

**SOLVENT EXTRACTION OF ZINC(II) AND MANGANESE(II)
WITH 5,10,15,20-TETRAPHENYL-21H,23H-PORPHINE (TPP)
THROUGH THE METAL EXCHANGE REACTION OF
LEAD(II)-TPP**

إستخلاص الزنك Zn(II) و المنجنيز Mn(II) باستخدام 5,10,15,20 - تترافينيل بروفين (TPP) عن طريق التبادل الأيوني في وجود ايون الرصاص الذي يعمل كعامل مساعد

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المخلص:

في هذا العمل تم دراسة إستخلاص كلا من الزنك Zn(II) و المنجنيز Mn(II) باستخدام البروفيرين وذلك في وجود ايونات الرصاص . وقد اوضحت النتائج أن نسبة الإستخلاص لا تعتمد على تركيز ايونات الرصاص Pb(II) في الوسط المائي مما يدل على أن تأثير ايونات الرصاص Pb(II) يكون كعامل مساعد فقط لتسريع عملية الإستخلاص.

ABSTRACT

An investigation was carried out on the extraction of aqueous Zn(II) and Mn(II) with a hydrophobic porphyrin (5,10,15,20-tetraphenyl-21H,23H-porphine, TPP) through a metal exchange reaction of Pb(II)-TPP. The distribution ratios (D) of these metals were found to be independent of the Pb(II) concentration in the aqueous phase. Pb(II) in the aqueous phase acted as a catalyst which promoted the metal-TPP complexation.

KEYWORDS: Zn(II); Mn(II); TPP; metal exchange; Pb(II)

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1. INTRODUCTION

A variety of porphyrins have been prepared and used as complexing agents with trace metals in analytical chemistry[1-3]. Their characteristic Soret bands enable determination of pertinent metal ions spectrophotometrically at levels as low as 10^{-7} mol dm⁻³. As porphyrins are macrocyclic ligands with four nitrogen donors in their ring structure, metal ions can be coordinated by these nitrogen atoms. In order to overcome the slowness of metal-porphyrin complexation, kinetics in various metal-porphyrin systems have been investigated [4-7].

A general trend in the complexation and metal exchange reaction of porphyrin complexes was found with respect to the metal ion size, i.e., large metal ions such as mercury(II), cadmium(II) and lead(II) accelerate the incorporation of small ions like manganese(II), copper(II) and zinc(II) etc. into the porphyrin ring[8-12].

Such porphyrin complexation behavior would allow development of entirely new extraction systems. There have been only a few studies concerning porphyrin compounds as extraction reagents for metal ions [13].

In this work the possibility of using a hydrophobic porphyrin (5,10,15,20-tetraphenyl-21H,23H-porphine, TPP) as an extraction reagent for divalent metal ions Mn and Zn in the presence of Pb will be carried out.

2. EXPERIMENTAL

2.1 Reagents and Solutions

5,10,15,20-Tetraphenyl-21H,23H-porphine (TPP) (M.Wt. = 614 g/mole) was obtained from Tokyo Kasei Co. Ltd. (Japan). All the reagents used in this study were purchased from Wako Pure Chemical Industry Co. Ltd. (Japan) and were of analytical reagent grade. Pb, Zn and Mn are in the form of

chlorides purity of 99.90 % for both. A TPP standard solution (1.31×10^{-2} M) 500 cm³ in volume was prepared by dissolving TPP (4.0205 g) in chloroform.

2.2 Apparatus

pH of the aqueous Solution was measured with a Horiba D-22 pH meter (Horiba Co.Ltd., Japan). Concentration of Pb, Zn and Mn in the aqueous phase before and after the extraction was measured by Perken Elemer AAS.

2.3 Procedure

The TPP concentration of the organic phase was varied as shown under each figure. In the aqueous phase, concentrations of both Zn(II) and Mn(II) were kept constant (mainly 2.42×10^{-5} M and 4.84×10^{-5} M). The initial Pb(II) concentration of the aqueous phase was adjusted to $0 \sim 1.94 \times 10^{-4}$ M. Acidity of the aqueous phase was adjusted with several pH buffer solutions which

contained either potassium dihydrogenphosphate and disodium hydrogenphosphate or sodium tetraborate and sodium hydroxide (or nitric acid) depending on the required pH value.

A mixture of aqueous and organic (chloroform) phases (10 ml each) was shaken vigorously in a glass vial with a mechanical shaker for one hour at room temperature to reach equilibrium. Phase separation was carried out. The concentration of Pb(II), Zn(II) and Mn(II) in the aqueous phase was measured. Concentration of Zn(II) and Mn(II) in the organic phase was calculated by difference. Distribution ratios (D) of Zn(II) and Mn(II) were then calculated by the standard method.

3. RESULTS AND DISCUSSION

In the present extraction system, metalloporphyrin complexation occurs in the aqueous phase into which TPP is transferred from the organic phase. Chloroform was used

for the organic phase because of its high solubility in the aqueous phase. The high solubility is thought to be an advantage in metalloporphyrin formation. In the aqueous phase Pb(II) was present prior to the metalloporphyrin formation in order to accelerate the complexation reaction.

Fig.1 shows the distribution ratio of Mn(II) and Zn(II) as a function of aqueous pH ($5.0 < \text{pH} < 12.0$). The distribution ratios (D) of Mn(II) and Zn(II) were affected by the pH value of the aqueous phase. D values increased with increasing pH up to pH at 10.0. The amount of Pb(II)-TPP formed in the solution depends on the aqueous pH. A high pH (pH \approx 10) would be preferable for Pb(II)-TPP complexation[14], whereas most metals in aqueous phase at this pH exist in the form of hydroxides. The catalytic effect of Pb(II) on the Zn(II)-TPP and Mn(II)-TPP complexation reaction may be more effective at high pH. Considering that almost all the metals exists as

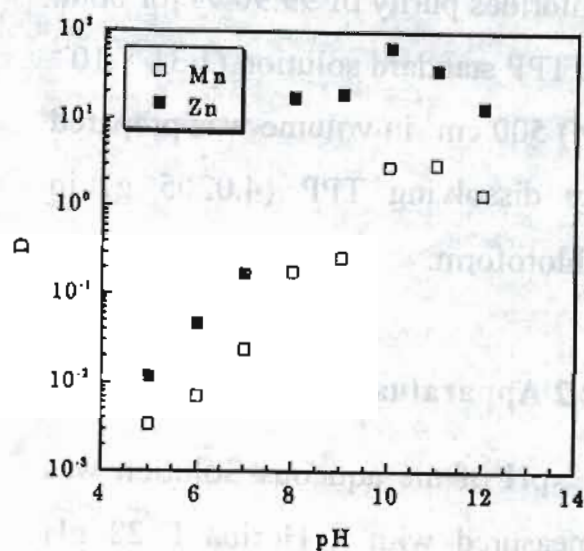


Fig. 1. Effect of pH on the extraction of Mn(II) and Zn(II) with TPP in the presence of Pb(II): $[\text{TPP}]_{\text{T}} = 2.93 \times 10^{-2} \text{ M}$; $[\text{Pb(II)}] = 5.89 \times 10^{-5} \text{ M}$; $[\text{Mn(II)}] = 4.84 \times 10^{-5} \text{ M}$, $[\text{Zn(II)}] = 2.42 \times 10^{-5} \text{ M}$

free ions at $\text{pH} < 6.0$ [15], the aqueous pH was set to be 6.0 in the subsequent investigations.

Fig. 2 shows the effect of TPP concentration on the distribution ratios of Mn(II) and Zn(II), in which TPP in the organic phase was varied from 5.24×10^{-3} to $2.93 \times 10^{-2} \text{ M}$. It is clear that Zn(II) D values were about one order of magnitude higher than those of Mn(II) at each TPP concentration. Such a difference in the distribution ratios between Zn(II) and Mn(II) is in agreement with the

general trend of stability constants of porphyrine complexes (...Zn(II)>Mn(II)>....»Pb(II)) [16]. In both cases, the plots of $\log D$ versus $\log[TPP]$ were almost linear with a slope close to 1. This means that the metal ion extracted with TPP would be in the form of a 1 to 1 complex (M-TPP).

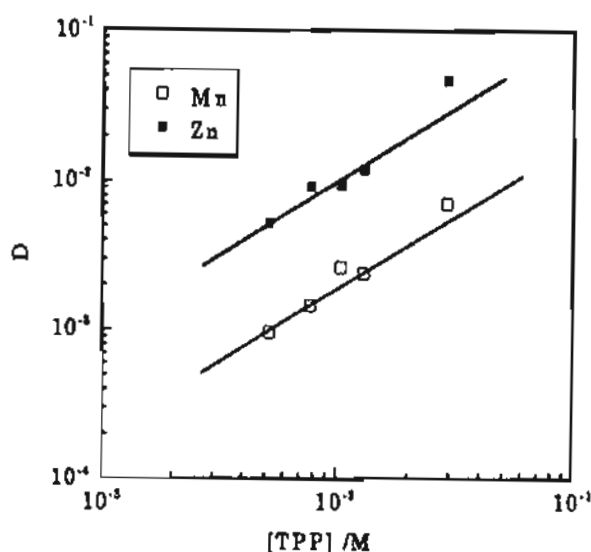


Fig. 2. Relationship between $\log D$ vs. $\log[TPP]$ for the Mn(II) and Zn(II) extraction with TPP pH6.0; $[Pb(II)]=5.89 \times 10^{-5} M$; $[Mn(II)]=4.84 \times 10^{-5} M$, $[Zn(II)]=2.42 \times 10^{-5} M$; $[TPP]=5.24 \times 10^{-3} \sim 2.93 \times 10^{-2} M$

Figure 3 shows the effect of Pb(II) added to the aqueous phase on the extraction of Mn(II) and Zn(II) with TPP. The results show that the D values of both Mn(II) and Zn(II)

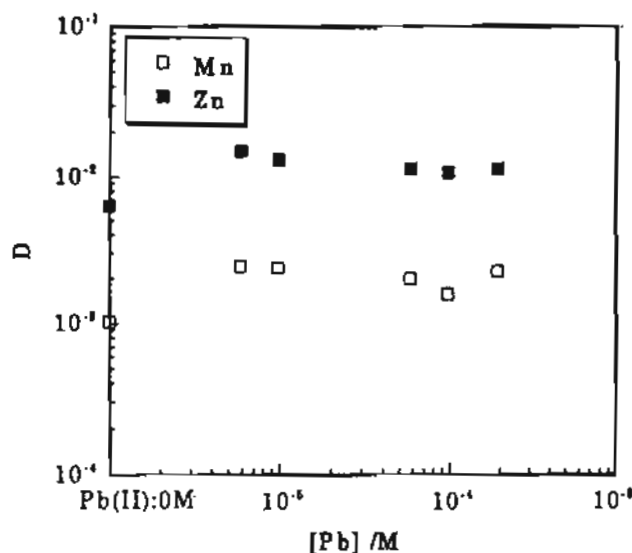
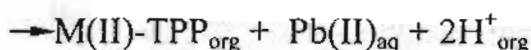
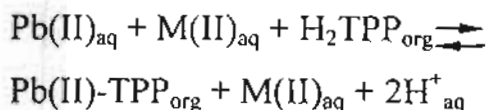


Fig.3. Effect of aqueous Pb(II) concentration on the extraction of Mn(II) and Zn(II) with TPP pH6.0; $[Mn(II)]=4.84 \times 10^{-5} M$, $[Zn(II)]=2.42 \times 10^{-5} M$; $[Pb(II)]=5.93 \times 10^{-6} \sim 1.94 \times 10^{-4} M$; $[TPP]=1.30 \times 10^{-2} M$

were almost constant and independent of the amount of Pb(II) present in the aqueous phase. The results suggest that Pb(II) in the aqueous phase would work as a catalyst on the TPP extraction, i.e., Pb(II) accelerates the complexation of Mn(II) and Zn(II) with TPP, but does not influence the equilibrium state of the system. If so, the metal exchange reaction must occur between (Mn(II) & Zn(II)) and Pb(II)-TPP. And the products, Mn(II)-TPP and also Zn(II)-TPP, are then to be extracted into the organic

phase. The extraction reaction probably occurring in the present solution system are summarized as follows:



Where, M is metal ions Zn(II) or Mn(II)

Figure 3 also shows that both Mn(II) and Zn(II) were extracted to a certain degree in the absence of Pb(II) in the aqueous phase when the mixture was kept standing for 24 hours. However, the D values of both metals were small compared to those obtained after 1 hour of standing in the presence of Pb(II), which was explained by the slow complexation of Mn(II)- and Zn(II)-TPP under the present experimental conditions [17]. The results also support the catalytic effect of Pb(II) on the metalloporphyrin complexation.

4. CONCLUSION

Solvent extraction of Zn(II) and Mn(II) was carried out with 5,10,15,20-tetraphenyl-21H,23H-porphine (TPP) as a complexing agent through the metal exchange reaction with Pb(II)-TPP. The distribution ratio of both metals depends on aqueous pH and the difference in the ratios is consistent with the general trend of the stability constants of porphyrine complexes. The extracted species was estimated to be Mn(II)-TPP (or Zn(II)-TPP) which was formed through the metal exchange of Mn(II) (or Zn(II)) with Pb(II)-TPP. In the absence of Pb(II), it took more than 24 hours for the metalloporphyrin extraction to achieve equilibrium. It was thus considered that Pb(II) in the aqueous phase works as a catalyst which accelerates the complexation of Mn(II) and Zn(II) with TPP. The distribution ratio of both metals was not so large compared with other extraction reagents such as 6-diketones which had been

investigated so far. However, the results of the present study suggest the possibility of developing new extraction systems with porphyrins by using their characteristic metal exchange reactions. The hydrophobic porphyrin, TPP, used in this study is one of the most simple porphyrin compounds. It is also possible to establish new extraction systems with other porphyrins and macrocyclic ligands such as pentaphyrins.

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