Synthesis of Dithia Diaza Calix[4]arene Derivative and Its Extraction Properties towards Zn^{2+}, Ni^{2+}, Cu^{2+} and Cr^{3+}

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ABSTRACT: In this work, a novel cation receptor of dithia diaza calix[4]arene derivative was synthesized and used to study its extraction properties on Zn^{2+}, Ni^{2+}, Cu^{2+} and Cr^{3+} from an aqueous nitrate medium into a chloroform layer. The influence of extraction parameters such as pH and extractant concentration was studied in order to determine the optimal conditions for extractions. The results showed that the extraction order was $Zn^{2+} > Ni^{2+} > Cu^{2+} > Cr^{3+}$ and the extracted species at a 1:1 ratio were obtained for Zn^{2+}, Ni^{2+} and Cu^{2+} at pH 10.2.

Key words: calixarene, extraction, cation, receptor

INTRODUCTION

A rapid growth in industry often results in a corresponding increase in the production of waste some of which may contain heavy metals such as Pb^{2+}, Cd^{2+} and Hg^{2+}. A solvent extraction system is one among many techniques used for metal removal. It is a method for extracting heavy metal for various purposes. For example; sample preparation of an incompatible matrix to a suitable matrix(1); for the hydrometallurgical processing of copper, nickel, cobalt, zinc, uranium, molybdenum, tungsten, vanadium, rare earths, zirconium, hafnium, niobium, tantalum, indium, gallium, germanium, the platinum group metals and boron; reprocessing nuclear fuels; purification of wet process phosphoric acid; nitric acid recovery and other uses.(2) Because this technique is very easy and doesn't require any complicated instruments, solvent extraction is an interesting technique to develop further. The calixarenes are particularly attractive molecules because they have two chemically distinct rims that can be selectivity modified to incorporate any desired properties(3) and they also have a high degree of preorganization.(4) They are widely used as extractants for metal ions in solvent extraction. The modification of the upper rim of calixarene with various functional groups bearing N and S donor atoms can greatly improve the molecular recognition of calixarene to the heavy metal ions.(3) Selectivity of the extractant is a key point in the design of a new molecule based on not only hard/soft acid-base theory, but also on the geometry of the molecule +as described by R. Seangprasertkij *et al.*(5) They studied the binding efficiencies of calix[4]arene containing Shiff's base group by solvent extraction of metal picrates into dichloromethane under neutral conditions. Pb^{2+}, Fe^{2+} and Cu^{2+} ions were extracted most efficiently. D. Isabelle *et al.*(6) also showed a good affinity and selectivity of β-ketoimine calix[4]arene towards $Pb^{2+}$and the best efficiency for the extraction of Cu^{2+} and Ag^{+} belonged to the homologous thiacalix[4]arene derivatives.

In this work, we report the synthesis and characterization of a novel extractant based on calix[4]arene containing N and S donor atoms (Scheme 1) and its extraction properties for some heavy metals from aqueous solution into chloroform.

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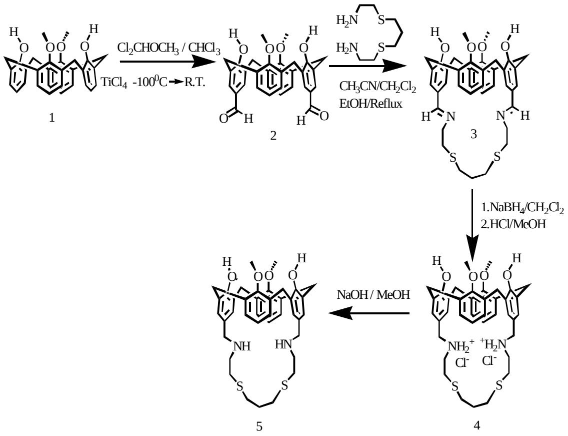

Scheme 1. Synthetic pathway of dithia diaza calix[4] arene containing N and S donor atoms (compound 5).

EXPERIMENTS

Reagents and analytical procedures

All solvents and chemicals were of analytical grade and used without further purification. Commercial grade solvents such as dichloromethane and methanol were distilled and stored over 4 Å molecular sieve. Reagents were purchased from Merck, J. T. Baker or Fulka. The stock solutions of metal ions (concentration 1,000 mg/l) were obtained from BDH and used as received. ^{1}H-NMR spectra were obtained on a Bruker ACF 200 or 400 MHz instruments. Elemental analyses were carried out on a Perkin Elmer Elemental Analyser 2400 CHN at the Scientific and Technological Research Equipment Center of Chulalongkorn University. A flame atomic absorption spectrometer, PE100 Perkin Elmer equipped with air-acetylene flame, was used for metal ion determination. The wavelengths used for Zn, Ni, Cu and Cr were 213.9, 232.0, 324.8, and 357.9 nm, respectively.

Synthetic procedures

Synthesis of diformyl dimethoxy calix[4]arene (compound 2)(7)

A 100 ml 2-necked, round-bottomed flask, containing dimethoxy calix[4]arene (0.54 g, 1.2 mmol) and dried chloroform (20 ml) was magnetically stirred at –10°C under nitrogen atmosphere for 20 min. 1,1-Dichlorodimethyl ether (2.4 ml, 26.5 mmol) and titanium(IV)chloride (1.5 ml, 13.6 mmol) were quickly added and the mixture was stirred for 1 hour at room temperature. To quench the reaction, 3 M HCl (100 ml) was added. The product was extracted by adding dichloromethane (200 ml). The organic phase was separated and dried over magnesium sulfate and filtered. After evaporating the organic solvent, the crude product was purified on a column chromatography (SiO_2) apparatus using dichloromethane as eluent. A white powder (0.36 g, 60%) was obtained.

^{1}H-NMR ($CDCl_3$, 200 Mz, δ (ppm)): 9.81 (s, 2H, ArC**H**O), 8.76 (s, 2H, ArO**H**), 7.66 (s, 4H, HOAr**H**), 6.92 (d, J_{H-H} = 7.6 Hz, 4H, *m*-Ar**H**OR), 6.78 (t, J_{H-H} = 7.6 Hz, 2H, *p*-Ar**H**OR), 4.30 and 3.53 (AB system, J_{H-H} = 13.6 Hz, 8H, ArC$\mathbf{H}_A\mathbf{H}_B$Ar and 4.03 (s, 6H, -OC$\mathbf{H}_3$)

Synthesis of Shiff base (compound 3)

A mixture of diformyl dimethoxy calix[4]arene (**compound 2**) (0.32 g, 0.6 mmol), dichloromethane (5.5 ml), ethanol (28 ml) and acetonitrile (28 ml) in a 100 ml 2-necked round-bottomed flask, was refluxed under nitrogen atmosphere. A solution of 2-[3-(2-amino-ethylsulfanyl)-propylsulfanyl]-ethylamine (**compound 3**)(8) (0.13 g, 0.7 mmol) in dichloromethane (10 ml) was added slowly. The mixture was heated at reflux for 20 hours. The organic solvents were evaporated. A solid product was obtained.

Synthesis of dithia diaza calix[4]arene (compound 5)

Shiff base (**compound 3**) (0.10 g, 0.15 mmol) was dissolved in dichloromethane (20 ml). The mixture was stirred at room temperature for 20 min and sodium borohydride (0.10 g, 2.64 mmol) was added. The mixture was stirred under N_2 at room temperature for 20 hours. The reaction was quenched by addition of H_2O. The organic layer was washed with H_2O until the pH of the aqueous phase reached 7. The organic phase was acidified with HCl/MeOH (0.74% v/v). After evaporating of solvents, the **product 4** precipitated as a yellow solid (0.07 g, 70% yield). mp. = 239-240°C (decompose) ^{1}H-NMR (DMSO-d_6, 400 Mz, δ (ppm)) : 9.30 (s, 4H, RN$\mathbf{H}^+_2$R), 8.18 (s, 2H, ArO**H**), 7.36 (s, 4H, HOAr**H**), 7.03 (d, J_{H-H} = 7.6 Hz, 4H, *m*-Ar**H**OR), 6.74 (t, J_{H-H} = 6.8 Hz, 2H, *p*-Ar**H**OR), 4.16 (d, J_{H-H} = 12.0 Hz, 4H, ArCH$_A\mathbf{H}_B$Ar), 3.95 (s, 6H, -OC$\mathbf{H}_3$), 3.90 (s, 4H, ArC$\mathbf{H}_2$N-), 3.02 (br, 4H, NCH$_2$C$\mathbf{H}_2$S), 2.80 (br, 4H, NC$\mathbf{H}_2$CH$_2$S), 2.56 (br, 4H, SC$\mathbf{H}_2$CH$_2$C$\mathbf{H}_2$S) and 1.61 (br, 2H, SCH$_2$C$\mathbf{H}_2$CH$_2$S) *Anal Found* C, 59.66; H, 5.70; N, 3.37 *Calc. For* $C_{39}H_{48}N_2O_4S_2Cl_2.CH_2Cl_2$ C, 60.58; H, 6.70; N, 3.45

The **compound 4** dissolved in dichloromethane was deprotonated by using a solution of 1 g NaOH dissolved in MeOH (15 ml). The mixture was stirred for 2 hours. The organic layer was washed with water (3×30 ml). The organic layers were combined and dried with magnesium sulfate and filtered. The organic solvents were evaporated and the dithia diaza calix[4]arene **(compound 5)** was obtained as yellow-white solid mp. = 230-231°C (decompose) ^{1}H-NMR ($CDCl_3$, 400 Mz, δ (ppm)): 7.77 (s, 2H, ArO**H**), 7.02 (s, 4H, HOAr**H**), 6.88 (d, J_{H-H} = 7.6 Hz, 4H, *m*-r**H**OR), 6.72 (t, J_{H-H} = 7.4 Hz, 2H, *p*-Ar**H**OR), 4.27 and 3.38 (AB system, J_{H-H} = 13.2 Hz, 8H, ArC$\mathbf{H}_A\mathbf{H}_B$Ar), 3.93 (s, 6H, OC$\mathbf{H}_3$), 3.67 (s, 4H, ArC$\mathbf{H}_2$N-), 2.81 (t, J_{H-H} = 5.6 Hz, 4H, NC$\mathbf{H}_2$C$\mathbf{H}_2$S), 2.68 (t, J_{H-H} = 6.0 Hz, 4H, NHC$\mathbf{H}_2$R), 2.49 (s, 4H, $SCH_2CH_2CH_2S$) and 1.65 (br, RNHR (2H), $SCH_2CH_2CH_2S$ (2H))

Solvent extraction procedure

5 ml of a 10 mM KNO_3 aqueous phase containing Zn^{2+} (4 mg/l), Ni^{2+} (6 mg/l), Cu^{2+} (4 mg/l) or Cr^{3+} (10 mg/l) and 5 ml of dithia diaza calix[4]arene **(compound 5)** dissolved in chloroform (twice as much metal concentration (M) for the study of pH effect and medium effect) were magnetically stirred for 30 min, which was sufficient to reach equilibrium, at 25.0 ± 1.0°C.

The aqueous and organic phases were separated by Heraeus Christ medifuge. The pH was measured by Schott pH-meter CG 825 (reference electrode: Ag/AgCl). The metal in aliquots was determined by FAAS.

RESULTS AND DISCUSSION

Synthesis and characterization

The synthesis of dithia diaza calix[4]arene is illustrated on Scheme 1 starting from dimethoxy-calix[4]arene **(compound 1)** which was prepared as described in the literature.(9) The diformyl dimethoxy **(compound 2)** was synthesized via electrophilic aromatic substitution of **compound 1** and 1,1-dichloro dimethyl ether in the presence of titanium(IV) chloride as catalyst. The addition of 2-[3-(2-amino-ethylsulfanyl)-propylsulfanyl]-ethylamine dissolved in dichloromethane into a solution of **compound 2** (1:1 equiv.) gave a Schiff base **(compound 3)** in 88% yield. This Schiff base was reduced by 17.5 equiv. of $NaBH_4$ and the reduced product was then protonated by a solution of HCl in methanol (0.74% v/v) to give a more stable **product 4**. Moreover, the **compound 4** was deprotonated by a solution of NaOH in MeOH before using for metal extraction studies.

The **compounds 2, 4** and **5** were characterized by ^1H-NMR spectoscopy and elemental analysis. ^1H-NMR spectrum of **compound 2** shows a singlet signal at 9.81 ppm due to an aldehyde proton. After reduction and protonation of **compound 3**, the signal of R^+NH_2 was observed at 9.30 ppm. The cone conformation of calixarenes **compounds 2, 4** and **5** was confirmed by a pair of doublet signals due to methylene bridge protons (J≈13 Hz).

Solvent extraction studies of metal ions

Extraction of metal ions (Zn^{2+}, Ni^{2+}, Cu^{2+} or Cr^{3+}) from a 10 mM nitrate medium were carried out by magnetically stirring for 30 min. The effect of pH was studied to determine the optimal condition. As shown in Figure 1. % extraction of Zn^{2+}, Ni^{2+} and Cr^{3+} increased when pH increased. However, %extraction of Zn^{2+} and Cr^{3+} decreased when pH was about 10.2. On the other hand, % extraction of Cu^{2+} decreased when pH increased. This indicates that the formation of copper anion complex as $[Cu(OH)_4]^{2-}$ under basic condition might have occurred. The highest extraction efficiency for each metal were found under pH ranges: pH 9.2-10.0, pH 10.2-10.7, pH 7.5-7.8 and pH 10.2 for Zn^{2+}, Ni^{2+}, Cu^{2+} and Cr^{3+}, respectively. Moreover, it also showed the quantitative extraction of Ni^{2+} at pH ≥ 10.2. However, the pH of aqueous solutions after the extraction process decreased indicating that partial deprotonation of this compound had occurred. In order to control a constant pH, the extraction was carried out in a buffer medium ($NaHCO_3$-NaOH, pH 10.2) with and without nitrate ion. The results are shown in Figure 2. Extractions under buffer and buffer/KNO_3 solutions showed no different extraction efficiency. No extraction of Cr^{3+} was observed under this condition.

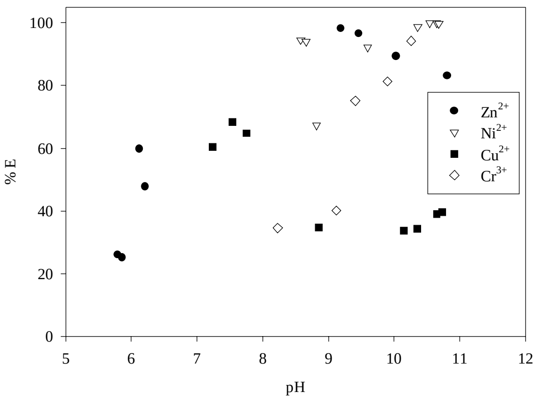

Figure 1. Effect of pH on metal ions extraction.

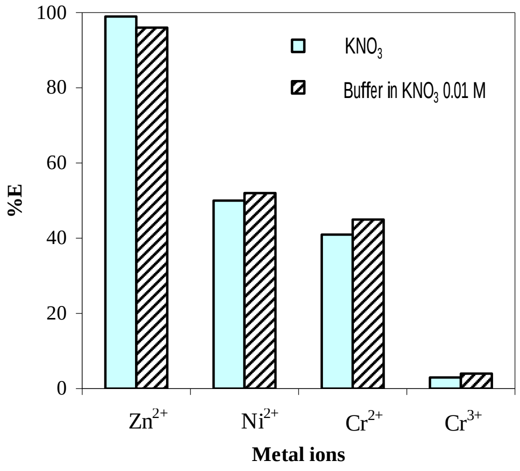

Figure 2. Effect of medium on metal ions extraction (n =3).

The extracted species was analyzed by using the classic slope analysis method. We considered the simple extraction equilibrium as follow:

$$e\,L_{org} + M^{n+} + n\,X^{-} \rightleftharpoons (ML_eX_n)_{org}$$

where L is extractant, M^{n+} is metal ion and X^- is counter anion.

The slope of e (plots of log D vs. log $[L]_{org}$ where D = $[(ML_eX_n)]_{org}$ / $[M^{n+}]$) indicates the stoichiometry of the extracted species. Extraction constant (log K'_{ex} where log K'_{ex} = log K_{ex} + n log $[X^-]$) can be calculated from intercept of the graph. Figure 3 represents the extraction of Zn^{2+}, Ni^{2+} and Cu^{2+} into chloroform at pH 10.2. The obtained slopes are close to 1 which indicate the extraction of species of 1:1 ratio. The results also show the extraction order under this optimal condition as follow: $Zn^{2+} > Ni^{2+} > Cu^{2+}$. Log K'_{ex} values were calculated from the experimental data and found to be log K'_{ex} = 4.40, 4.10 and 3.05 for Zn^{2+}, Ni^{2+} and Cu^{2+}, respectively.

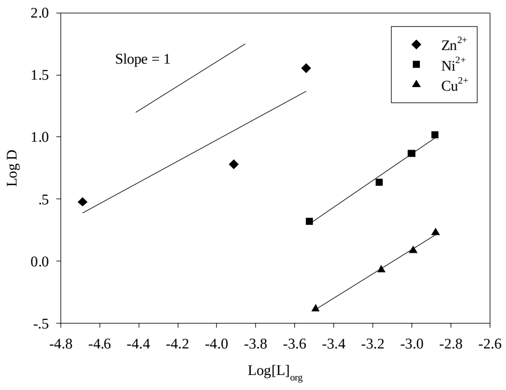

Figure 3. Extraction of Zn^{2+}, Ni^{2+}, Cu^{2+} from buffer medium ($NaHCO_3$-NaOH, pH 10.2) in 10 mM nitrate by compound 5 in chloroform at 25°C, n=3.

CONCLUSIONS

We have synthesized a novel calix[4]arene derivative containing N and S donor atoms and demonstrated its extraction potential towards Zn^{2+}, Ni^{2+}, Cu^{2+} and Cr^{3+} at pH 10.2 from an aqueous nitrate medium to chloroform. It was found that extraction order was $Zn^{2+} > Ni^{2+} > Cu^{2+} > Cr^{3+}$. The extracted species of 1:1 ratio was obtained for Zn^{2+}, Ni^{2+} and Cu^{2+}. Thus these results should be useful for further development for removal of Zn^{2+}, Ni^{2+} and Cu^{2+} from water sample or wastewater. It should also be useful for a preconcentration step in a spectrophotometric determination of such the metal ions.

ACKNOWLEDGMENT

The authors thank “Development Grants for New Faculty/Researchers”, Chulalongkorn University and “Senior Project Supporting Fund”, Faculty of Science, Chulalongkorn University for financial support.

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Received: January 23, 2006
Accepted: August 7, 2006