphyrins series, could be observed the following order of the photodegradation reaction rate: $Mg > Zn > Cd$, the same with the singlet oxygen quantum efficiency order.

As a general rule, the fluorescence decay of all the porphyrins is adequately fitted to a single exponential function, Figure 10. This has been the general behavior of nearly all planar fluorescent probe molecules in pure solvents.

IV. CONCLUSIONS

This paper is deals with some aspects about the photodegradation kinetic of some metallo-porphyrins in benzene and micellar solutions. The studied porphyrins (metal complexes with Mg, Zn and Cd of 5,10,15,20-tetraphenylporphyrin, TPP and 5,10,15,20-tetranaphthylporphyrin, TNP), due to the molecular dimensions permit their enclosure inside of the micelle, yielding to the photostabilization of these porphyrins. The stability of the micelle is not affected by the presence of the porphyrin, while the photostability of all these porphyrins are significantly increased.

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Table 1. The electronic spectrum of the metallo-porphyrins in benzene and micellar media

Compound	Medium	λ [nm]/ ϵ [M ⁻¹ cm ⁻¹]
TPP-Cd	benzene	432/343241; 574/17910; 618/9247
TNP-Cd		423/437000; 575/18661; 606/10786
TPP-Zn		418/462300; 549/23300; 600/12700
TNP-Zn		422/391000; 548/32000; 604/17400
TPP-Mg		425/594000; 564/19600; 604/11100
TNP-Mg		426/608000; 561/24700; 602/12900
	micellar solutions	
TPP-Cd		425/318000; 582/23000; 600/30000
TPP-Cd		429/340000; 585/20000; 615/28000
TPP-Zn		430/300000; 565/16000; 592/8000
TNP-Zn		438/350000; 595/13400; 630/6890
TPP-Mg		430/600000; 570/20000; 610/10000
TNP-Mg		432/560000; 578/19000; 613/9000