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Extraction of Soft Metals from Acidic Media with Nitrogen-Donor Ligand TPEN and its Analogs

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Abstract: Soft metals were extracted from acidic solution (pH 1 to 4) using two hydrophobic analogs of *N,N,N′,N′*-tetrakis[2-pyridyl-methyl]-1,2-ethylenediamine (TPEN). *N,N,N′,N′*-tetrakis[4-(2-butyloxy)-2-pyridyl-methyl]-1,2-ethylenediamine (TBPEN) and *N,N,N′,N′*-tetrakis(2-quinolinylmethyl)-1,2-ethylenediamine (TQEN) have shown enhanced extraction performance in more acidic media than TPEN. TBPEN showed enhanced extraction of Cd(II) from highly acidic solutions (pH < 2). This is because the distribution of this ligand to the aqueous phase is suppressed by the formation of a metal complex encapsulating Cd(II) with TBPEN. The percent extraction of Cd(II) for TBPEN was 100% at pH 1, whereas TPEN extracts less than 10% of the Cd(II) under these conditions. TBPEN also exhibited selective extraction of a variety of soft metals, such as Au(III), Pt(II), Pd(II), and Cd(II), from the acidic solution at pH 1. These results suggest that a hydrophobic TPEN analog combining alkyl chains to four pyridyl groups is applicable to the practical extraction process of soft metals.

Keywords: Acidic media, *N*-donor; Solvent extraction; TPEN

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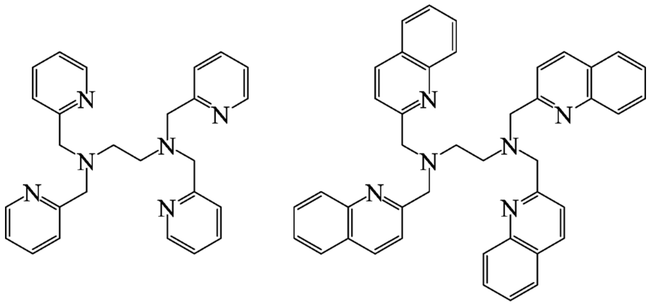
INTRODUCTION

N,*N*,*N*′,*N*′-tetrakis(2-pyridylmethyl)-1,2-ethylenediamine (TPEN) is a hexadentate ligand with six nitrogen donors, as shown Fig. 1 (a). It is well-known that soft metals, such as Hg, Cd, Au, and Pd, which are classified by Pearson's HSAB principle (1,2), are complexed selectively with a soft-donor ligand containing nitrogen or sulfur (3). Previously, TPEN was used as a masking agent in an aqueous solution. Jensen et al. studied the complex formation of Am(III) and Eu(III) with TPEN in an aqueous solution and determined the stability constants (4). The difference in these stability constants was evaluated to be about 100. TPEN recognized the slight difference in the softness between Am(III) and Eu(III). Takeshita et al. proposed and tested the synergistic extraction process of soft metals with TPEN, in which an organophosphoric acid or a carboxylic acid is used as a synergist (5–7). These studies demonstrated that TPEN, along with its masking properties, is an excellent extractant for soft metals. However, due to the enhanced solubility of


(a)TPEN (b)TQEN

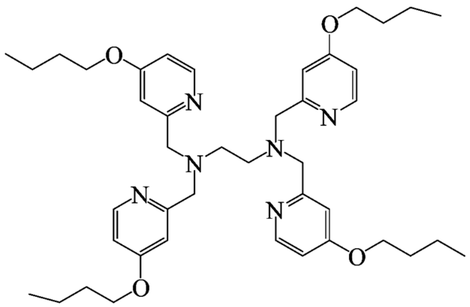

(c) TBPEN

Figure 1. Chemical structures of (a) TPEN, (b) TQEN, and (c) TBPEN.

the protonated TPEN in the acidic aqueous phase (pH < 4), the extraction performance of TPEN suffers in that region. The application of TPEN to a practical process is restricted, because of the high solubility of protonated TPEN to the acidic aqueous phase.

The extraction performance of TPEN for soft metals in acidic aqueous solutions must be improved for the extractant to have any practical use. The object of this study is to find a TPEN analog that extracts soft metals effectively and selectively in highly acidic solutions below pH 2. Cordier et al. reported that the hydrophobicity of a nitrogen-donor extractant, terpyridine, was improved by introducing hydrophobic groups to the compound and that the extraction separation of Am(III) and Eu(III) was attained successfully in highly acidic solutions (8). Our recent work suggested that the extraction performance of TPEN is reduced remarkably by the introduction of alkyl groups into the molecular framework (N-C-C-N structure). The positioning of alkyl functional groups is very important to preserve TPEN's extraction performance and its selectivity for soft metals (9). This study attempted to improve the extraction performance of TPEN for soft metals in the highly acidic solution by increasing the hydrophobicity of the alteration of the pyridyl groups.

In this way, we synthesized two TPEN analogs, *N*,*N*,*N'*,*N'*-tetrakis-(2-quinolinylmethyl)-1,2-ethylenediamine (TQEN), where all pyridyl groups are replaced with the quinoline groups, and *N*,*N*,*N'*,*N'*-tetrakis-[4-(2-butyloxy)-2-pyridylmethyl]-1,2-ethylenediamine (TBPEN), in which the butyloxy groups are connected directly to the pyridyl groups (Fig. 1). The extraction of Cd(II) by TPEN and its new analogs was investigated with a goal of finding an optimal structure-extraction relationship.

EXPERIMENTAL

Preparation of TPEN, TQEN, and TBPEN

TPEN was purchased from Dojindo Laboratories, Japan. TQEN was synthesized according to the previous paper (10). A mixture of 2-chloromethylquinoline hydrochloride (5 mmol), ethylenediamine (1.25 mmol), and potassium carbonate (15 mmol) in 20 mL of acetonitrile was refluxed for 2 days. After the solvent was removed under reduced pressure, the resulting solid was dissolved in water. TQEN was extracted from the water with chloroform. The chloroform phase was dried and evaporated. TQEN was purified by washing the residue with acetone. ES-MS: *m*/*z* 625.5. $C_{42}H_{36}N_6$ ($[M+H]^+$) requires 625.3. Anal. Calc. for $C_{42}H_{36}N_6$ ($Mw = 624.78$): C, 80.74; H, 5.81; N, 13.45. Found: C, 79.88; H, 5.59;

N, 13.51. TBPEN was synthesized by combining 2-chloromethyl-4-butoxypyridine (7.5 mmol), ethylenediamine (1.75 mmol), potassium carbonate (7.5 mmol) and sodium iodide (0.08 mmol). TBPEN was formed in the mixed solution by stirring at 70°C for 4 days and purified by an alumina column. All chemicals and solvents used for the synthesis of TQEN and TBPEN were reagent grade and were used without further purification. ^{1}H NMR($CDCl_3$, 500 MHz, 298 K), 8.25 (d, J = 5.7 Hz, 4H), 7.01 (d, J = 2.0 Hz, 4H), 6.63 (dd, J = 5.7, 2.0 Hz, H), 3.92 (t, J = 6.5 Hz, 8H), 3.84 (t, J = s, 8H), 2.93 (s, 4H), 1.70–1.75 (m, 8H), 1.41–1.48 (m, 8H), 0.95 (t, J = 7.4 Hz, 12H). ES-MS: m/z 713.9 $C_{42}H_{60}N_6O_4$ ($[M+H]^+$) requires 713.5. Anal. Calc. for $C_{42}H_{60}N_6O_4$ (Mw = 712.96): C, 70.75; H, 8.48; N, 11.79. Found: C, 68.66; H, 8.51; N, 11.52.

Distribution of TPEN, TQEN, and TBPEN into an Aqueous Phase

The distribution of TPEN, TQEN, and TBPEN in the organic phase to the aqueous phase was measured in the pH range of 1 to 7.5. TPEN and its analogs were dissolved in chloroform to form 20 μM TBPEN and 40 μM TPEN and TQEN. The ionic strength of the aqueous phase was maintained at 0.1 M by adding hydrochloric acid and sodium chloride solutions. Equal volumes (1.5 mL) of the aqueous and the organic phase were combined in a glass vial and shaken vigorously at 25°C (room temperature) for 1 day. After the aqueous phase was separated by a centrifugal separator, UV spectra of the solutions were measured by a UV-VIS spectrometer (JASCO, V-650). The absorbance for TPEN, TBPEN, and TQEN was observed at 261, 243, and 319 nm, respectively. The concentrations of TPEN, TBPEN, and TQEN in the aqueous phase were evaluated by analytical curves which were drawn from the absorbance of the aqueous solutions with different contents of TPEN and its analogs. The ionic strength and pH in these aqueous solutions were maintained at 0.1 M and 1.0, respectively.

Extraction of Cd(II) with TPEN, TQEN, and TBPEN

An aqueous solution with 1 mM $Cd(NO_3)_2$ was prepared. The pH was adjusted by adding nitric acid to be between 1 to 3.2. The ionic strength was maintained at 0.1 M by the addition of sodium nitrate solution. Each ligand was dissolved to form a 2 mM solution in chloroform. Equal volumes (1.5 mL) of the aqueous and the organic phase were combined in a glass vial and shaken vigorously at 25°C (room temperature) for 1 day. After the phases were separated by a centrifugal separator and the concentration of Cd(II) in the aqueous phase, $C_{\mathrm{Cd,W}}$, was measured by an inductively coupled plasma-atomic emission spectroscopy (Shimadzu, ICPE-9000). The concentration of Cd(II) in the organic phase, $C_{\mathrm{Cd,O}}$, was calculated as

$$C_{\mathrm{Cd,O}} = \frac{V_{\mathrm{W}}(C_{\mathrm{Cd,W,init}} - C_{\mathrm{Cd,W}})}{V_{\mathrm{O}}} \tag{1}$$

where $C_{\mathrm{Cd,W,init}}$, V_{W}, and V_{O} denote the initial concentration of Cd(II) in the aqueous phase, the volume of the aqueous phase, and the volume of the organic phase, respectively. The distribution ratio, D, and the percent extraction, E, were calculated as follows:

$$D = \frac{C_{\mathrm{Cd,O}}}{C_{\mathrm{Cd,W}}} \tag{2}$$

$$E = \frac{D}{D + V_{\mathrm{W}}/V_{\mathrm{O}}} \times 100 \tag{3}$$

Extraction of Various Metals with TBPEN

An aqueous solutions was prepared containing $CdCl_2$, $ZnCl_2$, $FeCl_3$, $CuCl_2$, $NiCl_2$, $HAuCl_4$, $PdCl_2$, H_2PtCl_6, $MgCl_2$, and $CaCl_2$, each at 1 mM concentrations. By adding hydrochloric acid, the pH and ionic strength were adjusted to 1 and 0.1 M, respectively. The experiment procedure was the same as those for the extraction of Cd(II) in the previous section. The percent extraction of each metal ion was evaluated from the concentration of the metal ion in the aqueous phase.

RESULTS AND DISCUSSION

Distributions of TPEN, TQEN, and TBPEN into an Aqueous Phase

The distributions of TPEN, TQEN, and TBPEN to the aqueous phase were examined in the pH range of 1 to 7.5 and was defined as:

$$\mathit{Distribution}\ [\%] = (L_{aq}/L_{total}) \times 100 \tag{4}$$

where L_{aq} and L_{total} denote the moles of extractant dissolved into the aqueous solution and the total moles of extractant in the aqueous phase and the organic phase, respectively. The relationships between the distribution of the extractants and the equilibrium pH are shown in Fig. 2. The distributions of the extractants into the aqueous phase increase with decreasing pH. These results were attributed to the protonation of

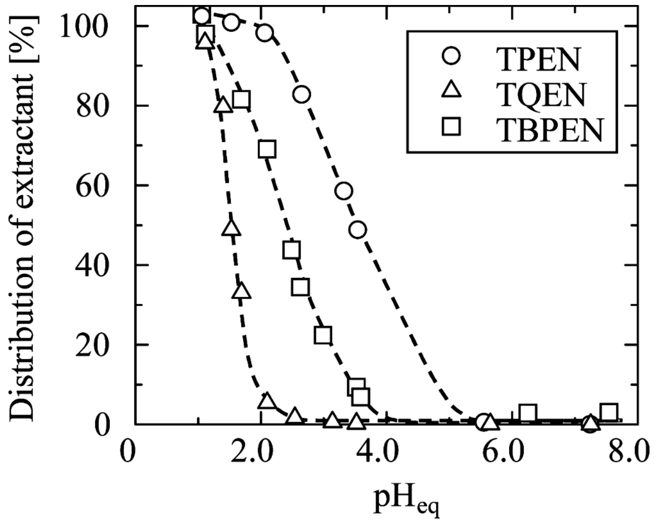


Figure 2. Distributions of TPEN, TQEN, and TBPEN into the aqueous phase in the pH range of 1 to 7.5.

extractant nitrogen donors under more acidic conditions. The partitioning of TPEN into the aqueous phase under mildly acidic conditions limits the potential application of the extractant. On the other hand, the distributions of TQEN and TBPEN in the aqueous phase are much lower than that of TPEN in the same media. Note that these extractants remain in the organic phase even in the pH range below 3, whereas TPEN is dissolved completely into the aqueous phase. These results suggest that the distributions of TQEN and TBPEN into the aqueous phase were suppressed by the enhancement by introducing the hydrophobic groups. The half pH values ($pH_{1/2}$) of TPEN and its analogs were compared to evaluate the hydrophobicity of these extractants and indicates the increase in the hydrophobicity of extractant. The order of $pH_{1/2}$ is given as TQEN (pH 1.5) < TBPEN (pH 2.5) < TPEN (pH 3.5) from Fig. 2.

Extraction Behavior of Cd(II) with TPEN, TQEN, and TBPEN

Extraction tests of Cd(II) with TPEN, TQEN, and TBPEN were carried out in the pH range of 1 to 4. Figure 3 shows the equilibrium pH dependence on the extraction of Cd(II). In the pH range of 1 to 4, less than 10% of the Cd(II) was extracted by TPEN. The greater part of extracted

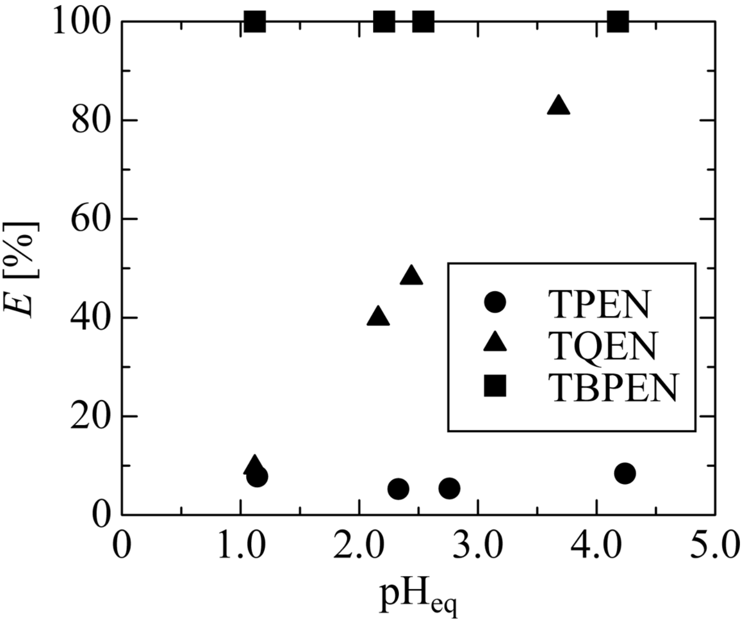


Figure 3. Extraction of Cd(II) with TPEN, TQEN, and TBPEN and at pH 1 to 4.

Cd(II) is caused by the direct extraction of Cd(II) with chloroform. TQEN and TBPEN showed enhanced extraction of Cd(II) from acidic solutions. It should be noted that TBPEN extracted Cd(II) effectively in the acidic solution with nearly all of the Cd(II) being portioned in the organic phase even at pH 1. Consequently, the extraction of Cd(II) under these conditions followed the order TBPEN > TQEN > TPEN.

As shown in Fig. 2, the distribution of TBPEN to the acidic solution ($pH \leq 3$) was larger than that of TQEN but TBPEN demonstrated better extraction of Cd(II) than TQEN. The distributions of TQEN and TBPEN between chloroform and the Cd-containing aqueous solution were tested in the pH range of 1 to 3.5. The initial concentrations of TQEN and TBPEN in the organic phase were adjusted to 40 and 20 μM, respectively. The initial concentration of Cd(II) in the aqueous phase was equimolar as the ligands in the organic phase. Figure 4 shows the distributions of TQEN and TBPEN for two water-chloroform systems with and without Cd(II). The solid lines represent the experimental data for the water-chloroform system with Cd(II) and the broken lines for that without Cd(II). In the case of TQEN (Fig. 4a), there was no difference between the two systems. On the contrary, in the case of TBPEN (Fig. 4b), the distribution data in the water-chloroform system with

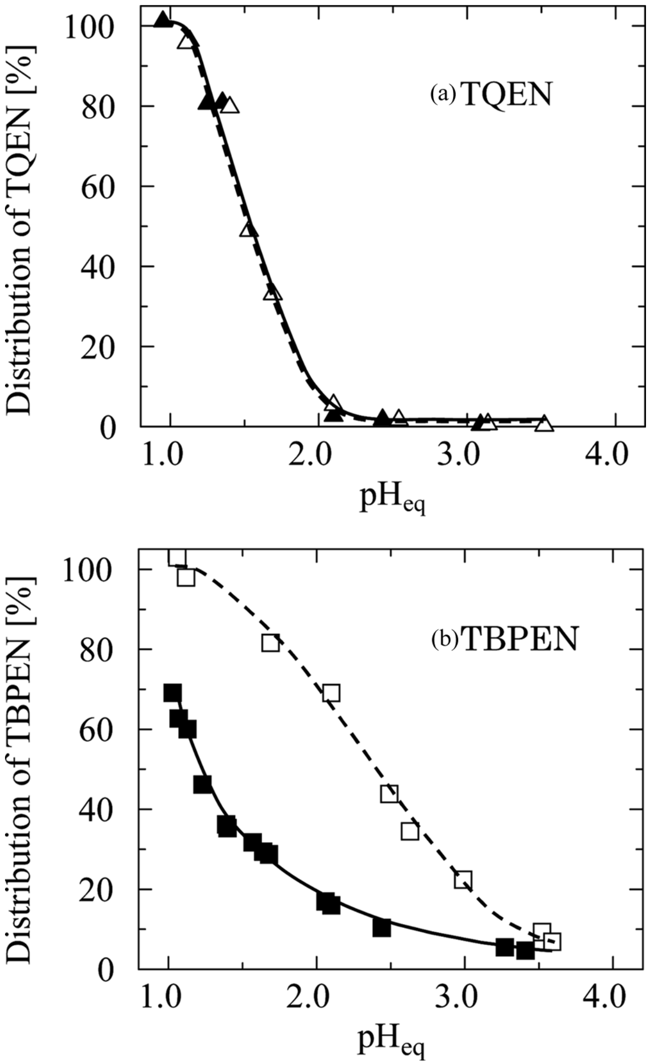


Figure 4. Distributions of (a) TQEN and (b) TBPEN into the aqueous phase. The solid lines represent the experimental data for the water-chloroform system with Cd(II) and the broken lines for that without Cd(II).

Cd(II) (solid line) were lower than those without Cd(II) (broken line). These results suggests that the hydrophocity of TBPEN is enhanced by the complex formation between Cd(II) and TBPEN.

This may be due to the encapsulation of Cd(II) inside TBPEN. Hydrophilic nitrogen donors of TBPEN are involved in the Cd-TBPEN complex. Then, the hydrophobicity of TBPEN may be further increased by the complex formation. These results give us an important suggestion for the molecular design of the TPEN analogs. The introduction of long-chain alkyl groups into four pyridyl groups for the synthesis of TPEN analog appear to improve extraction of soft metals in acidic aqueous solutions. However, further investigation is required to explain the relation between the hydrophobicity of TPEN analog and the complex structure.

Applicability of TBPEN to Recovery of Metals in an Acidic Solution

Nine metal ions (Au(III), Pt(II), Pd(II), Fe(III), Ca(II), Mg(II), Cu(II), Ni(II), and Zn(II)) were extracted by TBPEN in chloroform. On the basis of Pearson's HSAB principle, these metals are classified as follows: soft metals (Au(III), Pt(II), Pd(II), and Cd(II)), hard metals (Fe(III), Ca(II), and Mg(II)), and intermediate metals (Cu(II), Ni(II), and Zn(II)). Both the metal ions and TBPEN were present in equimolar concentrations (1 mM). As shown in Fig. 5, TBPEN extracted the soft and intermediate metals selectively from the pH 1 solution. The experimental results suggest that a hydrophobic TPEN analog with long-chain alkyl groups is

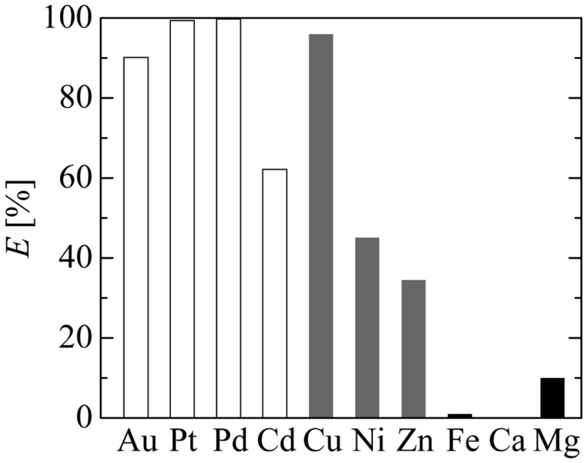


Figure 5. Extraction of various metals with TBPEN at pH 1. These metals are classified as soft (white bars), hard (black bars) and intermediate (grey bars) by Pearson's HSAB principle.

applicable to practical soft-metal separation processes, such as the separation of precious metals (Au, Pt, Pd, and Rh) and the recovery of highly toxic metals (Hg and Cd) from industrial wastes.

CONCLUSIONS

1. In the acidic pH range of 1 to 4, the distributions of TQEN and TBPEN to the aqueous phase were lower than that of TPEN, because of the increase in the hydrophobicity of these extractants. The extraction of Cd(II) from the acidic aqueous solution was improved by the use of hydrophobic TPEN analogs, TQEN and TBPEN.
2. TBPEN is suitable for the extraction of Cd(II) in highly acidic solutions below pH 2. The distribution of TBPEN to the aqueous phase was further suppressed by the formation of Cd-TBPEN complex in the organic phase. The percent extraction of Cd(II) for TBPEN was 100% at pH 1, whereas that for TPEN was less than 10%.
3. TBPEN showed high selectivity for the extraction of soft metals, such as Au(III), Pt(II), and Pd(II), in the highly acidic solution at pH 1. A hydrophobic TPEN analog obtained by introducing long-chain alkyl groups is applicable to practical soft-metal separation processes.

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