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Ion Flotation of Zinc(II) and Cadmium(II) in the Presence of Side-Armed Diphosphaza-16-Crown-6 Ethers

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ABSTRACT

Competitive flotation of zinc(II) and cadmium(II) ions from dilute aqueous solutions by side-armed lariat ether-type derivatives of diphosphaza-16-crown-6 ethers in the presence of nonylphenol nonylethylene glycol ether as the non-ionic foaming agent has been investigated. The influence of the type of group attached to the PNP-lariat ether molecule on the selectivity and efficiency of Zn(II) and Cd(II) ion flotation is studied. An effect of alkali metal cations, i.e., Li^+ and Na^+, on

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Cd(II) ion-flotation removal is also reported. It was shown that the removal of Cd^{2+} increases with increase of pH values and decreases with alkali metal cations concentration increase in aqueous solutions. The correlation between selectivity coefficients of Cd(II)/Zn(II) and pH of aqueous solution as well as molar intrinsic volume and hydrophilic–lipophilic balance of studied ethers was found.

Key Words: Ion flotation; Zinc(II); Cadmium(II); Diphosphaza-16-crown-6 ethers.

INTRODUCTION

Crown ethers and their derivatives were successfully used for metal-ions separation in liquid–liquid extraction, transport through liquid membranes, and ion-exchange systems.[1–3] A few papers have been concerned with the selective removal of zinc(II) and cadmium(II) cations with neutral crown ethers. The extraction of Zn^{2+} and Cd^{2+} cations with benzo-18-crown-6 into benzene organic phase in the presence of picric acid was studied by Katsuta et al. [4] Also, Billah and Hohjo[5] extracted the mixture of cadmium(II) and zinc(II) from aqueous solutions using neutral crown ethers. They extracted Zn(II) and Cd(II) as their thenyltrifluoroacetone complexes with dibenzo-18-crown-6 into o-dichlorobenzene. At pH 4.9 only Zn(II) was extracted quantitatively, whereas Cd(II) remained in the aqueous solution.

A reverse selectivity in Zn^{2+} and Cd^{2+} separation was obtained by Izatt et al.[6,7] in transport across liquid membranes containing 18-membered crown ethers. In competitive transport of zinc(II), cadmium(II), and mercury(II) through emulsion-liquid membranes, near quantitative selectivity for Cd(II) over Zn(II) and Hg(II) has been achieved. This can be explained by the preferential transport of neutral cation–anion species of CdA_2 from Zn^{2+} and $HgA_2{}^{2-}$, where $A = SCN^-$, I^-, Br^-, or Cl^-. Zinc(II) was also quantitatively transported as $Zn(SCN)_4{}^{2-}$ by supported liquid membrane using dicyclohexyl-18-crown-6 in presence of L- cysteine as metal-ion acceptor in the strip solution, whereas Cd(II) and the other metal ions remained in the solution.[8] Cho et al.[9–11] found that a single transport of Cd(II) across emulsion-liquid membranes by diazo-18-crown-6 (DA18C6) from 0.4 M SCN^- aqueous solutions is much more effective in comparison with Zn(II). On the other hand, Dadfarnia and Shamsipur[12] discovered quantitative transport of Zn(II) (90%) and only 1% of Cd(II) across bulk liquid membrane by DA18C6 and palmitic acid. Surprising results were received by Gupta and Kumar,[13] who used poly(vinyl chloride) matrix membranes containing neutral carrier with very large cavity size, i.e., dibenzo-24-crown-8, for cadmium-selective sensors.

Recently, macrocyclic compounds were applied in the ion flotation process. Koide et al.[14] have used the resorcinol-type calix[4]arenas with alkyl side chains as collectors in competitive flotation of alkali metal cations. They also applied phosphate esters of C-undecylcalix[4]resorcinarene for uranium-ions removal from seawater by ion flotation.[15] Schultz and Warr[16] investigated removal of alkali metal cations using anionic surfactant, i.e., bis(2,2′)-ethylhexylsulfosuccianate (AOT) and macrocycles, i.e., Cryptand 222 (C222) and 18-crown-6. They proved that C222 addition allows the achievement of better separation of alkali metal cations. The native separation, i.e., with AOT only, was as follows: $Li^+ < Na^+ < K^+ \leq Rb^+ \leq Cs^+$. With equimolar C222 added to AOT, the selectivity order was changed as follows: $Li^+ < Na^+ < Cs^+ < K^+$, Rb^+. Another approach to application of macrocycles for flotation of metal cations was done by Charewicz et al.[17] They used as macrocycles proton-ionizable dibenzo-16-crown-5 lariat ethers with sulfonic, phosphonic, and carboxylic groups. Sulfonic derivative of lariat ether exhibit sufficient foaming ability, while the others must be used together with a nonionic foaming agent, i.e., octylphenol decaethylene glycol ether (Triton X-100). Lariat ether with carboxylic group used together with Triton X-100 was found to have strong affinity towards Sr^{2+} cations.

Now we present results for competitive ion flotation of zinc(II) and cadmium(II) cations from dilute aqueous solutions ($c_{Me} = 1.0 \cdot 10^{-5}$ M) by side-armed PNP 16-crown-6 derivatives (PNP-lariat ethers) with nonylphenol nonylethylene glycol ether as nonionic foaming agent. Effects of structural modification of PNP-lariat ethers upon the efficiency and selectivity of ion flotation of Zn(II) and Cd(II) is reported. The influence of Li^+ and Na^+ on Cd^{2+} ions flotation is also studied.

EXPERIMENTAL SECTION

Apparatus and Procedure

The flotation experiments were carried out in a glass column 45.7 cm in height and 2.4 cm in diameter. The nitrogen gas was saturated with water and the flow rate was maintained at 12 mL/min through a sintered-glass sparger of 20–30 μm, nominal porosity. The initial volume of each feed solution was 100 mL. The temperature was maintained at 20 ± 2°C. The time dependence of the concentration of each metal in the bulk solution (c) was recorded continuously during ion-flotation experiments by means of radioactive analytical tracers and gamma-radiation spectrometry following a procedure described previously by Charewicz and Niemiec[18] and recently improved by Walkowiak and Ulewicz.[19] A single-channel, gamma-radiation spectrometer was used as the detector of radiation intensity of specific energy. The maximal percent removal (M) was calculated by an equation:

$$M = \left(1 - \frac{c_r}{c_i}\right)100\% \tag{1}$$

where c_i is the initial metal ion concentration and c_r is the metal ion concentration in the residual solution after foam ceased.

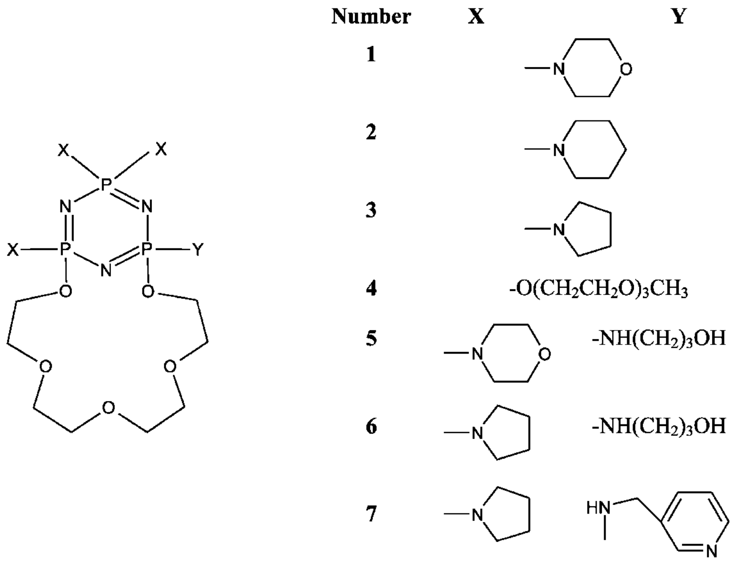
Selectivity coefficient (S) was calculated as:

$$S_{Me1/Me2} = \frac{M_{Me1}}{M_{Me2}} \tag{2}$$

where M_{Me1} is the maximal percent removal of the first metal and M_{Me2} is the maximal percent removal of the second metal.

Reagents

All aqueous solutions were prepared by using double-distilled water of conductivity 0.1 μS/m at 25°C. Reagent-grade inorganic chemicals, i.e., LiCl, NaCl, $ZnCl_2$, $CdCl_2$, NaOH, and HCl were obtained from POCh (Gliwice, Poland). Homogenously substituted diphospha-16-crown-6 lariat ethers **1** through **4** were synthesized according to the previously described procedure,[20] whereas the mixed ligands **5** through **7** were prepared by the stepwise incorporation of (a) one hydroxypropylamino (**5**, **6**) or 2-methylamino-pyridinyl (**7**) substituent, and (b) three cyclic amino-[morpholinyl (**5**) or pyrrolidinyl (**6**, **7**)] substituents.[21] As a nonionic foaming agent, nonylphenol nonyloethylene glycol ether (Rokafenol N-8, **8**) obtained from Rokita (Poland) was used. As the anionic surfactant sodium dodecylbenzene sulfonate (DBSNa) (**9**), BHD reagent, was applied.



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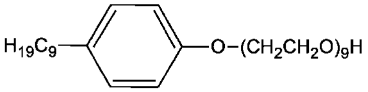

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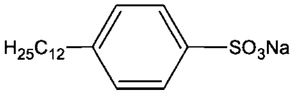

The gamma-radioactive isotopes, i.e., Zn-65 and Cd-115m, were from the Atomic Energy Institute (Świerk/Otwock, Poland). They were of sufficiently high specific activity to neglect the effect of carrier concentration, i.e., 9.2 GBq/g for Zn-65 and 2.3 GBq/g for Cd-115 m, respectively.

RESULTS AND DISCUSSION

Previously, it was found that competitive ion flotation of zinc(II) and cadmium(II) by the classical anionic surfactant, i.e., sodium dodecylbenzene sulfonate (**9**), allows the removal of both metals from acidic and neutral dilute aqueous solutions.[22] There was no selectivity in Zn(II) and Cd(II) removal since almost the same efficiency and rate of both metal cations was observed. Now we applied lariat ethers-type macrocycles with cyclophosphazene subunits for zinc(II) and cadmium(II) removal from $1.0 \cdot 10^{-5}$ M aqueous solutions. The macrocycles (**1**–**7**) i.e., side-armed ligands with diphosphaza-16-crown-6 rings and seven different sets of substituents were synthesized for the purpose of this study.[20,21] The detailed study on molecular structure-complexing property relationships with respect to several monovalent cations has been recently reported for the ligand **3**,[23] but even in that case no data were given on complexation of divalent cations. The other PNP-ligands (**1**, **2**, **4**–**7**) have been completely unexplored with respect to their complexing abilities, except for the ligand **4**, for which some results of TLC screening test have been reported.[20] It was disclosed that all lariat ethers studied do not exhibit sufficient foam ability and so they cannot be used solely as sufficient surfactants. For this reason all lariat ethers were used together with nonionic foaming agent, i.e., nonylphenol nonyloethylene glycol ether. We noticed that the nonionic foaming agent **8** does not float either Cd(II) or Zn(II).

Flotation-kinetics curves of zinc(II) and cadmium(II) that were floated from aqueous solutions containing single metals and an equimolar mixture of both metals by lariat ether **2** in the presence of foaming agent **8** are presented in Fig. 1. As can be seen in Fig. 1a, from single metal aqueous solutions, cadmium(II) is floated much better than zinc(II). Cadmium(II)/Zinc(II) selectivity in competitive ion-flotation process is very high since practically only cadmium(II) is floated, whereas zinc(II) remains in residual aqueous solutions. Similar trends were also observed when other PNP16C6 lariat ethers were used.

One important factor that influences Cd(II) and Zn(II) removal in ion-flotation process is the acidity of aqueous-phase solution. The relationship between maximal percent removal and pH of aqueous solutions for all diphosphaza-16-crown-6 derivatives is shown in Fig. 2. For all side-armed substituents (**1**–**7**) removal of both metals increases with pH increase. Selectivity coefficients of cadmium(II) over zinc(II) at pH equal to 7.0 and 11.0 for all studied lariat ethers are shown in Fig. 3. The highest values of $S_{Cd(II)/Zn(II)}$ are observed for lariat ethers **1** and **2**. At pH = 11.0, selectivity coefficients of Cd(II) over Zn(II) decrease in the following order of lariat ether-type macrocycles: $\mathbf{2} > \mathbf{1} > \mathbf{3} > \mathbf{7} > \mathbf{4} > \mathbf{6} > \mathbf{5}$.

The obtained results prove that the selectivity of cadmium(II) and zinc(II) separation with use of the PNP-lariat ethers **1** through **7** depends upon pH of aqueous solution and the nature of the substituents at the N_3P_3 ring, playing part of the side arms. The chemical behavior of these PNP-lariat ethers with the same internal-crown cavity size involving five oxygen and one nitrogen atoms is affected by the external substituents (side arms) with additional oxygen and nitrogen atoms influencing their total basicity, i.e., electron pair

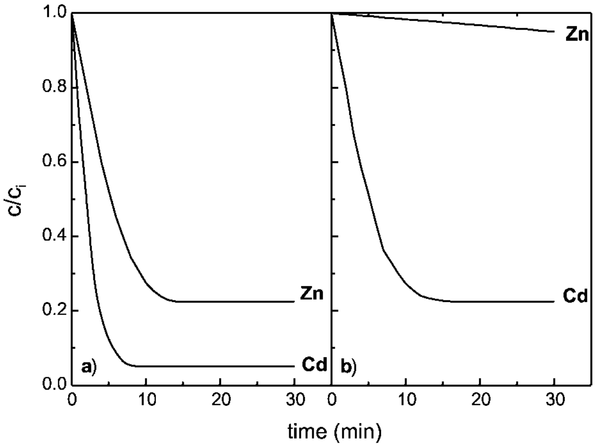

Figure 1. Flotation-kinetics curves of Zn(II) and Cd(II) with crown ether **2** and foaming agent **8** from single metal (a) and mixture of both metals in aqueous solutions (b); $[Zn^{2+}] = [Cd^{2+}] = 1.0{\cdot}10^{-5}$ M, pH = 11.0, $c_{ether} = 1.0{\cdot}10^{-4}$ M, [Rokafenol N−8] = $2.0{\cdot}10^{-4}$ M.

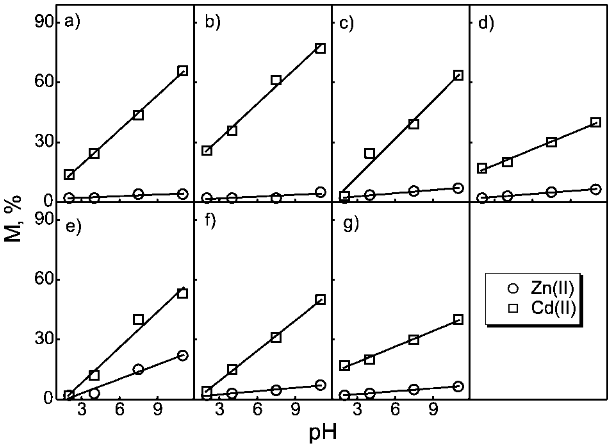

Figure 2. Influence of pH solution on removal of Zn(II) and Cd(II) ions from aqueous solutions using nonionic foaming agents **8** and diposhazaethers **1** (a), **2** (b), **3** (c), **5** (d), **6** (e), **7** (f), and **4** (g); $[Zn^{2+}] = [Cd^{2+}] = 1.0{\cdot}10^{-5}$ M, [Rokafenol N − 8] = $2.0{\cdot}10^{-4}$ M, $c_{ether} = 2.0{\cdot}10^{-4}$ M.

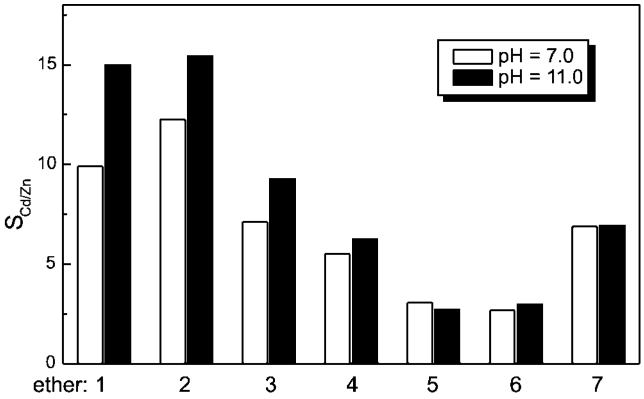

Figure 3. Cd(II)/Zn(II) selectivity coefficients in competitive flotation of Zn(II) and Cd(II) ions with PNP-lariat ethers and nonionic foaming agent **8** at pH 7.0 and 11.0; $[Zn^{2+}] = [Cd^{2+}] = 1.0 \cdot 10^{-5}$ M, $c_{ether} = 2.0 \cdot 10^{-4}$ M, [Rokafenol N − 8] $= 2.0 \cdot 10^{-4}$ M.

donicity and/or hydrogen-bond accepting ability. Therefore, the considered lariat ethers could be specifically characterized by means of their molar intrinsic volume, V_x (cm^3/mol), and hydrophile–lipophile balance, HLB, both calculated according to McGowan et al.[24–26]:

$$V_x = \Sigma n_i V_{x,i} - 6.56B \tag{3}$$

where $V_{x,i}$ is a volume specific for the ith kind of atom in the solute molecule, the number of which is n_i, and B are altogether bonds between the atoms (irrespective whether single or multiple). The number of bonds could be easily calculated with the following algorithm:

$$B = N - 1 + R \tag{4}$$

where N and R stand for the total number of atoms and rings in the molecule, respectively.

The HLB value was calculated as:

$$HLB = 7 - 0.337 \cdot V_x + 1.5 \cdot n \tag{5}$$

where n denotes the total number of oxygen and nitrogen atoms in the molecule.

The experimental separation coefficients have been correlated with pH of aqueous solution, the molar intrinsic volumes, and HLB of considered ethers

(Table 2) in accordance with the following linear model:

$$\log S_{Cd/Zn} = a + b \cdot pH + c \cdot V_x + d \cdot HLB \qquad (6)$$

The final equation that permits us to predict the separation coefficient of cadmium(II) over zinc(II) is as follows:

$$\log \mathrm{S_{Cd/Zn}} = (0.0288 \pm 0.0121)\mathrm{pH} + (3.26 \pm 0.49)10^{-3} \cdot \mathrm{V_x} - (0.0920 \pm 0.0195)\,\mathrm{HLB}$$

$$(\mathrm{R}^2 = 0.9200,\ \mathrm{s.d.} = 0.23,\ \mathrm{F} = 104,\ \mathrm{N} = 28) \qquad (7)$$

Where R^2 stands for the determination coefficient, s.d. is a standard deviation, F denotes the Fischer–Sedecor test function (F-statistic), and *N* represents the number of experimental data. From the statistical point of view, the obtained correlation is significant. It is also important that the deviations of experimental points from the correlation are lower than ± 3 s.d. According to Eq. (5), the values of HLB of homologs with constant number (*n*) heteroatoms (*O* and *N*, respectively) depends only on their molar intrinsic volumes. On the other hand, for the analogs of the same molar volume, the values of HLB depend only on the number of heteroatoms. The reagents studied differ in their molar intrinsic volumes and the numbers of oxygen and nitrogen atoms that interact with water

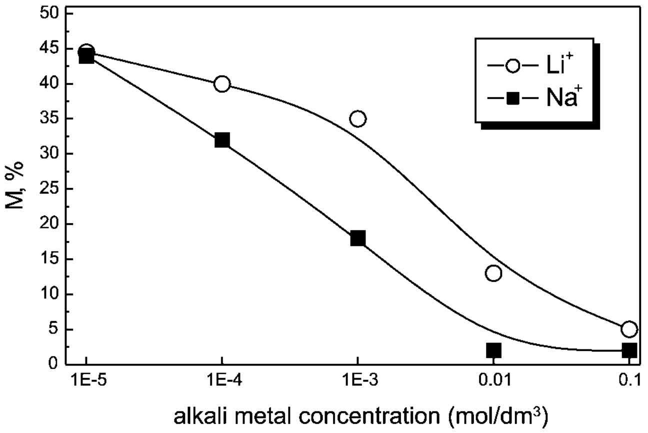

Figure 4. Influence of LiCl and NaCl concentrations on maximal percent removal of Cd(II) ions in competitive ion flotation with crown ether **1** in the presence of Rokafenol N-8; $[Zn^{2+}] = [Cd^{2+}] = 1.0 \cdot 10^{-5}$ M, pH = 11.0, $c_{ether} = 1.0 \cdot 10^{-4}$ M, [Rokafenol N − 8] = $2.0 \cdot 10^{-4}$ M.

Table 1. Diameters of crown ether cavities and metal cations studied.

Crown ether	Diameter (Å)[27,28]	Cation	Diameter[a] (Å)[29]
15-crown-5	1.7 ÷ 2.2	Zn^{2+}	1.7
		Cd^{2+}	2.1
18-crown-6	2.6 ÷ 3.2	Li^{+}	1.2
		Na^{+}	1.9

[a] For coordination number 6.

molecules through hydrogen bonding. As a result, the separation factors, $S_{Cd/Zn}$ depend on the properties of the reagents. From Eq. (7) comes that the contribution of molar intrinsic volume of the reagents reflects the effect of their hydrophobicity, whereas the contribution of HLB reflects the differentiation of their hydrophilicity. It may be also concluded that increase of molar intrinsic volume and increase of HLB of the reagents favor the flotation of larger Cd(II) cations in a greater extent than the flotation of smaller Zn(II) cations (Table 1).

The practical utility of cadmium(II) over zinc(II) separation strongly depends on its resistance to ionic strength of the aqueous solutions. Therefore, the effect of lithium and sodium chlorides concentration on efficiency of Cd(II) flotation was studied, and results obtained are shown in Fig. 4. As concentration of LiCl and NaCl increases the removal of Cd(II) decreases, and at the concentration equal to 0.10 M, cadmium(II) is floated with very low efficiency. Sodium(I) influences on Cd(II) flotation removal are stronger than lithium(I). Cavity size of PNP-16-crown-6, which is between 15-crown-5 and 18-crown-6,[23] fits much better to Na^+ than to Li^+ cations (Table 1). This causes higher interference of Na^+ than Li^+ on Cd(II) flotation.

Table 2. Molar intrinsic volume (V_x) and hydrophilic–lipophilic balance (HLB) values for diposphaza-16-crown-6 ethers.

Number of ether	V_{x}, cm^3/mol	HLB
1	539.0	12.8
2	524.8	7.3
3	471.0	9.8
4	717.5	18.8
5	414.1	11.0
6	427.9	12.1
7	442.6	10.1

CONCLUSIONS

PNP lariat ethers **1** through **7** allow, the separation of cadmium(II) over zinc(II) from dilute aqueous solutions by ion-flotation process using nonylphenol nonylethylene glycol ether as the foaming agent. The flotation removal and Cd(II)/Zn(II) selectivity is controlled by the type of substituents attached to the crown ether molecules. Within the series of ionophores, individual members with good selectivity for Cd^{2+} over Zn^{2+} (i.e., **1** and **2**) are identified. They both are uniformly substituted PNP-lariat ether-type derivatives with four six-membered cyclic amino rings [morpholinyl (**1**) or piperidinyl (**2**)] *N*-linked to the cyclophosphazene phosphourus atoms. All lariat ethers with a crown ether ring of PNP-16-crown-6 exhibit selectivity order $Cd^{2+} > Zn^{2+}$. The removal of Cd^{2+} increases with increase of pH value. The efficiency of Cd(II) flotation decreases with alkali metal cations concentration increase. The highest influence of alkali metal cations was observed for Na^{+}. A correlation was found between selectivity coefficients of Cd(II)/Zn(II) and pH of aqueous solution, as well as molar intrinsic volume and hydrophilic–lipophilic balance (HLB) of studied ethers. The increase of the molar intrinsic volume and the decrease of the HLB value of the side-armed diphosphaza-16-crown-6 ethers highly favor the flotation of larger Cd(II), rather than smaller Zn(II),cations.

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