

# Liquid Extraction of Zinc and Nickel Ions Using a Cryptand-like Calix[4]-arene Derivative

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The liquid-liquid extraction of Zn(II) and Ni(II) ions in aqueous solution by a cryptand-like calix[4]arene derivative as extractant in chloroform was studied. The extraction efficiency was investigated by means of flame atomic absorption spectrophotometry. The extraction behavior of the metal ions was closely related to the pH at equilibrium and the matrix of the aqueous solution. The results showed that the calix[4]arene derivative was able to extract 80-94 % of 1 mg/L Zn(II) at the pH range of 8-12 and more than 98 % of 1 mg/L Ni(II) at the pH range of 6-12. The ionic strength ( $I=0.001-0.1$ ) of the solutions had no significant effect on the extraction of the Ni(II) ion, but it had a slight effect on the Zn(II) ion.

**Key words:** Liquid-Liquid Extraction, Zinc, Nickel and Calix[4]arene.

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## การสกัดไอออนสังกะสีและนิกเกิลด้วยของเหลวโดยใช้อนุพันธ์ ของคาลิกซ์[4]เอรีนที่มีลักษณะคล้ายคริปแทนด์

อภิชาติ อิ่มยิ้ม สุชน ดีจึงวิภาต และ ธวัชชัย ต้นทุลانی (2548)

วารสารวิจัยวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย 30(1)

ทำการศึกษาการสกัดไอออนของโลหะสังกะสี(II) และนิกเกิล(II) ในสารละลายเอเคเวียสโดยใช้สารละลายของอนุพันธ์ของคาลิกซ์[4]เอรีนที่มีลักษณะคล้ายคริปแทนด์ในคลอโรฟอร์มเป็นตัวสกัด ประสิทธิภาพในการสกัดศึกษาด้วยเทคนิคอะตอมมิกแอบซอร์ฟชันสเปกโทรโฟโตเมตรีแบบเปลวไฟ การสกัดของไอออนทั้งสองชนิดขึ้นกับค่าพีเอชที่สมดุลและเมทริกซ์ของสารละลายเอเคเวียส ผลการทดลองแสดงให้เห็นว่าอนุพันธ์ของคาลิกซ์[4]เอรีนที่ใช้สามารถสกัดสังกะสี(II) เข้มข้น 1 mg/L ได้ 80-94 % โดยค่าพีเอชที่เหมาะสมอยู่ในช่วง 8-12 และสามารถสกัดนิกเกิล(II) เข้มข้น 1 mg/L ในน้ำได้มากกว่า 98% ที่ค่าพีเอช 6-12 ความแรงไอออนในสารละลาย ( $I=0.001-0.1$ ) ไม่มีผลต่อการสกัดไอออนของนิกเกิล(II) อย่างมีนัยสำคัญ แต่มีผลต่อการสกัดไอออนของสังกะสี(II) เพียงเล็กน้อย

**คำสำคัญ** การสกัดด้วยของเหลว สังกะสี นิกเกิล และ คาลิกซ์[4]เอรีน



## INTRODUCTION

Liquid-liquid extraction (LLE) or solvent extraction is based on differences in the solubilities of elements and their compounds in two immiscible liquid media. The method is usually used to remove metals from an aqueous solution. This requires organic solvents immiscible with water and appropriate ligands or complexing agents to form metal complexes. Since LLE is a fast and simple process, which demands only very simple equipment, it is very useful for a wide range of applications such as separation, preconcentration or enrichment of heavy metals prior to determination by an appropriate analytical technique; for example, AAS and ICP-OES.<sup>(1-3)</sup>

Derivatives of calix[4]arene recently have been used for metal chelating agents.<sup>(4)</sup> Because of the high selectivity and high stability of these complexes, they have become an alternative to conventional extractants for separation of metal ions.<sup>(4-6)</sup> However, solvent extraction of transition and toxic metal ions has been less studied in comparison to alkali and alkaline earth metals extraction. This study has extended the procedure to separate transition metals from aqueous solution.<sup>(4,5)</sup> To date, all studies have focused on the extraction from aqueous solutions and water samples using a single batch solvent extraction.<sup>(7-9)</sup> Cryptand-like calix[4]arene derivatives containing nitrogen donors with their binding ability towards Co(II), Ni(II), Cu(II), and Zn(II) have been reported by Tuntulani *et al.*<sup>(10)</sup> The investigation of the extraction behavior of the ligand for metal ions in aqueous solution will be very useful for future applications; i.e. LLE, ion-selected electrode development,<sup>(11)</sup> liquid membrane extraction,<sup>(12)</sup> and hollow-fiber membrane extraction.<sup>(13)</sup>

This study aims to develop a new LLE procedure to extract toxic transition metals including Zn(II) and Ni(II) from an aqueous solution using a cryptand-like calix[4]arene derivative and chloroform as extractant. In this study, extraction of single metal ion species from model solutions has been carried out. The extraction efficiency under different conditions of pH and the ionic strength was studied.

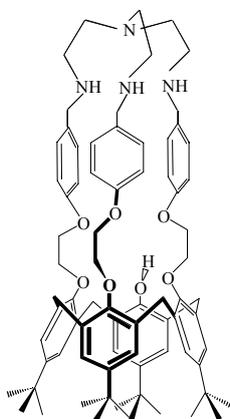
## MATERIALS AND METHOD

### Materials

The selected chelating agent was 25,26,27-N,N',N''-tris((4-ethoxy)benzyl)ethylene tetraamine-*p-tert*-butylcalix[4]arene (Figure 1). It was synthesized and purified by the Supramolecular Chemistry Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University.

All reagents and solvents were standard analytical grade, purchased from Carlo BDH, Fluka, and Merck, and used without further purification. Deionised (DI) water was obtained from the purification via cation and anion exchange resin columns, the conductivity of the DI water was less than 18  $\mu\text{S}/\text{cm}$ .

Borosilicate glassware and HDPE plasticware were cleaned by the following procedure: rinsed with tap water, washed by a detergent, rinsed with tap water, rinsed with DI water, immersed in 2 % v/v nitric acid solution for 12 hours, rinsed with abundant DI water, air-dried in ambient temperature, and stored in closed polyethylene boxes.



**Figure 1.** 25,26,27-N,N',N''-tris((4-ethoxy)benzyl)ethylenetetraamine-*p-tert*-butylcalix[4]-arene ( $\text{C}_{77}\text{H}_{98}\text{O}_7\text{N}_4$ , 1191.65 g/mol).

### Extraction Method

The solutions used for the batch liquid-liquid extractions were prepared as follows :  $10^{-3}$  mol of the ligand was dissolved in 100 mL of chloroform in a 100 mL volumetric flask to give a stock solution of  $10^{-2}$  M. Five millilitres of the stock solution was pipetted and quantitatively diluted with chloroform in a 500 mL volumetric flask to give a  $10^{-4}$  M solution. The model solutions of Zn(II) were prepared by diluting a 1000 mg/L stock nitrate solution to 1 mg/L with DI water, 0.001 M, 0.01 M, and 0.1 M  $\text{KNO}_3$ . The desired pH of the model solutions was adjusted by 1 %w/v KOH and 1 %v/v  $\text{HNO}_3$ . The Ni(II) model solutions were prepared in the same manner. The solutions were freshly prepared daily.

### Influence of pH on extraction efficiency

Ten different pH model solutions ranging from pH 3-12 were prepared by adjusting the pH with 1 %w/v KOH and 1 %v/v  $\text{HNO}_3$  in a beaker before transferring and making an exact volume in a volumetric flask with DI water. Equal volumes of each phase (10 mL) were mixed in an extraction bottle and carefully shaken for 2 hours and left for phase separation for 30 minutes at 25°C. Three replicates of each batch were prepared. The blank extractions were performed at the same time using the same procedure with the model solution and pure chloroform. Nine millilitres of the aqueous phase was taken, the pH value was measured and then acidified to  $\text{pH} \leq 2$  by 65%  $\text{HNO}_3$ . The metal concentration was compared to that of the blank extraction.

### Influence of ionic strength on extraction efficiency

Six different pH model solutions ranging from pH 7-12 were prepared by adjusting the pH

with 1 %w/v KOH and 1 %v/v  $\text{HNO}_3$  in a beaker before transferring and making an exact volume in a volumetric flask with 0.001 M, 0.01 M, and 0.1 M  $\text{KNO}_3$ . The extraction procedure was performed in the same procedure as before. Three replicates of each batch were performed.

### Metal concentration determination

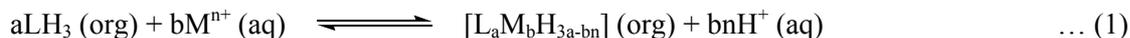
Final blank and working concentrations ( $C_0$  and  $C_{aq}$ ) of the metals were measured (3 replicates) on a Perkin Elmer AAnalyst-100 Atomic Absorption Spectrophotometer, at analytical wavelengths ; Zn 213.9 nm and Ni 232.0 nm. The external standard calibration was used with the limit of detection equal to 0.01 and 0.02 mg/L for Zn and Ni respectively.

## RESULTS AND DISCUSSION

### Influence of pH on extraction efficiency

It has been reported that pH has a strong influence on the percent extraction of metal ions.<sup>(8,9,11,14-16)</sup> Herein, to investigate the effect of pH on extraction efficiency of Zn(II) and Ni(II) ions from aqueous solution by the cryptand-like calix[4]arene dervative, pHs of the initial solutions were varied from 3 to 12. The mole ratio of metal to ligand is 1:10. This ratio was chosen to ensure an excess amount of the ligand. After extraction, each unbuffered aqueous solution was separated, the pH value was measured, and the metal concentration was determined. Figure 4 shows the pH values before and after extraction of the metal ions. It is obvious that the pH of the aqueous solutions remarkably decreases after extraction.

The LLE of metal ion ( $\text{M}^{2+}$ ) in the presence of the protonated complexing agent ( $\text{LH}_3$ ) can be represented as a proton-cation exchange process:<sup>(9)</sup>



Which gives:

$$\log D_M = \log K_M + a \log[\text{LH}_3] + bn \text{pH} \quad \dots (2)$$

where  $D_M$  is a distribution coefficient given by the ratio of metal concentration in the organic and in the aqueous phases, and  $K_M$  is a thermodynamic extraction equilibrium constant. The slope of the curve  $\log D_M$  versus the pH

gives the number of protons exchanged (parameter  $bn$  in Eq. (2)). Figures 2 and 3 show the plot between  $\log D_M$  versus pH for zinc and nickel respectively. The slopes are about 1 for all cases.

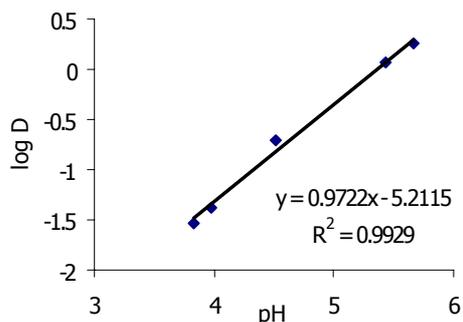


Figure 2. Extraction of 1 mg/L Zn(II) ion as a function of pH at equilibrium in DI water.

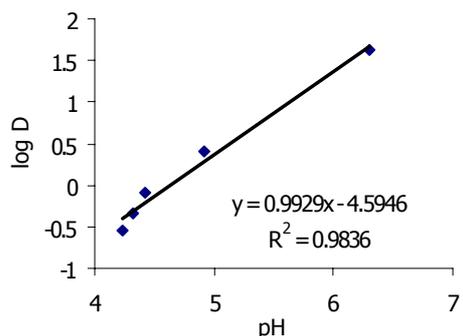


Figure 3. Extraction of 1 mg/L Ni(II) ion as a function of pH at equilibrium in DI water.

From the literature, the stoichiometry of metal-ligand was 1:1.<sup>(10)</sup> The decrement of pH values may be attributed to the exchange between ligand

protons and metal ions according to the following equation:

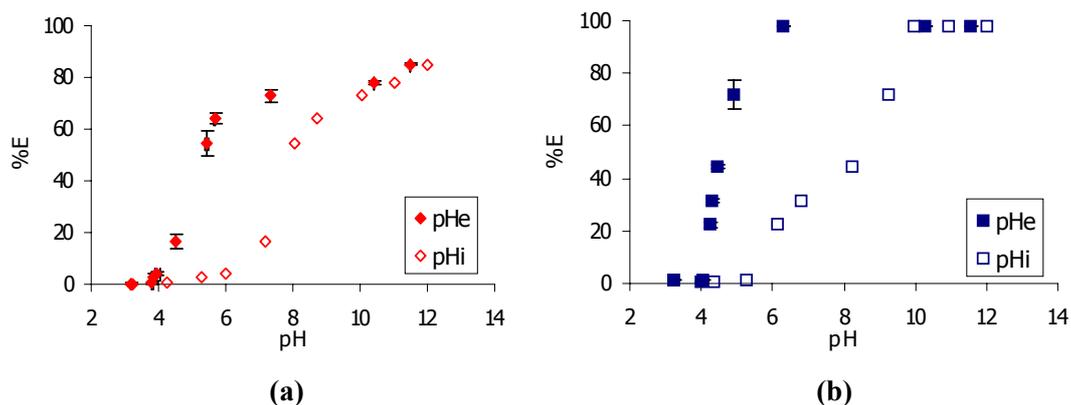


The percent extraction was calculated by the equation expressed as:

$$\%E = \frac{C_0 - C_{\text{aq}}}{C_0} \times 100 \quad \dots (4)$$

where  $C_0$  and  $C_{\text{aq}}$  are the final blank and working concentrations of metal ion in aqueous phase. The overall standard deviations (SD) of %E of three replicates were generally less than 5. The

average percent extractions (mean  $\pm$ SD,  $n=3$ ) of zinc and nickel ions versus initial pH and pH at equilibrium in the aqueous phase are illustrated in Figure 4.



**Figure 4. Relationship between the percent extractions (%E) of (a) Zn(II) and (b) Ni(II) ions and initial pH (pHi) and pH at equilibrium (pHe) in aqueous solution.**

From Figure 4, it can be seen that changes in initial pH affect the percent extraction of both metal ions. In the acidic region, with the  $\text{pH} \leq 5$ , neither metal ion could be extracted. This extraction behavior may be attributed to the hypothesis that in a high acidic medium ( $\text{pH} \leq 5$ ), the cryptand-like calix[4]arene derivative could be protonated on nitrogen atoms. This resulted in a positive charge on the ligand, which could not coordinate the positive metal ions. The percent extraction of zinc increased quantitatively with increasing initial pH in the range of 6–12 while the percent extraction of nickel increased in the pH range of 5–10. Zinc shows maximum percent extraction (85%) with the pH 12. Nickel shows maximum percent extraction (>98%) in the initial pH above 10. In basic solution, the ligand is neutral or slightly negatively charged resulting in an affinity to Zn(II) and Ni(II) ions.

#### **Influence of ionic strength on extraction efficiency**

The influence of ionic strength ( $I$ ) on the percent extraction of metal ions has been reported.<sup>(9,10,14)</sup> The effect of ionic strength on

extraction efficiency ions was investigated by using 0.001 M ( $I = 0.001$ ), 0.01 M  $\text{KNO}_3$  ( $I = 0.01$ ), and 0.1 M  $\text{KNO}_3$  ( $I = 0.1$ ) at different pH values ranging from 7–12. The pH values before and after extraction of the metal ions were measured, and the decrease of pH values was observed. The relationship between the average percent extractions (mean  $\pm$ SD,  $n=3$ ) of Zn(II) and Ni(II) in different ionic strength solutions and pH values is shown in Figures 5 and 6, respectively. The SD values were less than 5. From Figure 5, the percent extractions of Zn(II) in 0.1 M and 0.01 M  $\text{KNO}_3$  were higher than that of DI water and 0.001 M  $\text{KNO}_3$  in the pH range of 7–12. This can be explained by the salting out effect. The highest percent extraction (94%) for Zn(II) was found at pH 9.3. The percent extraction decreased slightly when pH increased from 9 to 12, probably due to the formation of negatively charged zinc hydroxide complex,  $[\text{Zn}(\text{OH})_3]^-$ . Regarding Figure 6, the percent extractions of Ni(II) was almost unchanged at different ionic strengths, thus ionic strength hardly affects the extraction efficiency in this case.

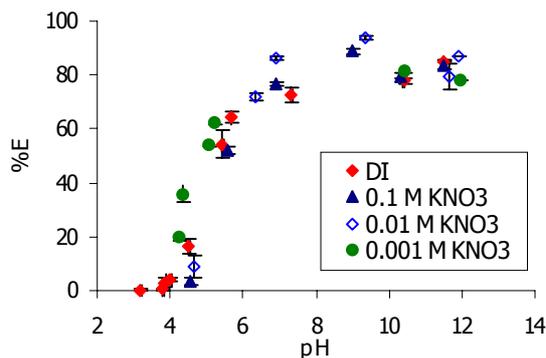


Figure 5. Relationship between the average percent extractions (%E) of Zn(II) in DI water, 0.001 M, 0.01 M, and 0.1 M KNO<sub>3</sub> and pH values at equilibrium in aqueous solution.

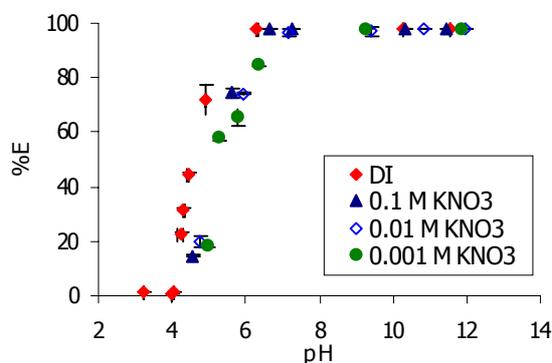


Figure 6. Relationship between the average percent extractions (%E) of Ni(II) in DI water, 0.001 M, 0.01 M, and 0.1 M KNO<sub>3</sub> and pH values at equilibrium in aqueous solution.

## CONCLUSIONS

Using a cryptand-like calix[4]arene derivative as an extractant in chloroform, Zn(II) and Ni(II) ions can be extracted from aqueous solution. The percent extractions of both ions were about 94% at equilibrium pH 9 and 98% at equilibrium pH 6-12. The pH showed a remarkable increase on the extraction efficiency, while the ionic strength only had slight effect for the Zn(II) ion and no effect on the Ni(II) ion.

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