Title	Studies on Syntheses and Analytical Applications of Macrocyclic Polythiaethers
Author(s)	大植, 正敏
Citation	大阪大学, 1989, 博士論文
Version Type	VoR
URL	https://hdl.handle.net/11094/1853
rights	
Note	

STUDIES ON
SYNTHESES AND ANALYTICAL APPLICATIONS OF MACROCYCLIC POLYTHIAETHERS

（大環状ポリチアエーテルの合成とその分析化学的応用に関する研究）

1989

MASATOSHI OUE

PREFACE

The works in this thesis were carried out under the guidance of Professor Toshiyuki Shono at Faculty of Engineering, Osaka University.

The object of this thesis is the designing and preparation of silver ion-selective thiacrown ether derivatives for solvent extraction reagents and neutral carriers of ion selective electrodes and their applications to the separation of silver ion from other heavy metal ions and the potentiometric determination of silver ion.

Masatoshi Oue

LIST OF PUBLICATIONS

The contents of this thesis are composed of the following papers.

1. New Poly- and Bis(thiacrown Ether)s as Extraction Reagents

   Masatoshi Oue, Akira Ishigaki, Yousuke Matsui, Takumi Maeda,
   Keiichi Kimura, and Toshiyuki Shono,
   Chem. Lett., 1982, 275-276.

2. Synthesis and Cation-Binding Properties of Poly- and Bis(thiacrown Ether)s

   Masatoshi Oue, Akira Ishigaki, Keiichi Kimura,
   Yousuke Matsui, and Toshiyuki Shono,
   J. Polym. Sci., Polym. Chem. Ed., **23**, 2033-2042(1985).

3. Liquid-Liquid Extraction of Silver Ion with Benzothiacrown Ether Derivatives

   Masatoshi Oue, Keiichi Kimura, and Toshiyuki Shono,
   Anal. Chim. Acta, **194**, 293-298(1987).

4. Neutral Carrier-Type Silver Ion-Selective Electrode Based on Lipophilic Monothiacrown Ether

   Masatoshi Oue, Keiichi Kimura, Kazuhiro Akama,
   Minoru Tanaka, and Toshiyuki Shono,
   Chem. Lett., 1988, 409-410.

5. Extraction-Spectrofluorimetric Determination of Silver Ion Using Benzothiacrown Ether and Eosin

   Masatoshi Oue, Keiichi Kimura, and Toshiyuki Shono,
   Analyst(London), 113, 551-553(1988).

6. Silver Ion-Selective Polymeric Membrane Electrode Based on Lipophilic Monothiacrown Ether

   Masatoshi Oue, Kazuhiro Akama, Keiichi Kimura,
   Minoru Tanaka, and Toshiyuki Shono,
   Anal. Sci., 5, 165-169(1989).

7. Lipophilic Thiacrown Ether Derivatives Selective as Silver Ion Neutral Carriers

   Masatoshi Oue, Kazuhiro Akama, Keiichi Kimura,
   Minoru Tanaka, and Toshiyuki Shono,
   J. Chem. Soc., Perkin Trans. 1, in press.

8. Substituent Effect of Thiacrown Ethers on Silver Ion Selectivity as Neutral Carrier for Ion-Selective Electrodes

   Masatoshi Oue, Kazuhiro Akama, Minoru Tanaka,
   and Toshiyuki Shono,
   in contribution.

CONTENTS

GENERAL INTRODUCTION

One of the targets in analytical chemistry is separation and detection of particular metal ions, which is widely used for medical and environmental analyses. Macrocyclic ligands or ionophores, which are able to easily bind and discriminate cations or anions, are considerably excellent compounds for solvent extraction or membrane transport. Though macrocyclic polyethers, crown ethers, which were discovered and coined by Pedersen[1] are simple compounds, their selectivities on crown ether-metal ion complex formation for the alkali and alkaline-earth metal ions are predominant. These crown ethers form not only 1:1 macrocycle-cation complexes, but also 2:1 complexes. Specifically, polymers carrying monocyclic crown ether moieties in the side chain, poly(crown ether)s, are most likely to form 2:1 macrocycle-cation complexes by cooperative action of the two neighboring crown rings.[2] Taking the 2:1 complexes formation into consideration, poly(crown ether)s have been synthesized and used as solvent extraction reagents. Moreover, since the appearance of the K^+-selective electrode based on valinomycin, naturally-occurring ionophore,[3] many studies on neutral carrier-type ion-selective electrode by using of artificial ionophore, such as crown ethers, have been carried out.[4]

On the other hand, replacement of some or all oxygen atoms in crown ether rings by sulfur atoms changes the ion selectivities of the crown ethers from alkali and alkaline-earth metal ions to silver ion or other heavy metal ions.[5,6] For the sake of their attractive complexing properties, various kinds of macrocyclic polythiaethers with oxygen and sulfur atoms as ring heteroatoms have been synthesized, even though it may be somewhat dangerous to use mustard gas-like starting materials for the synthesis of the thiacrown ethers.[7-11]

Izatt et al.[12] have shown that the Ag^+ and Hg^{2+} affinities of several sulfur derivatives of 15-crown-5 and 18-crown-6 which partially substitute sulfur atoms for oxygen ones as the ring heteroatoms are greatly increased as compared with the corresponding crown ethers, but that those for Tl^+ and Pb^{2+} remain unchanged. The stoichiometries of the cation-crown ether complexes were 1:2 (cation / crown) for Ag^+ or Hg^{2+} and 1:1 for Tl^+ or Pb^{2+}. Similar tendencies have been found in the complex of the cations with dithia-18-crown-6 (1,4,10,13-tetraoxa-7,16-dithiacyclooctadecane) in non-aqueous solvents.[13] Consequently, the cation-complex formation properties of the thiacrown ether derivatives depend on the following factors:(1)the replacement of oxygen donor atoms by sulfur atoms, (2)the number of sulfur atoms in the molecule, (3)the position of sulfur atoms in the crown ring, and (4)the ring cavity size.

Few thiacrown ether has been employed as neutral carriers for ion-selective electrode due to their coordination bonding property.[14] However, Lai et al.[15] have studied Ag^+- and Hg^{2+}-selective electrodes by using dithia-15-crown-5 as the neutral carriers of liquid membrane-type ion-selective electrodes, and have revealed that the electrode response toward Ag^+ was not very good (40 mV/decade) due to the anion interference, but the response toward Hg^{2+} was almost Nernstian. However, it is necessary to further improve the sensitivity and selectivities of the Ag^+-selective electrodes.

This thesis is concerned with syntheses of thiacrown ether derivatives which contain oxygen and sulfur atoms in the crown ring and their applications to analytical chemistry. In chapter I, the syntheses of various poly- and bis(thiacrown ether)s and their cation-binding properties are described. In chapter II, solvent extraction of silver ion with the poly- and bis(thiacrown ether)s is reported. In chapter III, determination of trace amount of silver ion by ion-pair extraction with the thiacrown ethers and fluorimetric reagent is described. In chapter IV, syntheses of mono- or dithiacrown ethers possessing a lipophilic group and their applications to neutral carriers of Ag^+-selective electrode are mentioned.

References

1. C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017(1967).
2. S. Kopolow, T. E. Hogen-Esch, and J. Smid, *Macromolecules*, **6**, 133(1973).
3. L. A. R. Pioda, V. Stankova, and W. Simon, *Anal. Lett.*, **2**, 665(1969).
4. R. L. Solsky, *Anal. Chem.*, **60**, 106R(1988).
5. C. J. Pedersen, *J. Org. Chem.*, **36**, 254(1971).
6. D. S. C. Black, and I. A. McLean, *Tetrahedron Lett.*, **1969**, 3961(1969).
7. J. S. Bradshaw, J. Y. Hui, B. L. Haymore, J. J. Christensen, and R. M. Izatt, *J. Heterocycl. Chem.*, **10**, 1(1973).

8. J. S. Bradshaw, J. Y. Hui, Y. Chan, B. L. Haymore, R. M. Izatt, and J. J. Christensen, *J. Heterocycl. Chem.*, **10**, 1(1973).

9. J. S. Bradshaw, R. A. Reeder, M. D. Thompson, E. D. Flandeers, R. L. Carruth, R. M. Izatt, and J. J. Christenbsen, *J. Org. Chem.*, **39**, 2079(1974).

10. J. Buter, and R. M. Kellogg, *J. Org. Chem.*, **46**, 4481(1981).

11. L. A. Ochrymowycz, C. P. Mak, and J. D. Michna, *J. Org. Chem.*, **39**, 2079(1974).

12. R. M. Izatt, R. E. Terry, L. D. Hansen, A. G. Avondet, J. S. Bradshaw, N. K. Dalley, T. E. Jensen, and J. J. Christensen, *Inorg. Chim. Acta*, **30**, 1(1978).

13. C. Rounaghi, and A. I. Popov, *J. Inorg. Nucl. Chem.*, **43**, 911(1981).

14. E. Sekido, K. Suzuki, and K. Hamada, *Anal. Sci.*, **3**, 505 (1987).

15. M. T. Lai, and J. S. Shih, *Analyst(London)*, **111**, 891(1986).

CHAPTER I

Synthesis and Cation-Binding Properties of Poly- and Bis(thiacrown Ether)s

Introduction

Crown ether polymers possess attractive cation-binding properties toward alkali and alkaline-earth metal ions.[1] Especially, polymers carrying crown ether moiety at the side chain, called poly(crown ether)s, are specific on binding metal cations. It is most likely that on complexation by poly(crown ether)s a cation is sandwiched intramolecularly by two crown ether rings in the polymer. In other words, by the cooperative action of crown ether moieties, poly(crown ether)s can easily form 2:1 crown ether ring to cation complexes with particular metal ions which slightly exceed the crown ether cavities in size. Therefore, poly(crown ether)s often exhibit excellent cation-binding selectivities as compared with the corresponding monomeric analogs.[2] For instance, poly(15-crown-5) derivatives are selective for K^+, poly(18-crown -6) derivatives for Cs^+, and poly(12-crown-4) derivatives for Na^+ on complexing alkali metal ions.[3] The corresponding dimeric model compounds, so-called bis(crown ether)s, behave in a similar way, forming the sandwich-type complexes.[4,5]

Crown ethers in which some or all of the oxygen atoms are replaced by sulfur atoms, thiacrown ethers, are known to show great affinity for softer metal ions than alkali and alkaline-earth metal ions.[6-9] Also, the replacement of oxygen by sulfur causes a decrease in cavity size of crown ethers. It is of much interest to see how specific cation-binding abilities are realized with polymers and dimers of thiacrown ether. To this end, polymers and dimers of benzothiacrown ether containing three or four sulfur atoms were synthesized.

This chapter describes the syntheses of the poly- and bis(thiacrown ether)s, and their cation-binding properties which have been elucidated by a solvent extraction method. A comparison with the corresponding monomeric thiacrown ethers is also discussed.

Experimental

Chemicals

All chemicals were of analytical-reagent grade and purchased from Wako Pure Chemicals. Poly- and bis(thiacrown ether)s employed were synthesized as follows.

Syntheses

2,3-(4'-Nitrobenzo)-1,4-dioxa-7,10,13-trithiacyclopentadeca-2-ene or Nitrobenzo-trithia-15-crown-5

Sodium hydroxide (2 g, 0.05 mol) was dissolved in 100 ml of absolute ethanol under a nitrogen atmosphere. To this solution bis(2-mercaptoethyl)sulfide (2.31 g, 0.015 mol) was slowly added and the mixture was refluxed gently. To the mixture 1,2-bis(2'-chloroethoxy)-4-nitrobenzene (4.2 g, 0.015 mol) dissolved in 200 ml of hot ethanol was added cautiously for 1 h while stirring. After the addition the mixture was refluxed for 1 h. The hot solution was filtered and cooled. The yellow crystals were precipitated from the filtrate. The crystals were collected by filtration and then recrystallized from heptane to yield a solid of 2,3-(4'-nitrobenzo)-1,4-dioxa-7,10,13-trithiacyclopentadeca-2-ene; yield, 40%; mp 122-125.3 °C; IR(KBr) 1580(NO_2), 1060(CO), 645 cm^{-1} (CS); ^{1}H-NMR($CDCl_3$, δ) 2.7-3.3(12H,m,CH_2S), 4.3-4.5(4H,t, CH_2O), 6.8-7.0(1H,d,aromatic), 7.7-8.0(2H,m,aromatic); MS, m/e 361. Anal. Calcd for $C_{14}H_{19}NO_4S_3$: C,46.52%; H,5.30%; N,3.87%. Found: C,46.48%; H,5.12%; N,3.94%.

The 1,2-bis(2'-chloroethoxy)-4-nitrobenzene was obtained by chlorination of 1,2-bis(2'-hydroxyethoxy)benzene[10] in refluxing benzene using thionyl chloride and pyridine, followed by nitration. To a solution of 1,2-bis(2'-chloroethoxy)benzene[11] (47 g, 0.2 mol) in chloroform (750 ml) and acetic acid (650 ml), nitric acid (200 ml) was added while stirring at room temperature over 1 h and the stirring was continued for 24 h. And then, after the solution was neutralized with sodium bicarbonate, organic layer was separated. The chloroform layer was washed with water, and dried with anhydrous $MgSO_4$. Evaporation of the solvent yielded a product of yellow crystals; yield, 93%; mp 89-92 °C(from heptane); IR(KBr) 1590(NO_2), 670 cm^{-1}(CCl); ^{1}H-NMR($CDCl_3$, δ) 3.7-4.0(4H,m,CH_2CH_2), 4.2-4.5(4H,m,CH_2CH_2), 6.8-7.0(1H,d,aromatic), 7.7-8.0 (2H,m,aromatic); MS, m/e 279. Anal. Calcd for $C_{10}H_{11}NO_4Cl_2$: C,42.88%; H,3.96%; N,5.00%. Found: C,42.64%; H,3.88%; N,4.77%.

Bis(2-mercaptoethyl)sulfide was prepared as follows: In a 1-L 3-necked flask were placed bis(2-hydroxyethyl)sulfide (24.5 g, 0.2 mol), thiourea (32 g, 0.4 mol), and concentrated HCl

(105 ml). The mixture was allowed to reflux while stirring for 12 h under a nitrogen atmosphere. After cooling the solution, NaOH (67 g, 1.2 mol) dissolved in water (400 ml) was added gradually. The mixture was refluxed and stirred for additional 3 h under a nitrogen atmosphere. After phase separation on cooling, the aqueous layer was acidified with dilute HCl and then extracted with diethyl ether (200 ml). The combined organic layer was dried with anhydrous $MgSO_4$ and the solvent was evaporated off. By vacuum distillation bis(2-mercaptoethyl)-sulfide was obtained as a colorless oil: bp 125-128 $^oC/7$ mmHg (lit.[12,13] 135-136 $^oC/10$ mmHg) [1 mmHg = 133.32 Pa]; yield, 63%.

2,3-(4'-Nitrobenzo)-1,4-dioxa-7,10,14,17-tetrathiacyclononadeca-2-ene or Nitrobenzo-tetrathia-19-crown-6

The synthetic procedure of this compound using 3,7-dithia-1,9-nonanedithiol was similar to that of the 2,3-(4'-nitrobenzo)-1,4-dioxa-7,10,13-trithiacyclopentadeca-2-ene. Recrystallization from heptane yielded slightly yellow crystals; yield, 20%; mp 138-139 ^oC; IR(KBr) 2850(CH), 1590(NO_2), 640 cm^{-1}(CS); ^1H-NMR ($CDCl_3$,δ) 1.8-2.1(2H,m,CH_2), 2.6-3.1(12H,m,SCH_2), 4.1-4.4(4H,t,OCH_2), 6.8-6.9(1H,d,aromatic), 7.7-7.9(2H,m,aromatic); MS, m/e 435. Anal. Calcd for $C_{17}H_{25}NO_4S_4$: C,46.87%; H,5.78%; N,3.22%. Found: C,46.82%; H,5.67%; N,3.31%.

3,7-Dithia-1,9-nonanedithiol was synthesized according to the literature[11] by using 1,3-dichloropropane instead of 1,3-dibromopropane. The diol was converted to the corresponding thiols in a similar way to the literature[6]; bp 160-165 $^oC/2$ mmHg (lit.[6] 159-161 $^oC/0.5$ mmHg).

2,3-(4'-Acryloylaminobenzo)-1,4-dioxa-7,10,13-trithiacyclopentadeca-2-ene or Acryloylaminobenzothiacrown Ether (**1a**)

In a dioxane solution (100 ml) of nitrobenzothiacrown ether (4.0 g, 0.01 mol), palladium carbon (1 g, ca. 0.008 mol) was suspended and then the mixture was stirred at room temperature under a hydrogen pressure of 0.5 MPa(5 atm) in a glass autoclave. After the hydrogen absorption ceased, the palladium carbon was filtered off. The filtrate was concentrated to a volume of about 10 ml, and stirred on cooling in an ice bath. To this solution acrylic anhydride (1.4 g, 0.011 mol) was added dropwise. After completing the addition the mixed solution was stirred for 4 h at room temperature and allowed to stand overnight. The resulting white precipitate was washed with diethyl ether (10 ml), and redissolved in acetone (50 ml). This solution was treated with activated charcoal and filtered. The solvent was removed under a reduced pressure. The residue gave a white crystal of acryloylaminobenzothiacrown ether (**1a**); yield, 54%; mp 170-172 ^{o}C; IR(KBr) 3300(NH), 1660(CO), 1625(C=C), 620 cm^{-1}(CS); ^{1}H-NMR($CDCl_3$,δ) 2.7-3.2(12H,m,SCH_2), 4.2-4.3(4H,t,OCH_2), 5.6-5.8 (1H,m,-CH), 6.2-6.4(2H,m,CH_2-), 6.8-7.5(3H,m,aromatic), 7.5-7.6 (1H,s,NH); MS, m/e 385. Anal. Calcd for $C_{17}H_{23}NO_3S_3$: C,52.96%; H,6.01%; N,3.63%. Found: C,52.81%; H,5.99%; N,3.54%.

2,3-(4'-Acryloylaminobenzo)-1,4-dioxa-7,10,14,17-tetrathiacyclononadeca-2-ene or Acryloylaminobenzothiacrown Ether (**1b**)

This compound was synthesized by the similar procedure to that for (**1a**), with a slight modification of the workup. The resulting white precipitate was filtered off, washed with methanol (10 ml) and redissolved in acetone (50 ml). This solution was stirred with activated charcoal and then activated charcoal was filtrated. Evaporation of the acetone under a reduced pressure gave a solid of (**1b**); yield, 58%; mp 137-140 °C; IR(KBr) 3300(NH), 1660(CO), 1610(C=C), 1020 cm^{-1}(COC); ^1H-NMR ($CDCl_3$,δ) 1.7-2.1(2H,m,CH_2), 2.6-3.1(16H,m,SCH_2), 4.1-4.3(4H,t, OCH_2), 5.6-5.8(1H,m,-CH), 6.0-6.4(2H,m,CH_2-), 6.7-7.5(3H,m,aromatic), 7.5-7.7(1H,s,NH); MS, m/e 459. Anal. Calcd for $C_{20}H_{29}NO_3S_4$: C,52.25%; H,6.36%; N,3.05%. Found: C,51.96%; H,6.34%; N,3.00%.

Poly(thiacrown Ether)s (**2a**)

In 10 ml of N,N-dimethylformamide (DMF), 1 g (2.6 mmol) of acryloylaminobenzothiacrown ether (**1a**) and 18 mg (0.11 mmol, 4 mol% to the monomer) of α,α'-azobisisobutyronitrile were dissolved. The solution was degassed by a freeze-and-thaw method, and then polymerization was carried out at 55-60 °C for 20 h in a sealed tube. Poly(thiacrown ether)s were obtained by pouring the tube content into a large excess of diethyl ether, and the resulting white precipitate was filtered off. Purification of the product was performed by reprecipitation from chloroform in diethyl ether; conversion, 53%.

Poly(thiacrown Ether)s (**2b**)

The polymerization procedure was almost the same as that for (**2a**), but the tube content was poured into a large excess of methanol. Furthermore, by the reprecipitation from DMF in methanol the polymer was purified; conversion, 62%. The molecular weights of poly(thiacrown ether)s (**2a**) and (**2b**) were evaluated by GPC(gel permeation chromatography) using polystyrene standards.

1,3-Bis[(3',4'-benzo-1",4"-dioxa-7",10",13"-trithiacyclopentadeca-2"-ene)aminocarbonyl]propane or Bis(thiacrown Ether)s (**3a**)

Nitrobenzo-trithia-15-crown-5 (3.0 g, 8.3 mmol) was reduced with palladium carbon using a method similar to that used for the monomer (**1a**). Palladium carbon was removed by filtration and the filtrate was concentrated to a volume of a few milliliters. The solution was again diluted with 30 ml of dry benzene and then to this solution 1.1 ml of triethylamine was added. While cooling under a nitrogen atmosphere, the solution was stirred, and then 0.42 ml of glutaryl dichloride in 10 ml of benzene was added dropwise over 1 h. The mixture was stirred for 10 min at room temperature and then refluxed for 3 h. After refluxing, the solution was allowed to stand overnight. The resulting brown residue was filtered off and redissolved in chloroform (400 ml). The chloroform solution was washed with a ca. 10% HCl (twice), water (once), aqueous NH_3 (once), and water (twice), and then dried with anhydrous $MgSO_4$. Solvent evaporation allowed a crude product. Recrystallization of the product was carried out from acetone; yield, 65%; mp(dec.) 265-270 ^{o}C; IR(KBr) 3400(NH), 2920(CH), 1650 cm^{-1}(CO); ^{1}H-NMR(DMSO-d_6,δ) 2.2-2.4(2H,m,-CH_2-), 2.7-3.2(24H,m,SCH_2), 3.3-3.4(4H,s,CH_2CO), 4.0-4.3(8H,t,OCH_2), 6.8-7.5(3H,m,aromatic), 9.7-9.9(1H,s,NH); MS, m/e 758. Anal. Calcd for $C_{33}H_{46}N_2O_6S_6$: C,52.22%; H,6.11%; N,3.69%. Found: C,52.05%; H,6.29%; N,3.66%.

1,3-Bis[(3',4'-benzo-1",4"-dioxa-7",10",14",17"-tetrathiacyclononadeca-2"-ene)aminocarbonyl]propane or Bis(thiacrown Ether)s (3b)

The method of the synthesis of this compound was similar to that of (2a); yield, 25.6%; mp 180-190 °C; IR(KBr) 3400(NH), 2930(CH), 1650(CO), 680 cm^{-1}(CS); ^{1}H-NMR(DMSO-d_6,δ) 1.7-2.0(2H,m, thiaether CH_2), 2.2-2.4(2H,m,CH_2), 2.5-3.1(32H,m,SCH_2), 3.2-3.4 (4H,s,-CH_2CO), 4.0-4.2(8H,t,OCH_2), 6.8-7.3(3H,m,aromatic), 9.7-9.8(1H,s,NH); MS, m/e 908. Anal. Calcd for $C_{39}H_{58}N_2O_6S_8$: C,51.62%; H,6.44%; N,3.09%. Found: C,51.31%; H,6.47%; N,2.90%.

Solvent Extraction

Equal volumes (10 ml) of a 5 x 10^{-5} M thiacrown ether chloroform solution and a mixed aqueous solution of 1 x 10^{-5} M metal nitrate and 1 x 10^{-4} M picric acid were placed in a stoppered flask. The concentrations for the poly- and bis(thiacrown ether)s are defined here in terms of thiacrown ether unit(ring). The stoppered flask was shaken for 40 min at 25.0 ± 0.1 °C. After phase separation, the metal ion concentration remaining in the aqueous phase was measured by atomic absorption spectrophotometry. Atomic absorption spectrophotometer was AA-855 type of Nippon Jarrell-Ash Co., Ltd.

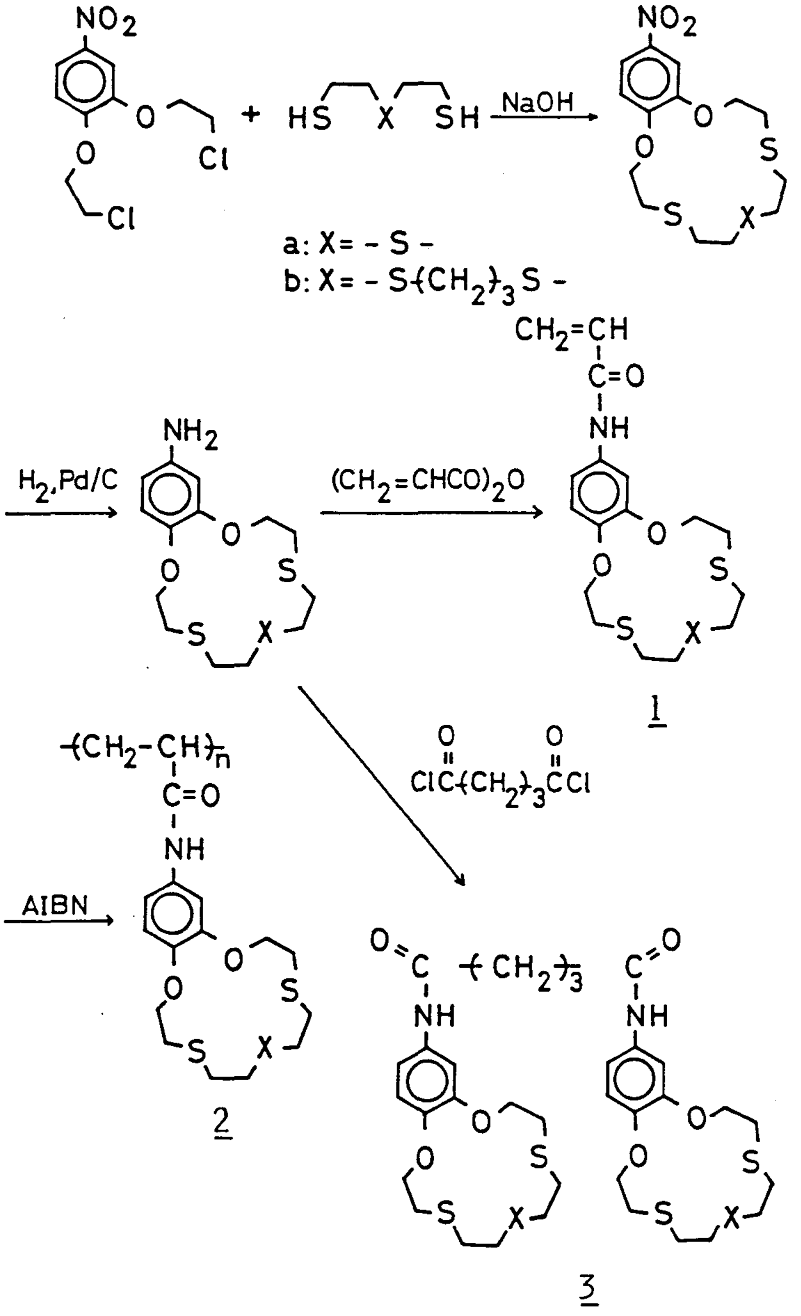
Conductometric Measurements

The conductivity of the silver nitrate-thiacrown ether acetone solution was measured at 25.0 ± 0.1 °C using a conductometer of CM-2A type of TOA Electric Co., Ltd. The concentrations were (1 - 3) x 10^{-4} M for thiacrown ether and 1 x 10^{-4} M for silver nitrate, the molar ratio of thiacrown to metal being changed from 0 to 3. In the case of bis(thiacrown ether)s, chloroform/acetone(2/3) was employed as the solvent. The cell constant was 0.995 cm^{-1}.

Results and Discussion

Syntheses of Poly- and Bis(thiacrown Ether)s

The synthetic process for the thiacrown ether monomer and poly- and bis(thiacrown ether)s is shown in Scheme I-I. There may be various synthetic routes to the thiacrown ether besides Scheme I-I, but they often suffer from some problems. For instance, if 4-nitrocatechol is used instead of 1,2-bis(2'-chloroethoxy)-4-nitrobenzene for the cyclization to the thiacrown ethers, one must treat it with 1,13-dichloro-4,7,10-trithiatridecane, which contains mustard-gas-like structure. Though nitration of benzocrown ethers by nitric acid is generally easy to proceed, it failed in the case of these thiacrown ethers. It is probably because nitric acid oxidizes the sulfur atoms to sulfide, which results in the scission of C-S linkage. On the other hand, the reactions in Scheme I-I proceeded successfully. Catechol was derivatized to the 1,2-bis(2'-chloroethoxy)benzene, and then nitrated quantitatively. Ethanol was chosen as the solvent of the cyclization to the benzothiacrown ether. Since the 1,2-bis(2'-chloroethoxy)-4-nitrobenzene is practically insoluble in ethanol at room temperature, the cyclization reaction was performed at 50 °C. The yields of the cyclization did not exceed 50% for both of the nitrobenzothiacrown ethers. Reaction temperature higher than 70 °C and reaction times longer


NO2
NaOH
a: X= - S -
b: X= - S(CH2)3S -
H2,Pd/C
NH2
(CH2=CHCO)2O
CH2=CH
C=O
NH
1
ClC(CH2)3CCl
AIBN
(CH2-CH)n
2
3

Scheme I-I

than 2 h produced more viscous by-products, decreasing the cyclization yields. Especially, in the thiacrown ethers containing four-ring sulfur atoms, nitrobenzo-tetrathia-19-crown-6, more viscous by-products, such as polysulfides, were obtained than in nitrobenzo-trithia-15-crown-5. The nitrobenzothiacrown ethers were reduced to the amino derivatives on palladium carbon. If the absorption of hydrogen gas stopped before completing the reduction due to poisoning of palladium carbon, additional amounts of palladium carbon were added. The resulting aminobenzothiacrown ether is labile to air oxidation, which was therefore subjected to the following condensation with acrylic anhydride without isolation. Since acrylamide-type monomers (**1a**) and (**1b**) easily polymerize by heating, the workup in the condensation reaction was performed at room temperature. The thiacrown ether monomers were polymerized radically by α,α'-azobisisobutyronitrile in a degassed, sealed tube. The molecular weight of the resulted poly(thiacrown ether)s was determined by

TABLE I-1

Solubilities of mono-, poly-, and bis(thiacrown ether)s at 25.0 ^{o}C

Solvent	**1a**	**2a**	**3a**	**1b**	**2b**	**3b**
Acetone	High	Good	Poor	High	Good	Poor
Chloroform	Fair	Fair	Good	Fair	Fair	Good
Ethanol	Good	Poor	Poor	Good	Poor	Poor
Tetrahydrofuran	Good	Poor	Poor	Good	Poor	Poor
Dioxane	Good	Poor	Poor	Good	Poor	Poor
Dichloromethane	Good	Good	Poor	Good	Good	Poor
Nitrobenzene	High	High	Good	High	High	Good
Toluene	Poor	Poor	Poor	Poor	Poor	Poor
Dimethylformamide	Fair	Fair	Good	Fair	Fair	Good
Diethylether	Poor	Poor	Poor	Poor	Poor	Poor
Dimethylsulfoxide	Fair	Fair	High	Fair	Fair	High

GPC, being about 2700 in terms of polystyrene for (**2a**) and about 2300 for (**2b**). In order to obtain poly(thiacrown ether)s with higher molecular weight, various polymerization conditions were attempted. The higher molecular weight of polymers could, however, not be attained. One possible reason for the low molecular weight of the poly(thiacrown ether)s is the existence of sulfur atoms in the monomer. The sulfur atoms might work as a chain transfer reagent like thiol derivatives. The solubility of the monomers, polymers, and dimers are shown in Table I-1. Chloroform is one of the best solvents for the thiacrown ether compounds. The bis(thiacrown ether)s were inferior in solubility to the corresponding polymers and monomers.

Cation-Binding Properties

It is likely that crown ethers complex hard cations such as alkali or alkaline-earth metal ions. However, thiacrown ethers, in which some or all of the oxygen atoms in crown ethers are replaced by sulfur atoms, are expected to possess affinity for soft cations such as transition or heavy metals. Also the cation-complexing selectivity depends on the cavity size or kinds of donor atoms in the crown rings. For screening of the cation-binding abilities of poly- and bis(thiacrown ether)s, (**2**) and (**3**), solvent extraction of various metal ions was carried out with them. The results of solvent extraction in a chloroform/water solvent system are shown in Table I-2. It should be noted that the poly- and bis(thiacrown ether)s extract Ag^+ effectively. This is also the case for the corresponding monocyclic analogs, but the poly- and bis(thiacrown ether)s are higher in the extractability for Ag^+ than the corresponding monocyclic analogs. The poly- and bis(thiacrown ether)s also possess great affinity for Hg^{2+}. The Hg^{2+} complexes of the poly(thiacrown ether)s are, however, quite insoluble in either the organic phase or the aqueous phase, being almost precipitated. This complex precipitation may be in favor of the apparent percent extraction. In contrast, the monocyclic analogs can hardly extract the ion, unlike the case of Ag^+. That is to say, the Hg^{2+} binding is specific to the poly- and bis(thiacrown ether)s, not to the monocyclic analogs. Alkali and alkaline-earth metal ions were hardly extracted by the thiacrown ethers (percent extraction of less than 1.0% for Na^+, K^+, and Ca^{2+}), although poly- and bis(crown ether)s not containing sulfur atoms in the crown rings are excellent extracting reagents for

TABLE I-2

Percent extraction of various kinds of metals by use of thiacrown ethers[a]

ThiaCr / Metals	Percent extraction[b] (%)					
	1a	2a	3a	1b	2b	3b
Cu^{2+}	0.0	0.8	0.6	0.2	1.5	0.7
Ag^+	70.3	90.6	86.7	71.6	90.6	88.4
Zn^{2+}	0.4	1.4	1.3	0.4	2.1	1.5
Hg^{2+}	0.0	90.4[c]	25.1	0.0	90.4[c]	25.3
Pb^{2+}	0.9	1.5	1.5	1.3	1.5	1.5

[a] [Thia Cr]/[M] = 5×10^{-5} M/1×10^{-5} M.

[b] Determined from the decrease of the metal ions concentration in the aqueous phase.

[c] Precipitates are formed at the interphase between the organic and aqueous phases. The values of percent extraction are, therefore, apparent ones.

alkali and alkaline-earth metal.[3] Also, the poly- and bis(thiacrown ether)s and the monocyclic analogs were ineffective in extraction of transition metals and the other heavy metals. For instance, the values of the percent extraction for Cd^{2+}, Co^{2+}, Pd^{2+}, and Fe^{3+} were less than 1.0%. Thus, the poly- and bis(thiacrown ether)s are highly selective for Ag^{+} and Hg^{2+}, and the monocyclic analogs for Ag^{+}.

Cation-binding abilities of thiacrown ethers have been so far investigated by using monomeric and immobilized thiacrown ethers. Pedersen[9] has carried out extraction of K^{+}, Na^{+}, and Ag^{+} by using monomeric thiacrown ethers in which some of the ring oxygens in benzo-15-crown-5 are replaced by sulfur atoms. Tomoi et al.[11] have also reported that Cu^{2+}, Ag^{+}, and Cd^{2+} ions were extracted by immobilized thiacrown ethers in which several thiacrowns containing only sulfur atoms as the ring heteroatom were immobilized on chloromethylated crosslinked polystyrene. The results have shown that those thiacrown ether derivatives are able to fairly bind metal ions other than Ag^{+}. The ion selectivities of the previous thiacrown ethers are, therefore, quite different from those for thiacrown ethers employed here.

The complex formations between $AgNO_3$ and bis(thiacrown ether)s (**3a**), (**3b**) and the monomeric analogs (**1a**), (**1b**) were investigated conductometrically. Molar conductivity (Λ) of $AgNO_3$ in acetone is rather low due to the strong association of the cation and anion. The molar conductivity increases with the complex formation because the dissociation of silver nitrate occurs by forming crown-metal complexes. In the case of stable complex formation, the stoichiometry of the complex was obtained from the [Cr]/[M] ratio at the break point. The values of molar conductivities were plotted against the ratios of thiacrown ether unit to Ag^+(Figs. I-1 and I-2). The plot for the monomeric thiacrown ether **(1)**reveals a sharp break point at 1:1 thiacrown to cation ratio, indicating the formation of 1:1 crown ether to Ag^+ complex. In the molar conductivities of the bis(thiacrown ether)s (**3a**), the break occurs at 2:1 thiacrown to cation ratio. Although the discontinuous conductivity change is not yet understood in the (**3a**) system, the clear break at the [Cr]/[M] ratio of 2 suggests that bis(thiacrown ether)s (**3a**) forms 2:1 thiacrown to Ag^+ complexes under conditions where an excess of the thiacrown ether is present, like the present solvent extraction condition. In contrast, the Λ value for the bis(thiacrown ether)s (**3b**) was increased gradually and a breaking point was observed at 1:1 thiacrown to cation ratio. The results indicate a 1:1 stoichiometry of crown ether unit and Ag^+ for the silver-(**3b**) complex. The poly(thiacrown ether)s may be considered to form Ag^+ complexes with the same stoichiometries as the corresponding bis(thiacrown ether)s. In the previous benzocrown ethers not containing sulfur atoms the easy formation of the sandwich-type 2:1 complex led to the high extractability of the poly- and bis(benzocrown ether)s. However, in the poly- and bis(thiacrown ether)s, (**2a**) and (**3a**), such drastic effects are not attained, probably because the high affinity of sulfur atoms for Ag^+ may surpass the bis(thiacrown ether)s effect on the complex formation. On the other hand, in the Hg^{2+} complexes of the thiacrown ethers, any information about the complex

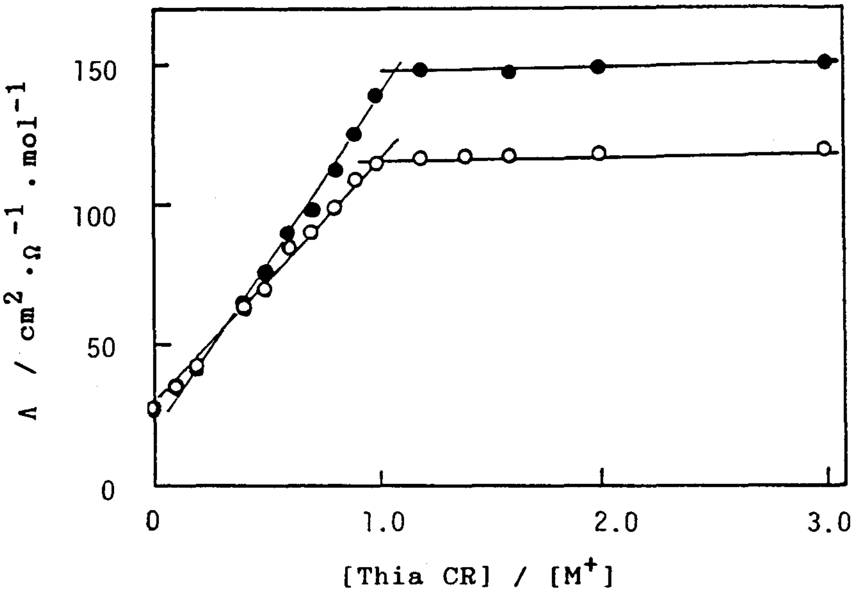


Figure I-1. Plot of molar conductivity versus the ratio of [mono-thiacrown ether] to [silver salt]: (○)(**1a**)-$AgNO_3$, (●)(**1b**)-$AgNO_3$.

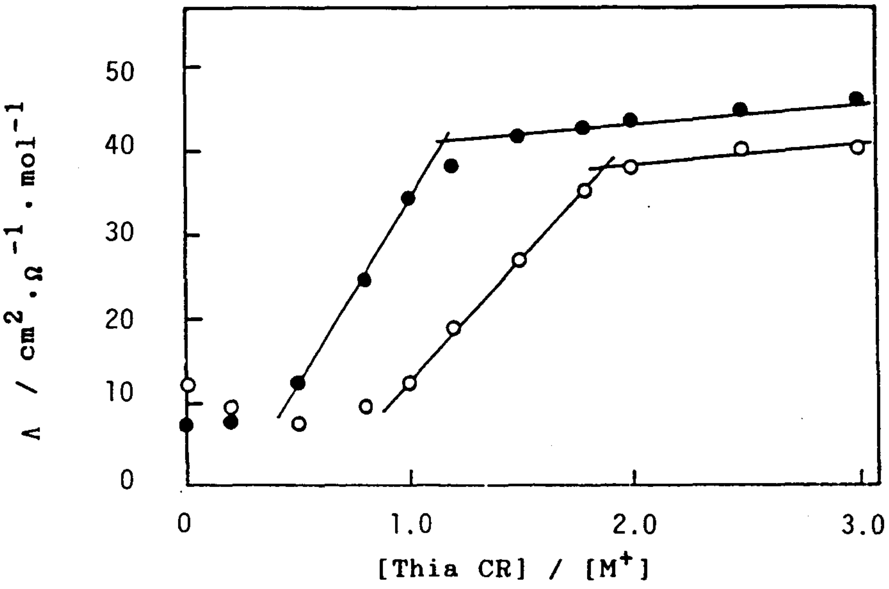


Figure I-2. Plot of molar conductivity versus the ratio of [crown ether ring] to [silver salt] for the bis(thiacrown ether)s systems:(○)(**3a**)-$AgNO_3$, (●)(**3b**)-$AgNO_3$.

stoichiometry was not obtained by the conductivity measurements due to the precipitate formation. However, taking account of the fact that only the poly- and bis(thiacrown ether) derivatives can bind Hg^{2+} strongly, some bis(crown ether)s effect might occur on complexing Hg^{2+}.

Summary

Poly- and bis(thiacrown ether) derivatives in which some oxygen atoms of benzocrown ether moiety are replaced by sulfur atoms have been synthesized. Their cation-binding abilities have been investigated by using the solvent extraction method. The poly- and bis(benzothiacrown ether)s showed great affinity for silver ion, being more excellent in the affinity than the corresponding monocyclic analogs. They, however, possess very poor cation-binding ability for alkali and alkaline-earth metal ions. The poly- and bis(thiacrown ether)s also bind mercuric ion effectively, whereas the corresponding monomeric analogs do not at all.

References

1. S. Kopolow, T. E. Hogen Esch, and J. Smid, *Macromolecules*, 6, 133(1973).
2. K. Kimura, T. Maeda, and T. Shono, *Talanta*, **26**, 945(1979).
3. T. Maeda, M. Ouchi, K. Kimura, and T. Shono, *Chem. Lett.*, **1981**, 1573.
4. K. Kimura, T. Maeda, and T. Shono, *Anal. Lett.*, **A11**, 821 (1978).

5. T. Maeda, K. Kimura, and T. Shono, *Z. Anal. Chem.*, **298**, 363 (1979).

6. W. Rosen, and D. H. Busch, *J. Am. Chem. Soc.*, **91**, 4694(1969).

7. J. S. Bradshaw, B. L. Haymore, R. M. Izatt, and J. J. Christensen, *J. Org. Chem.*, **40**, 1510(1975).

8. K. Saito, Y. Masuda, and E. Sekido, *Anal. Chim. Acta*, **151**, 447(1983).

9. C. J. Pedersen, *J. Org. Chem.*, **36**, 254(1971).

10. L. Dario, M. Fernando, and R. Franco, *Synthesis*, **1978**(3), 223.

11. M. Tomoi, O. Abe, N. Takasu, and H. Kakiuchi, *Makromol. Chem.*, **184**, 2431(1983).

12. G. B. Butler, and Q. S. Lien, *Am. Chem. Soc. Symp. Ser.*, **195**, 149(1982).

13. B. Peter, and W. Peter, *GWXXB Ger. Offen*, No. 2934948, 34 (1981).

CHAPTER II

Liquid-Liquid Extraction of Silver Ion with Benzothiacrown Ether Derivatives

Introduction

The liquid-liquid extraction of heavy and transition metals by poly- and bis(thiacrown ether) derivatives has been already described in chapter I and has proved to be efficient and highly selective for Ag^+. This chapter is concerned with the applications of extraction to Ag^+ recovery from several artificial samples, which are binary and quaternary metal ion systems, and from actual copper ore.

Experimental

Chemicals

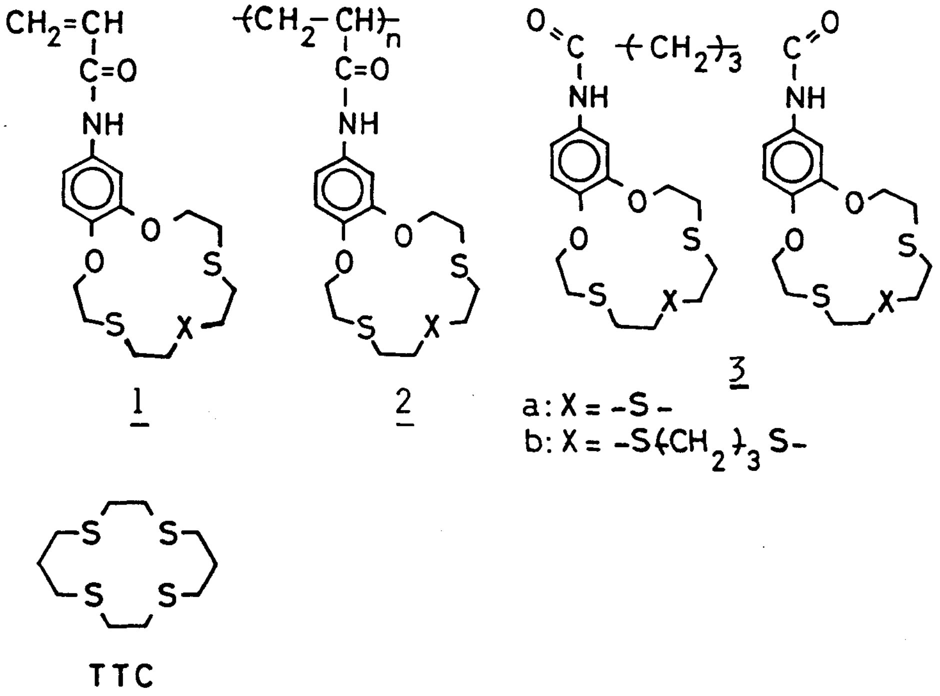
Benzothiacrown ether derivatives employed as extraction reagents have been already described in chapter I. 1,4,8,11-Tetrathiacyclotetradecane (TTC) was synthesized by a method similar to that of Rosen and Busch.[1] Metal nitrates were used for extractions (Wako Pure Chemicals).

Liquid-Liquid Extraction

The procedure was as noted in chapter I. Equal volumes(10 ml) of an aqueous solution of 1×10^{-5} M metal nitrate and 1×10^{-4} M picric acid and a chloroform solution of 5×10^{-5} M (for monomeric unit) benzothiacrown ether derivatives were placed into a stoppered flask. The stoppered flask was shaken for 40 min at 25.0 ± 0.1 °C. After complete phase separation, the metal ion concentration in the aqueous phase was determined by flame emission or atomic absorption spectrometry (A-185 Jarrel Ash Co., Ltd). When the percent extraction was small, the metal ion concentration was quantified in the organic phase; the organic phase was evaporated, the residue was dissolved in 10 ml of 6 N HNO_3, and the metal ion was determined as before mentioned.

Selective Separation of Ag^+ from Mixtures Containing Hg^{2+}, Zn^{2+}, Cu^{2+}, Pb^{2+}, Fe^{3+}, and Bi^{3+}

Extraction was carried out from an aqueous solution containing 1 x 10^{-5} M Ag^+, appropriate concentrations of the



Scheme II-I

interfering ions, and 1 x 10^{-4} M picric acid into a chloroform solution of 5 x 10^{-5} M (for monomeric unit) benzothiacrown ether derivatives. The ratio of the interfering ions over Ag^+ in the aqueous phase was 10 for the binary metal ion systems and 1 for the quaternary system.

Silver Recovery from a Copper Ore

A copper ore sample from South America, which was a gift from Mitsubishi-Kinzoku Co., Ltd, was employed here. This sample contains about 80 g silver per ton after drying. Dry copper ore (5.03 g) was ground finely in a mortar and then stirred with 10 ml of concentrated HNO_3 at room temperature until no further dissolution occurred. The residual insoluble material was filtered off. The filtrate was diluted 1000-fold with deionized water. Silver ion was extracted from a 10-ml aliquot as described above but without picric acid present. In some cases, after the Ag^+ determination, a further 5 ml of the diluted aqueous solution was again extracted with 5 ml of the chloroform solution of the reagent.

Results and Discussion

Liquid-Liquid Extraction

Previously, silver picrate was extracted efficiently by poly- and bis(thiacrown ether)s (2) and (3), while silver nitrate was extracted only slightly. Thus the cation extraction by the thiacrown ether derivatives depended on the counter anion and picrate was better than nitrate as the anion. However, for practical applications, one cannot consider only pure metal picrates. Therefore, picric acid was added to aqueous silver nitrate solutions to increase the percent extraction. Figure II-1 shows the relationship between picric acid concentration in the aqueous phase and Ag^+ percent extraction by compound (**2a**). Without picric acid, the percent extraction for Ag^+ was very low. Increasing picric acid concentrations enhanced the Ag^+ extraction and the percent extraction became constant (at about 90%) at a [picric acid]/[metal] ratio of about 8; a ratio of 10 was adopted routinely.

With that ratio of picric acid, various metal ions were extracted by using the thiacrown ethers with the results shown in

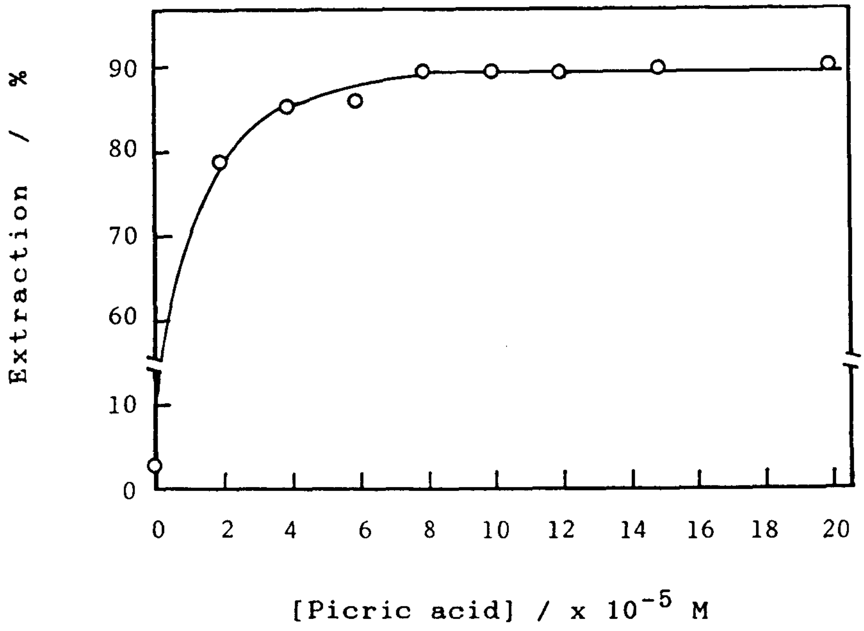


Figure II-1. Relationship between silver extraction and picric acid concentration in extraction with poly(thiacrown ether)s (**2a**). Silver ion concentration 1 X 10^{-5} M; crown ether unit concentration 5 X 10^{-5} M.

Table II-1. For comparison, TTC was also tested. Silver(I), Hg^{2+}, and Pd^{2+} were extracted by TTC, the percent extraction being 52.7, 33.3, and 27.3%, respectively. The other heavy or transition metals, and alkali and alkaline-earth metal ions were

TABLE II-1

Extraction of various metal ions by thiacrown ethers[a]

Metals	Percent extraction[b] (%)						
	1a	**2a**	**3a**	**1b**	**2b**	**3b**	TTC
Na^+	0.4	0.6	0.3	0.6	1.0	0.4	0.0
K^+	0.2	0.4	0.1	0.3	0.3	0.2	0.5
Ca^{2+}	0.0	0.6	0.0	0.0	0.8	0.0	0.8
Fe^{3+}	0.1	0.4	0.3	0.1	0.3	0.3	2.8
Co^{2+}	0.1	0.1	0.3	0.0	0.2	0.3	8.3
Cu^{2+}	0.0	0.8	0.6	0.2	1.5	0.7	7.1
Ag^+	70.3	90.6	86.7	71.6	90.6	88.4	52.7
Zn^{2+}	0.4	1.4	1.3	0.4	2.1	1.5	10.0
Cd^{2+}	0.0	0.2	0.2	0.1	0.4	0.5	2.6
Hg^{2+}	0.0	90.4[c]	25.1	0.0	90.4[c]	25.3	33.3
Pb^{2+}	0.9	1.5	1.5	1.3	1.5	1.5	5.0
Pd^{2+}	0.0	0.0	0.0	0.0	0.0	0.0	27.3

[a] [ThiaCr unit]/[Metal] = 5×10^{-5} M/ 1×10^{-5} M. In IUPAC nomenclature, **1a** is 2,3-(4'-acryloylaminobenzo)-1,4-dioxa-7,10,13-trithiacyclopentadeca-2-ene. **2a** is poly[2,3-(4'-acryloylaminobenzo)-1,4-dioxa-7,10,13-trithiacyclopentadeca-2-ene]s. **3a** is 1,3-bis[(3',4'- benzo-1",4"- dioxa-7",10",13"- trithiacyclopentadeca-2"-ene)aminocarbonyl]propane. **1b** is 2,3-(4'-acryloylaminobenzo)-1,4-dioxa-7,10,14,17-tetrathiacyclononadeca-2-ene. **2b** is poly[2,3-(4'- acryloylaminobenzo)-1,4-dioxa-7,10,14,17-tetrathiacyclononadeca-2-ene]s. **3b** is 1,3-bis[(3',4'-benzo-1",4"-dioxa-7",10",14",17"- tetrathiacyclononadeca-2"- ene)aminocarbonyl]propane.

[b] Evaluated from the metal ion concentration in the aqueous phase.

[c] Some precipitate was formed at the interface between organic and aqueous phases. The values of percent extraction are, therefore, apparent ones.

scarcely extracted. These results are supported by the affinity of thiacrown ethers, but TTC does not possess high ion selectivity for soft metal ions. In contrast, benzothiacrown ether derivatives (1)-(3)(a,b) showed excellent selectivities for Ag^+ and Hg^{2+}. Though the extraction abilities of the monocyclic thiacrown ethers are lower than those of the poly and bis derivatives, the mono derivatives are more selective for silver than the poly or bis compounds. The high affinity of the poly- and bis(thiacrown ether)s for Ag^+ and Hg^{2+} can be explained by the fact that the thiacrown ethers easily form 2:1(crown ether unit to cation) sandwich-type complexes which are more favorable than the 1:1 complexes for extraction.

Silver Ion Separation from Binary and Quaternary Metal Systems

Silver in actual samples often co-exists with Cu^{2+}, Zn^{2+}, or Pb^{2+}. Recovery of silver from silver-containing products(silver plate, batteries, jewel work, silver solder, photo materials, etc.) is now often used to conserve source materials. Separation of silver from such materials is difficult because of variety of materials.

It is clear that the benzothiacrown ether derivatives tested are efficient extractants for Ag^+ alone. To establish their behavior in the case of binary and quaternary cation systems containing silver and other heavy or transition metals, tests were made with various other metal ions present.

For the binary systems with Ag^+ and Cu^{2+}, Zn^{2+}, or Pb^{2+}(Table II-2), the extraction efficiency for Ag^+ did not vary much for the poly- and bis(thiacrown ether)s, but the monocyclic compounds were less effective than for silver alone. However, mercury(II) ions had a disastrous effect on all the Ag^+ extractions; compounds (**2a**), (**2b**), and (**3b**) extracted only Hg^{2+} from the binary mixture. This might be partly due to the formation of the 2:1 (thiacrown unit to Hg^{2+}) complex, which is apt to precipitate irreversibly in these systems. The silver separations from Cu^{2+}, Zn^{2+}, and Pb^{2+} in the binary systems were reasonably effective at 10:1 of M^{2+}/Ag^+ ratios.

TABLE II-2

Selective extraction of silver ion from binary cation systems[a]

Thiacrown ether	Percent extraction (%)							
	Ag^+	Cu^{2+}	Ag^+	Zn^{2+}	Ag^+	Pb^{2+}	Ag^+	Hg^{2+}
1a	39.7	0.1	33.0	7.0	37.8	1.1	1.3	0.5
2a	94.9	1.2	96.9	8.4	99.2	1.9	1.3	45.2
3a	96.2	0.6	96.3	4.7	97.2	1.9	0.0	0.6
1b	91.0	0.8	87.5	6.7	91.9	1.2	0.0	0.6
2b	97.4	1.6	98.2	6.1	99.2	1.9	0.0	47.6
3b	97.4	1.1	97.3	4.7	97.6	1.9	0.0	35.5

[a] $[MNO_3] = 1 \times 10^{-4}$ M, $[AgNO_3] = 1 \times 10^{-5}$ M, [crown ether unit concentration] = 5×10^{-5} M.

TABLE II-3

Selective extraction of silver ion from quaternary cation systems[a]

Thiacrown ether	Percent extraction (%)			
	Ag^+	Cu^{2+}	Fe^{3+}	Bi^{3+}
1a	40.7	0.3	0.9	0.1
2a	80.6	0.3	0.8	0.2
3a	73.8	2.0	1.4	0.3
1b	70.8	1.4	0.0	0.1
2b	83.7	0.4	1.0	0.2
3b	73.8	1.6	1.0	0.2

[a] $[MNO_3] = 1 \times 10^{-5}$ M, [crown ether unit] = 5×10^{-5} M.

In the quaternary system with Ag^+, Cu^{2+}, Fe^{3+}, and Bi^{3+}(Table II-3), there were no remarkable differences in the silver extraction ability compared with extractions of silver alone, and selectivity was good. These results suggest that even in the quaternary cation system, Ag^+ is also extracted selectively by the poly- and bis(thiacrown ether) derivatives.

Silver Ion Separation from Copper Ore

Separation of silver from copper ores, which generally contain a small quantity of silver, by using of the benzothiacrown ether derivatives was examined. Picric acid was not added because extraction of Ag^+ as the picrate proved to be impractical. Sevdić et al.[2] reported that a high concentration of acid in the aqueous phases enhances cation extraction with thiacrown ether derivatives. Therefore, the copper ore was dissolved in concentrated HNO_3 and then this solution was diluted with water. Table II-4 shows the results. Extraction was carried out twice successively from the aqueous phase. Although

TABLE II-4

Silver extraction from copper ore sample[a]

Thiacrown ether	First extraction (%)		Second extraction (%)	
	Ag^+	Cu^{2+}	Ag^+	Cu^{2+}
1a	6.0	2.8	—	—
2a	19.9	3.7	73.8	0.9
3a	14.3	2.9	66.7	0.7
1b	13.6	2.8	—	—
2b	14.7	3.7	68.8	1.4
3b	17.1	3.3	52.6	1.1

[a] The concentration ratio of Cu^{2+}/Ag^+ in the copper ore was about 5 X 10^3. Picric acid was not added.

the ratio of Cu^{2+} over Ag^+ was about 5 x 10^3 in the original sample, Ag^+ was extracted to the extent of 6-20% in the first extraction. Only a little copper was extracted with any of the reagents. The percent extraction of Ag^+ was 52.6-73.8% with the poly and bis derivatives in the second extraction. A maximum of about 80% total extraction of Ag^+ was attained. Thus the poly(thiacrown ether)s are quite promising for selective silver extraction from copper ore samples.

Summary

The extraction behavior of mono-, poly-, and bis(benzothiacrown ether)s was studied for alkali, alkaline-earth, heavy, and transition metal ions in the presence of picrate anion. These thiacrown ether derivatives show high selectivity for silver ion. Silver ion extraction from binary and quaternary mixtures of silver with heavy or transition metal ions was successful, except for mixtures with mercury(II) ion. Silver can be extracted successfully from a copper ore with ca. 80% recovery.

References

1. W. Rosen and D. H. Busch, *J. Am. Chem. Soc.*, **91**, 4694(1969).
2. D. Sevdić, Lj. Jovanovac and H. Meider-Gorican, *Mikrochim. Acta*, **1975**, 235(1975).

CHAPTER III

Extraction-Spectrofluorimetric Determination of Silver Ion by Using Benzothiacrown Ether and Eosin

Introduction

Ion-pair extraction systems with ternary complex formation among a metal ion, a neutral crown ether, and a chromogenic counter anion or with binary complex formation of a metal ion and an anionic chromogenic crown ether, are useful for the spectrophotometric determination of the metal ions.[1-4] The spectrofluorimetric determination of K^+ based on ion-pair extraction using a chromogenic counter ion has been attempted by using dibenzo-18-crown-6 and anilinonaphthalene sulfonate by Kina et al.,[5] and using 18-crown-6 and eosin by Sanz-Medel et al.[6] Similarly, Pb^{2+} was determined with 18-crown-6 and eosin.[7] Spectrofluorimetry using crown ethers has also been studied in order to increase the precision of the determination of cations. Nakashima et al.[8] reported the fluorimetry of Li^+ using a Li^+-selective fluoroionophore, in which a fluorescent group is introduced to a crown ring. El-Ghamry et al.[9] have determined 100 p.p.b. of silver ion spectrophotometrically by using a ternary complex system of silver ion, ligand and 2,4,5,7-tetrabromofluorescein.

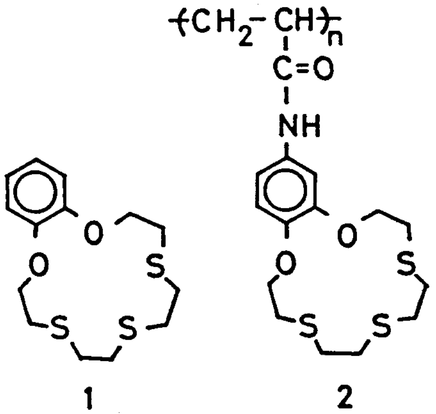
The author has already found that benzothiacrown ethers, in which some oxygen atoms in benzocrown ethers were replaced with sulfur atoms, possess high selectivities for silver ion in cation extraction. This chapter deals with extraction-spectrofluorimetric determination of trace amounts of silver ion by using benzothiacrown ether as the extractant and eosin as the fluorescent anion. The determination of silver ion in river water is described as a practical application of this extraction-fluorimetric method.

Experimental

Chemicals

All chemicals were of analytical-reagent grade and purchased from Wako Pure Chemicals. Demineralized and distilled water was used. Chloroform, 1,2-dichloroethane, and dichloromethane were distilled before use. The standard solution for fluorescence intensity, I_F, measurements was 5 x 10^{-5} M quinine sulfate in 0.5 M H_2SO_4. Eosin Y (2,4,5,7-tetrabromofluorescein, sodium salt) was dissolved in water to give a 9.27 x 10^{-4} M solution.[10] The metal nitrate concentrations ranged from 9.27 x 10^{-3} to 9.27 x 10^{-6} M. For the buffer solutions, 0.033 M and 0.1 M KH_2PO_4, 0.033 M $Na_2HPO_4 \cdot 12H_2O$, 0.05 M $Na_2B_4O_7 \cdot 10H_2O$, and 0.05 M Na_2CO_3 solutions were prepared. The pH 8.6 buffer was prepared by mixing 3.40 ml of 0.1 M KH_2PO_4 and 6.60 ml of 0.05 M $Na_2B_4O_7 \cdot 10H_2O$ solutions.

Benzothiacrown ether, 2,3-benzo-1,4-dioxa-7,10,13-trithiacyclopentadeca-2-ene and the corresponding poly(benzothiacrown ether)s, were synthesized according to the above described methods in chapter I. The benzothiacrown ether was identified as follows: Yield, 65%; colorless crystals; mp 98.5-100 ^{o}C; IR(KBr) 2900(CH), 1500(CH), 1060 cm^{-1}(COC); ^{1}H-NMR($CDCl_3$,δ) 2.8-3.1 (12H,



1 **2**

Scheme III-I

m,CH_2S), 4.2-4.4(4H,t,CH_2O), 6.9-7.0(4H,s,aromatic); MS, m/e 316; Anal. Calcd for $C_{14}H_{20}S_3O_2$: C,53.13%; H,6.37%; S,30.39%. Found: C,52.99%; H,6.33%; S,30.22%.

General Procedure for Extraction-Spectrofluorimetry

An aqueous solution with a total volume of 5 ml was prepared by pipetting 0.1 ml of 9.27×10^{-4} M eosin solution, 1.8 ml of buffer solution, 0.1 ml of 1-20 p.p.m. $AgNO_3$ solution, and 3 ml of water into a stoppered flask. After adding 5 ml of a 5×10^{-6} M solution of benzothiacrown ether or poly(benzothiacrown ether)s (for a crown ring unit) in dichloromethane to the flask, the contents were shaken vigorously and then allowed to stand for a few minutes until the two phases had completely separated. A small portion of organic phase was placed in a 1-cm quartz cell for fluorescence measurements, which was carried out using a Hitachi 885 Spectrofluorimeter. The band pass was adjusted to 5 nm for both the excitation and emission waves. The I_F values were measured immediately at an emission wavelength of 558.8 nm with an excitation wavelength of 536.0 nm. A reagent blank solution containing no silver ion was prepared similarly. When examining the effect of foreign ions, the above procedure was also followed, except that an appropriate solution of the foreign ions was additionally added. For the determination of silver ion in river water, 0.1 ml of a Yodo river sample was placed in a stoppered flask and then artificially spiked by adding appropriate amounts of silver ion.

Results and Discussion

Effect of Solvents

Extraction of silver ion was carried out by using benzothiacrown ethers (1) and (2) as the extractant and eosin Y as the fluorescent counter anion. Chloroform, 1,2-dichloroethane, and dichloromethane were tested as solvents for the ion-pair extraction and the order of extractability of silver ion was dichloromethane > chloroform > 1,2-dichloroethane. Poor extractability was observed with 1,2-dichloroethane and chloroform showed poor reproducibility at low silver ion concentrations. In contrast, not only the fluorescence intensity of the complex, but also that of the reagent blank was high in dichloromethane and the difference between the intensities of the complex and reagent blank was large and clear. Dichloromethane, therefore, seemed to be the most suitable extraction solvent.

Absorption and Emission Spectra

Representative excitation and emission spectra of the blank and the Ag^+-benzothiacrown ether-eosin ion-pair complex extracted into the dichloromethane phase from the aqueous phase at pH 8.6 are shown in Figure III-1. When the excitation spectrum was measured from 220 nm at a fixed emission wavelength of 558.8 nm, only one absorption peak appeared at 536.0 nm. The emission peak was at 558.8 nm when the excitation wavelength was fixed at 536.0 nm. The reagent blank spectrum based on eosin extracted into the dichloromethane phase without complex formation was similar to the spectrum of the ion-pair complex. As the I_F of reagent blank was not zero, the detection limit in this spectrofluorimetric determination depends on the I_F difference between the ion-pair complex and the reagent blank. It seems

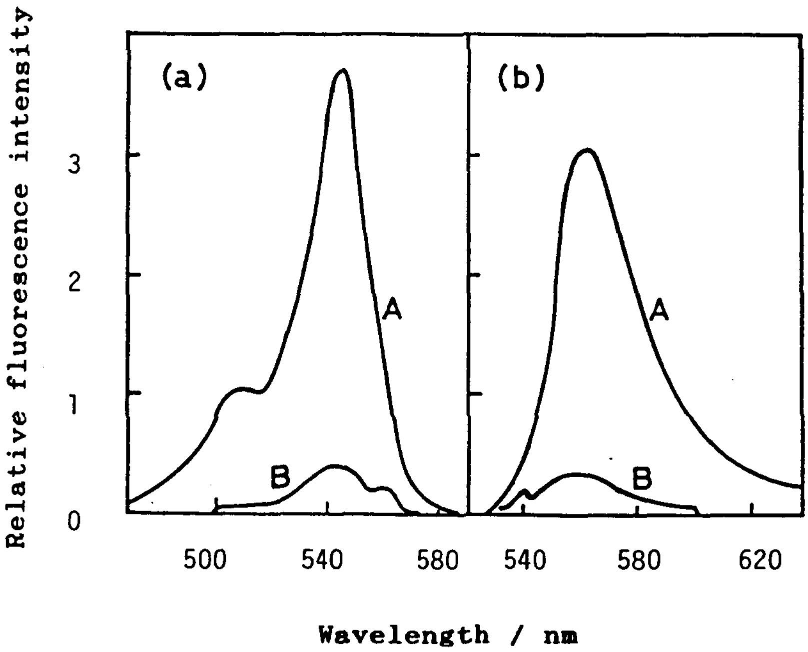


Figure III-1. (a)Excitation and (b)emission spectra for (A)ion-pair complex of benzothiacrown ether and (B)reagent blank.

necessary to prepare the eosin Y solution freshly each day in order to obtain large differences in I_F and a high reproducibility.[11,12] If not, the I_F of the ion-pair complex was not always reproducible in the extraction of the Ag^+-eosin complex.[8] The I_F values for the poly(benzothiacrown ether)s system were slightly higher than those for the monomeric benzothiacrown ether (1), but large differences in I_F were not observed when equimolar concentrations of the crown ring unit were employed.

Effect of pH

The pH of the aqueous phase is an important factor for the ion-pair extraction. It has been reported that fluorescein in an aqueous phase undergoes the pH-dependent formation of four ionic types, that is, cationic, electrically neutral, monoanionic and dianionic,[13,14] and that the cationic form of fluorescein appears at ca. pH 1 and the dianionic form at pH 12. Eosin, which is tetrabrominated fluorescein, is also expected to assume different forms at different aqueous phase pH. The relationship between pH and I_F is shown in Figure III-2. For each of the pH ranges 5.0-8.0, 8.0-9.0, and 9.0-11.0, buffer solutions were used. The I_F versus pH graphs in the pH range 5.0-11.0, at which eosin is considered to be neutral or monoanionic, exhibit a reversed U-shape with a maximum at pH 8.0-9.0 for both the benzothiacrown ether and the polymeric analogue.

Calibration Graph

Linearity of the calibration graph was studied at pH 8.6 [0.1 M KH_2PO_4-0.05 M $Na_2B_4O_7 \cdot 10H_2O$(34.0+66.0)]. Below 100 p.p.b.

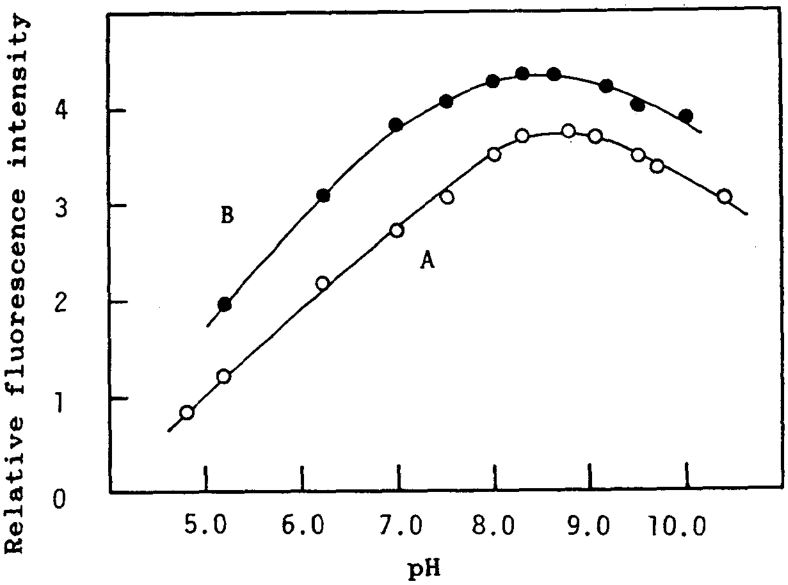


Figure III-2. Relationship between pH and relative fluorescence intensity for (A)benzothiacrown ether and (B)poly(thiacrown ether)s.

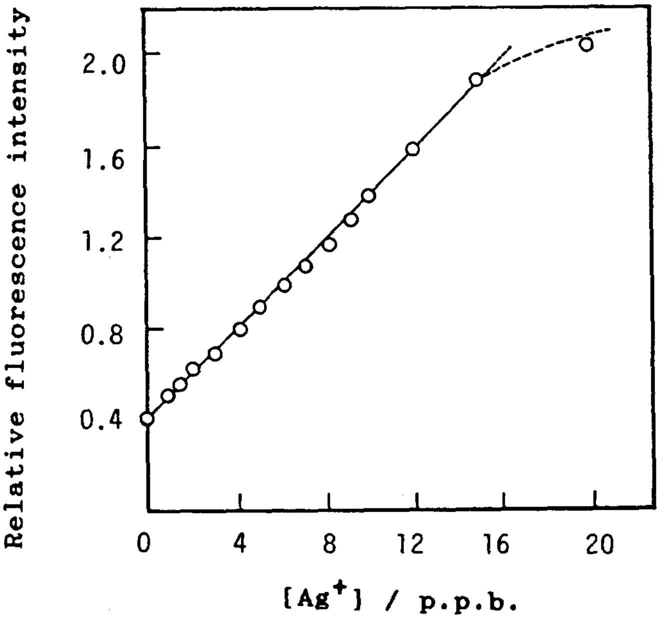


Figure III-3. Calibration graph for the fluorimetric determination of silver ion.

of silver ion the calibration graph showed good linearity and above this level I_F hardly increased with increasing concentration of silver ion. More detailed examination of the measurement concentration range showed that the detection limit of silver ion is 1 p.p.b. and that between 2 and 15 p.p.b. the calibration graph possesses good linearity(Figure III-3). The linear calibration graph did not pass through the origin, because eosin was distributed into the organic phase from the aqueous phase even without any silver ion present in the aqueous phase.

The concentration ratio of eosin to silver ion was adjusted to 10-100, as in the extraction method described in chapter I. At eosin to Ag^+ ratios below 10 or over 100, poor stability and reproducibility of the fluorescence were observed. The concentration ratio of benzothiacrown ether to silver ion was 5, being the same as described in chapter I.

Extractions were performed in two ways, viz., a mixture of aqueous and organic phases was shaken for 40 min at 25.0 ± 0.1 °C, or shaken vigorously for a few minutes at room temperature. Both methods gave almost the same cation extractability and I_F values in the organic phase, so for a fast extraction the latter method was adopted.

Effect of Foreign Ions

Thiacrown ethers generally possess affinity for silver ions. Benzothiacrown ethers, in which some oxygen atoms have been replaced by sulfur atoms, also exhibit high extractabilities for silver ion and mercury(II) ion. The author examined whether spectrofluorimetry of silver ions using benzothiacrown ethers

TABLE III-1

Effect of other cations on the determination of silver ion

Cation	Molar ratio (M^{n+}: Ag^+)[a]	Apparent recovery (%)
Li^+	1000 : 1	102.7
Na^+	1000 : 1	100.0
K^+	1000 : 1	100.0
NH_4^+	1000 : 1	100.4
Mg^{2+}	1000 : 1	99.7
Ca^{2+}	1000 : 1	97.5
Ba^{2+}	1000 : 1	101.1
Cr^{3+}	1000 : 1	101.7
Mn^{2+}	1000 : 1	95.7
Fe^{3+}	1000 : 1	103.3
Co^{2+}	1000 : 1	97.1
Ni^{2+}	1000 : 1	109.0
	500 : 1	104.2
Cu^{2+}	1000 : 1	110.4
	500 : 1	103.8
Zn^{2+}	1000 : 1	112.6
	500 : 1	103.9
Cd^{2+}	1000 : 1	113.5
	500 : 1	102.7
Hg^{2+}	500 : 1	130.4
	100 : 1	120.3
	10 : 1	100.6
Pb^{2+}	1000 : 1	98.3

[a] Constant silver ion concentration, 10.0 p.p.b.

suffered interference from co-existing alkali and alkaline-earth metal ions and heavy metal ions. The results are shown in Table III-1. In the system with benzothiacrown ether, which showed a similar extraction behavior to the poly(benzothiacrown ether)s, even 1000-fold excesses of alkali and alkaline-earth metal and some heavy metal ions do not seem to interfere significantly.

However, copper, zinc, cadmium, and nickel ions interfered severely at 1000-fold concentrations over silver ion, but at a 500-fold concentration, it was possible to obtain apparent recoveries within 105% of the true value. Mercury(II) ion interfered seriously, probably because the affinity of the thiacrown ether for the mercury(II) ion is as great as that for the silver ion. The apparent recovery with the silver-mercury ion system is higher than those with the systems with other heavy metals.

Determination of Silver Ion in River Water Samples

River water samples collected from the upper stream of the Yodo river, Osaka City, were first filtered to remove insoluble solid such as wood chips. In neither the unconcentrated sample nor a 100-fold concentrated sample could any silver ion be detected by atomic absorption spectrometry. The main foreign metal ions present in the sample were Zn 60, Pb<10, Cu<10, Fe 400, Cd<10, Mn 50 and Cr<10 p.p.b. The river water sample was, therefore, spiked with p.p.b. levels of silver ion. This level also could not be detected by atomic absorption spectrometry, but the author found that the silver ion concentration could be measured by extraction-spectrofluorimetry with the benzothiacrown

TABLE III-2

Determination of silver ion in river water samples

Sample No.	Ag^+ concentration (p.p.b.)		Relative standard deviation (%)
	Actual	Found[a]	
1	2.0	1.9 ± 0.1	4.3
2	4.0	4.1 ± 0.1	2.0
3	10.0	9.8 ± 0.2	2.0
4	20.0	16.6 ± 0.2	1.0

[a] n=4.

ether-eosin system. The results are shown in Table III-2.

Four artificial river sample waters prepared here contained 2.0, 4.0, 10.0 and 20.0 p.p.b. of silver ion. The standard deviation and accuracy were best for the samples containing 2.0 or 4.0 p.p.b. of silver. In the sample that contained 20.0 p.p.b. of silver ion, a lower value (16.6 p.p.b.) was determined, probably because of some concentration quenching. A determination range of 1.0 - 10.0 p.p.b. may be suitable for this method.

In the determination of silver ion by this extraction-spectrofluorimetric method, lower concentrations of silver ion can be determined than by atomic absorption spectrometry without pre-treatment. Hence this method seems promising for the determination of trace amounts of silver ion in aqueous solution.

Summary

As benzothiacrown ether exhibited high selectivities for silver ion over several heavy metals on cation extraction, silver

ion spectrofluorimetry was carried out by using an ion-pair extraction system with benzothiacrown ether as the extractant and eosin Y as the fluorescent anion. It was possible to determine 2-10 p.p.b. of silver ion, and the method was subject to only low interferences by alkali, alkaline-earth and heavy metal ions, except mercury(II) ion. This method was successfully applied to the determination of trace amounts of silver ion in river water.

References

1. W. Szczepaniak, and B. Juskowiak, *Anal. Chim. Acta*, **140**, 261(1982).
2. M. Takagi, H. Nakamura, Y. Sanui, and K. Ueno, *Anal. Chim. Acta*, **126**, 185(1981).
3. H-G. Löhr, and F. Vögtle, *Acc. Chem. Res.*, **18**, 65(1985).
4. E. Sekido, and K. Chayama, *Nippon Kagaku Kaishi*, **1986**, 907 (1986).
5. K. Kina, K. Shiraishi, and N. Ishibashi, *Bunseki Kagaku*, **27**, 291(1978).
6. A. Sanz-Medel, D. B. Gomis, and J. R. G. Alvarez, *Talanta*, **28**, 425(1981).
7. A. Sanz-Medel, D. B. Gomis, E. Fuente, and S. A. Jimeno, *Talanta*, **31**, 515(1984).
8. K. Nakashima, S. Nakatsuji, S. Akiyama, I. Tanigawa, T. Kaneda, and S. Misumi, *Talanta*, **31**, 749(1984).
9. M. T. El-Ghamry, and R. W. Frei, *Anal. Chem.*, **40**, 1986(1968).

10. The Society of Dyers and Colourists, " Colour Index," Third Edition, Volume 4, Lund Humphries, London, 1971, p.4426.
11. H. Elmgren, *J. Polym. Sci., Polym. Lett. Ed.*, **18**, 815(1980).
12. R. Markuszewski, and H. Diehl, *Talanta*, **27**, 937(1980).
13. E. Martin, A. Pardo, M. S. Guijarro, and J. I. Fernandez-Alonso, *J. Mol. Struct.*, **142**, 197(1986).
14. V. Zanker, and W. Peter, *Chem. Ber.*, **91**, 572(1958).

CHAPTER IV

Neutral Carrier-Type Silver Ion-Selective Electrode Based on Lipophilic Mono- or Dithiacrown Ether Derivatives

Introduction

Silver is one of the most familiar metals and used such as alloys, jewelry, silver materials, films and even preservative reagents of cut flowers in our life. It is important not only to yield silver from silver mine, but also to recover silver from waste-silver manufactures, photograph films, or waste water. Thus, it is very interesting to take notice of the silver-analysis or recovery.[1]

Since crown ethers have been employed as neutral carriers of liquid membrane-type ion-selective electrodes(ISEs), many studies about the K^+, Na^+, and Li^+-selective electrodes based on crown ether derivatives have been carried out, because of their expected applications to clinical and environmental analyses.[2-4] On the contrary, few studies concerning heavy metal-ISEs based on thiacrown ether derivatives have been carried out because of their poor solubilities and sluggish cation-complexing equilibrium. Kamata et al.[5] have fabricated a Cu^{2+}-selective electrode based on 13,14-benzo-1,4,8,11-tetrathiacyclopentadecane. Recently, Lai et al.[6] have reported Ag^+- and Hg^{2+}-selective electrodes based on dithia-15-crown-5, which contains two sulfur and three oxygen atoms. Those electrodes did not exhibit Nernstian response to Ag^+, the slope being 40 mV/decade, whereas an ideal Nernstian slope with respect to Hg^{2+} was attained at the region of 10^{-6} - 10^{-3} M. The selectivities toward heavy metal ions and alkali and alkaline-earth metal ions are superior to conventional solid membrane Ag^+ electrodes, although the interferences by Fe^{3+} and Hg^{2+} are severe.

The author has attempted to design highly soluble thiacrown ethers, which possess a lipophilic group such as a dodecyl one as the neutral carrier of Ag^+-selective electrode. The Ag^+-selective electrode based on a lipophilic monothiacrown ether, dodecyl-monothia-16-crown-5 (1), has proved to possess high ion selectivities, emf stability, electrode durability, and reproducibility. This chapter describes syntheses of a series of new lipophilic thiacrown ether derivatives , which contain one or two sulfur atoms and three or four oxygen atoms, and membrane optimization for the Ag^+-selective electrode based on lipophilic monothia-16-crown-5 and practical applications of the optimized Ag^+-selective electrode to Ag^+ determination. Furthermore, the properties and ion-selectivities of the thiacrown compounds as neutral carriers for Ag^+-selective polymeric membrane electrodes are also discussed.

Experimental

Chemicals

The membrane solvents or plasticizers, o-nitrophenyl octyl ether (NPOE)[7] and tris(2-ethylhexyl)phosphate (TEHP),[8] were prepared according to the literature. Commercially-available dioctyl phthalate (DOP) and bis(2-ethylhexyl) sebacate (DOS) were distilled under vacuum. Poly(vinyl chloride) (PVC, average polymerization degree of 1100) was purified by reprecipitation from tetrahydrofuran(THF) in methanol twice. All of the metal salts employed here were nitrates of analytical grade and were purchased from Wako Pure Chemicals. Water was deionized and distilled.

Syntheses

6-Dodecyl-1,4,8,11-tetraoxa-14-monothiacyclohexadecane or Dodecyl-monothia-16-crown-5 (1)

The monothiacrown ether, 6-dodecyl-1,4,8,11-tetraoxa-14-monothiacyclohexadecane or dodecyl-monothia-16-crown-5 (1), was synthesized in a similar way to that described previously.[9,10] Bis(2-hydroxyethyl)sulfide (230 mg, 1.88 mmol) was dissolved in 100 ml of dry dioxane. To this solution NaH (60% in oil)(200 mg, 50 mmol) was added and then the resulted solution was refluxed. To the refluxing solution 5-dodecyl-3,7-dioxanonane-1,9-diol ditosylate (1.20 g, 1.88 mmol) dissolved in 30 ml of dry dioxane was slowly added and the mixture was refluxed for 16 h. After the reaction the solvent was evaporated off and the residue was extracted with chloroform. The organic layer was washed with water and then dried over $MgSO_4$. Evaporation of the solvent yielded a crude product of yellow viscous liquid, which was purified by silica gel column chromatography (ethyl acetate/ n-hexane = 1/10, R_f = 0.3); white crystals; yield 25%; mp 37.5 ^{o}C; IR(KBr) 2920 and 2850(CH), 1120(CO), 730 cm^{-1}(CS); ^{1}H-NMR(CCl_4, δ) 0.88(3H,t,CH_3), 1.20-1.40(22H,m,CH_2), 1.60-1.80 (1H, br,CH), 2.68(4H,t,SCH_2), 3.42(4H,d,$OC\underline{H}_2CH(C_{12}H_{25})C\underline{H}_2O$); MS, m/e 418. Anal. Calcd for $C_{23}H_{46}O_4S$: C,65.99%; H,11.08%; S,7.66%.

Found: C,65.85%; H,11.06%; S,7.37%.

3-Dodecyl-1,5,11-trioxa-8,14-dithiacyclohexadecane
or Dodecyl-dithia-16-crown-5 (2)

Sodium hydroxide (0.2 g, 5 mmol) was added to 200 ml of ethanol and the mixture was refluxed. A solution of 5-dodecyl-3,7-dioxanonane-1,9-diol ditosylate (1 g, 1.56 mmol) and bis(2-mercaptoethyl) ether (0.216 g, 1.56 mmol) in 50 ml of ethanol was dropwise added to the refluxing solution in 4 h. After the addition, reflux was continued for 7 h. After the reaction, the solvent was removed under vacuum. Water (50 ml) was added into the residue and this mixture was extracted with $CHCl_3$ (50 ml each) three times. The organic layer was separated and dried over $MgSO_4$. The solvent was then removed under vacuum. The resulted crude product of yellow viscous liquid was purified by silica gel column chromatography (ethyl acetate/n-hexane = 1/5; R_f = 0.5) to yield a white crystal; yield 20%; mp 38.0-38.5 °C; IR(KBr) 2920 and 2850(CH), 1120 cm^{-1}(COC); ^{1}H-NMR(CCl_4, δ) 0.88 (t,3H,CH_3), 1.20-1.84(m,23H,$(CH_2)_{11}CH$), 2.60-3.00(m,8H,CH_2SCH_2), 3.26-4.08(m,12H,CH_2OCH_2); MS, m/e 434. Anal. Calcd for $C_{23}H_{46}O_3S_2$: C,63.54%; H,10.67%; S,14.75%. Found: C,63.55%; H, 10.56%; S,14.69%.

12-Dodecyl-1,4,9-trioxa-10,14-dithiacyclohexadecane
or Dodecyl-dithia-16-crown-5 (3)

A mixture of 2-dodecylpropane-1,3-diol ditosylate (2.09 g, 3.78 mmol) and NaI (1.5 g, 10 mmol) in 50 ml of acetone was refluxed for 3 h. After the reaction a resulted insoluble salt was filtered off, and the solvent was removed from the filtrate. To the residue, water (30 ml) and benzene (50 ml) were added. The organic layer was separated, washed successively with water, 5% $Na_2S_2O_3$ aqueous solution and saturated NaCl aqueous solution, and dried over Na_2SO_4. The solvent was removed to yield 2-dodecylpropane-1,3-diiodide (1.7 g).

Cesium carbonate (2.0 g, 6.1 mmol) in 500 ml of dry dimethyl formamide(DMF) was heated at 50 °C under a nitrogen atmosphere. To this solution, the diiodide (1.7 g) dissolved in dry DMF (100 ml) solution and tetraethyleneglycol dithiol (0.898 g, 3.97 mmol) was added dropwise in 5 h and the reaction was continued for over 8 h. After the reaction the solvent was removed under vacuum, and water (50 ml) was added to the residue. The mixture was extracted with $CHCl_3$ (50 ml each) three times. The organic layer was dried over $MgSO_4$ and the solvent was removed. A viscous liquid was obtained and then purified by silica gel column chromatography (ethyl acetate/n-hexane = 1/3, R_f = 0.3) to yield a colorless liquid of pure product (3); yield 22.0%; IR(neat) 2900 and 2825(CH), 1115 cm^{-1}(COC); ^{1}H-NMR($CDCl_3$, δ) 0.88(t,3H,CH_3), 1.12-1.60(m,22H,CH_2), 1.60-1.92(br,1H,CH), 2.64-2.88(m,8H,CH_2SCH_2), 3.60-3.88(m,12H,CH_2OCH_2); MS, m/e 434. Anal. Calcd for $C_{23}H_{46}O_3S_2$: C,63.54%; H,10.67%; S,14.75%. Found: C, 63.54%; H,10.65%; S,14.57%.

12-Hydroxymethyl-1,4,7-trioxa-10,13-dithiacyclopentadecane or Hydroxymethyl-dithia-15-crown-5 (4)

Dry DMF (1.5 l) containing Cs_2CO_3 (3.58 g, 11 mmol) was heated and stirred at 50 °C under a nitrogen atmosphere. To this solution, a dry DMF (200 ml) solution of 2,3-dimercapto-1-propanol (1.24 g, 10 mmol) and tetraethyleneglycol diiodide (4.14 g, 10 mmol) was gradually added in 5 h. The similar procedure for the above addition of the DMF solution was repeated. After the reaction, the solvent was removed, water (100 ml) was added to the residue, and the aqueous layer was extracted with $CHCl_3$ (100 ml each) several times. The organic layer was separated and dried over $MgSO_4$ and then the solvent was removed. The crude liquid was purified by silica gel chromatography (ethyl acetate/benzene = 3/2, R_f = 0.3) to yield a colorless liquid of pure product (4); yield 73%; IR(neat) 3400(OH), 2910 and 2860(CH), 1120 cm^{-1}(COC); ^{1}H-NMR($CDCl_3$, δ) 2.60-3.00(m,6H,CH_2SCH_2), 3.20-3.48(m,1H,CH), 3.60-3.88(m,15H, CH_2OCH_2,OH); MS, m/e 282. Anal. Calcd for $C_{11}H_{22}O_4S_2$: C,46.78%; H,7.85%; S,22.70%. Found: C,46.27%; H, 7.75%; S,22.10%.

15-Hydroxymethyl-1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane or Hydroxymethyl-dithia-18-crown-6 (5)

The synthetic procedure was similar to that for (4). In this case, pentaethyleneglycol diiodide (4.58 g, 10 mmol) was used instead of tetraethyleneglycol diiodide. A resulted crude product was purified by silica gel chromatography (ethyl acetate/benzene = 1/1, R_f = 0.2) to yield a colorless liquid of (5); yield 60%; IR(neat) 3400(OH), 2900 and 2830(CH), 1100 cm^{-1}(COC); ^{1}H-NMR($CDCl_3$, δ) 2.66-3.00(m,6H,CH_2SCH_2), 3.12-3.36(m,1H,CH), 3.60-3.88(m,19H,CH_2OCH_2,OH); MS, m/e 326. Anal. Calcd for $C_{13}H_{26}O_5S_2$: C,47.83%; H,8.03%; S,19.64%. Found: C,47.90%; H, 7.94%; S,19.27%.

12-Dodecanoyloxymethyl-1,4,7-trioxa-10,13-dithiacyclopentadecane or Dodecanoyloxymethyl-dithia-15-crown-5 (6)

A mixture of (4) (0.572 g, 2.03 mmol), dry benzene (40 ml) and triethylamine (0.85 ml) was cooled to 0 °C. A dry benzene (20 ml) solution of dodecanoyl chloride (1.4 ml) was gradually added to this solution while stirring and the solution was further stirred at room temperature for 6 h. After the reaction a resulted salt was filtered off and the filtrate was washed successively with saturated $NaHCO_3$ and NaCl aqueous solution. The organic layer was separated and dried over $MgSO_4$. The solvent was evaporated under vacuum. The residue was purified by silica gel chromatography (ethyl acetate/n-hexane = 1/3, R_f = 0.3) to yield a colorless liquid of pure product (6); yield 57%; IR(neat) 2900 and 2825(CH), 1720(CO), 1100 cm^{-1}(COC); ^{1}H-NMR($CDCl_3$, δ) 0.88(t,3H,CH_3), 1.20-1.80(m,18H,$CH_3(C\underline{H}_2)_9CH_2$), 2.32(t,2H,$OOCC\underline{H}_2(CH_2)_9CH_3$), 2.68-3.00(m,6H,$CH_2SCH_2$), 3.24-3.52 (m,1H,CH), 3.60-3.86(m,12H,CH_2OCH_2), 4.38(d,2H,$C\underline{H}_2OOC(CH_2)_{10}CH_3$); MS, m/e 464. Anal. Calcd for $C_{23}H_{44}O_5S_2$: C,59.45%; H,9.54%; S,13.80%. Found: C,59.33%; H,9.54%; S,13.84%.

15-Dodecanoyloxymethyl-1,4,7,10-tetraoxa-13,16-dithiacyclooctadecane or Dodecanoyloxymethyl-dithia-18-crown-6 (7)

Compound (7) was synthesized in a similar way to compound (6). The product was purified by silica gel chromatography (ethyl acetate/n-hexane = 1/1, R_f = 0.3) to yield a colorless liquid of (7); yield 80%; IR(neat) 2900 and 2840(CH), 1720(CO), 1115 cm^{-1}(COC); ^{1}H-NMR($CDCl_3$, δ) 0.88(t,3H,CH_3), 1.20-1.80(m,18H, $CH_3(C\underline{H}_2)_9CH_2$), 2.32(t,2H,$OOCC\underline{H}_2(CH_2)_9CH_3$), 2.68-3.00(m,6H,

CH_2SCH_2), 3.16-3.44(m,1H,CH), 3.60-3.84(m,16H,CH_2OCH_2), 4.34(d, 2H,$\underline{CH_2}OOC(CH_2)_{10}CH_3$); MS, m/e 508. Anal. Calcd for $C_{25}H_{48}O_6S_2$: C,59.02%; H,9.51%; S,12.60%. Found: C,59.06%; H,9.57%; S,12.54%.

Ag^+-Thiacrown Ether Complexes

The Ag^+-thiacrown ether (1:1) complexes were prepared as follows: Equal volumes (4 ml) of thiacrown ether (0.05 mmol) chloroform solution and 1 M $AgNO_3$ aqueous solution were taken into a stoppered test tube. After the solution was stirred in dark for 3 h, the organic layer was separated and then the solvent was evaporated. The residue was recrystallized from benzene to yield white crystals;

Ag^+-(1) complex (8); yield 44%; mp 104-105 °C; IR(KBr) 2920 and 2845(CH), 1120 and 1100 cm^{-1}(COC); Anal. Calcd for $C_{23}H_{46}O_4S.AgNO_3$: C,46.94%; H,7.88%; N,2.38%. Found: C,46.68%; H, 7.90%; N,2.39%.

Ag^+-(2) complex (9); white crystals; yield 78 %; mp 88-89 °C (from benzene); IR(KBr) 2910 and 2840(CH), 1120 cm^{-1}(COC); Anal. Calcd for $C_{23}H_{46}O_3S_2.AgNO_3$: C,45.69%; H,7.67%; N,2.32%. Found: C,45.38%; H,7.61%; N,2.29%.

Ag^+-(3) complex (10); white crystals; quantitatively yield; mp 37.5-38.5 °C; IR(KBr) 2900 and 2840(CH), 1120 cm^{-1}(COC); Anal. Calcd for $C_{23}H_{46}O_3S_2.AgNO_3$: C,45.69%; H,7.67%; N,2.32%. Found: C, 45.31%; H,7.79%; N,2.18%.

The other Ag^+-thiacrown ether complexes could not be crystallized. However, these complexes were quantitatively yielded as liquid. The analytical data for the Ag^+-thiacrown ether complexes are as follows:

Ag^+-(6) complexes (11); IR(neat) 2900 and 2850(CH), 1730(CO), 1100 cm^{-1}(COC); Anal. Calcd for $C_{23}H_{44}O_5S_2 \cdot AgNO_3$: C,43.53%; H,6.99%; N,2.21%. Found: C, 44.28%; H,7.25%; N,1.95%.

Ag^+-(7) complexes (12); IR(neat) 2920 and 2850(CH), 1740(CO), 1120 cm^{-1}(COC); Anal. Calcd for $C_{25}H_{48}O_6S_2 \cdot AgNO_3$: C,44.25%; H,7.13%; N,2.06%. Found: C,44.39%; H, 7.23%; N,2.09%.

Fabrication of Electrodes

The PVC membranes containing the neutral carrier-Ag^+ complex were cast from the THF solutions according to the previous procedure.[11] The typical membrane consisted of 27.5 wt% PVC, 3.3 wt% Ag^+-thiacrown ether complex, 68.9 wt% membrane solvent (plasticizer), and 0.3 wt% lipophilic salt (0.1 mol% to the Ag^+-thiacrown ether complex). DOP was used as the membrane solvent unless otherwise stated. The electrode body of a Philips IS-561 was equipped with a 7 mm diameter disc of the PVC membrane. The internal filling solution was a 1 x 10^{-3} M (or 1 x 10^{-1} M) $AgNO_3$ aqueous solution. The electrodes were conditioned by soaking in 1 x 10^{-3} M $AgNO_3$ solution overnight.

Measurements of EMF

The measurements were carried out with a pH/mV meter of Corning Model M-130 at 25.0 ± 0.1 °C. The electrochemical cell was Ag-AgCl / 10^{-3} M $AgNO_3$ / membrane / measured solution / 0.1 M NH_4NO_3 / 4 M KCl / AgCl-Ag.

The potentiometric selectivity coefficients, k_{AgM}^{Pot}, were determined by a mixed solution method (fixed interference method) according to the IUPAC recommendations.[12] The constant background concentrations were 5×10^{-1} M for alkali and alkaline-earth metal ions and NH_4^+, 5×10^{-2} M for H^+ and heavy metal ions, and 5×10^{-5} M for Hg^{2+}.

Silver Ion Determinations

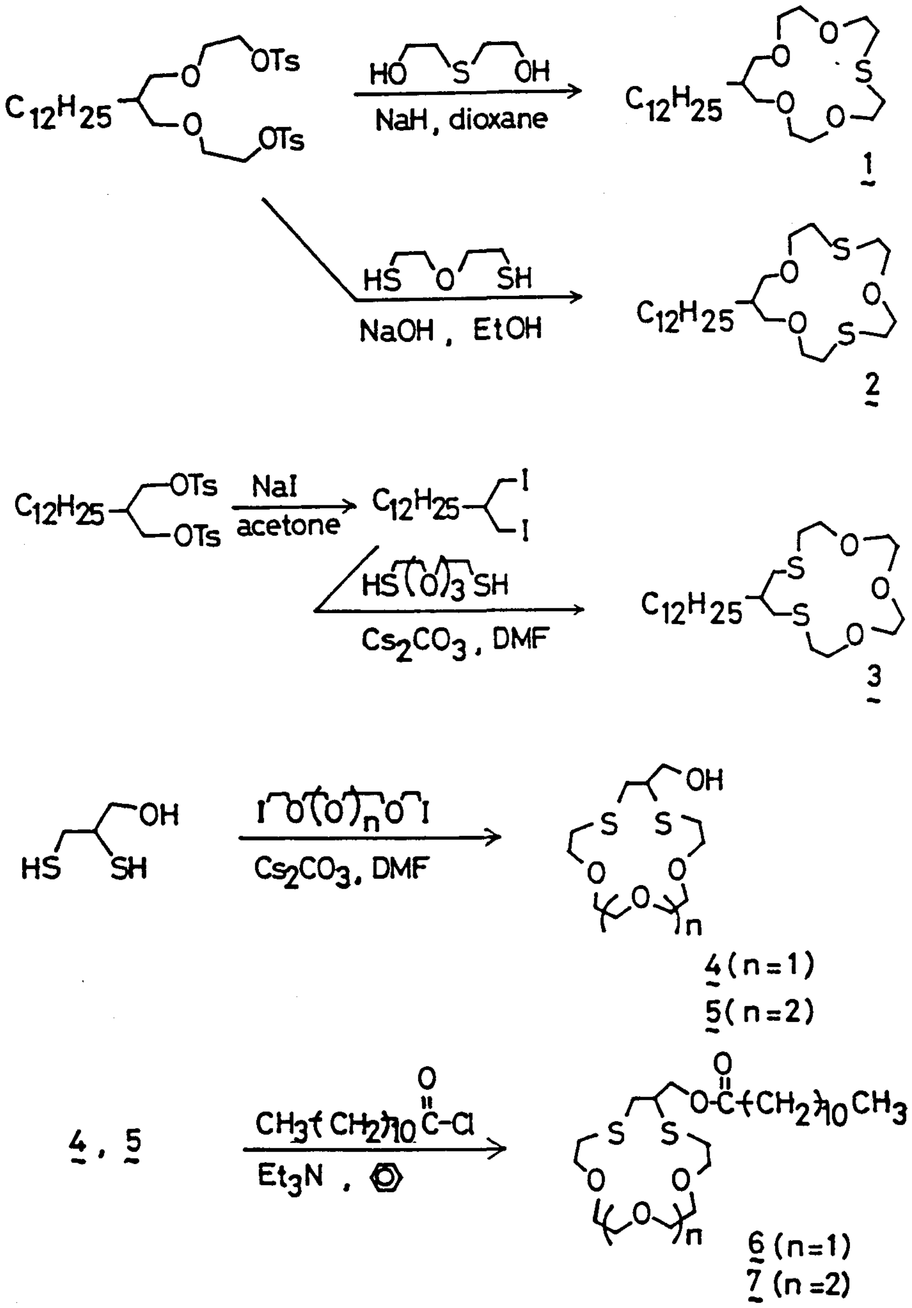
Concentrations of artificial Ag^+ samples were determined by a standard addition method (Gran's plot method).[13] Aqueous sample solutions of 5×10^{-4} M, 7.5×10^{-4} M, 1×10^{-3} M, and 2.5×10^{-3} M $AgNO_3$ were prepared by dilution of 1 M $AgNO_3$ aqueous solution. To 10 ml of this sample solution, 0.1 ml of 1×10^{-1} M $AgNO_3$ standard solution was added stepwise, except for the 5×10^{-4} M sample solution to which 0.1 ml of 1×10^{-2} M standard solution was added.

In silver ion potentiometric titrations, 1×10^{-3} M NaCl, 1×10^{-3} M KBr, and 1×10^{-3} M KI aqueous solutions were prepared as artificial samples, and the sample solutions were titrated with 1×10^{-2} M $AgNO_3$ standard solution. Also, 10 ml of 1×10^{-3} M $AgNO_3$ was titrated with halogen ion solutions, which were 1×10^{-2} M NaCl, KBr, and KI aqueous solutions.

Results and Discussion

Synthesis

Five kinds of lipophilic mono- or dithia crown ether were synthesized as shown in the scheme IV-1. In compounds (1), (2), and (3), a dodecyl group was introduced to the diols before the cyclization. 2-Dodecylpropane-1,3-diol was obtained by reduction of the reaction product of diethyl malonate with dodecyl bromide. The cyclization reaction by the diiodide and the dithiol was


C12H25
OTs
OTs
HO S OH
NaH, dioxane
1
HS O SH
NaOH, EtOH
2
NaI
acetone
HS(O)3SH
Cs2CO3, DMF
3
HS SH OH
I O(O)nO I
Cs2CO3, DMF
4(n=1)
5(n=2)
4, 5
CH3(CH2)10C-Cl
Et3N
O-C(CH2)10CH3
6 (n=1)
7 (n=2)

Scheme IV-1

carried out under a variety of conditions and methods, but the cyclization yields by the method of Buter and Kellogg[14] using Cs_2CO_3 were better than the methods using other base (Na_2CO_3)[15] and Williamson reaction. Only dithiacrown ether (**2**) was prepared by 5-dodecyl-3,7-dioxanonane-1,9-diol ditosylate and bis(2-mercaptoethyl) ether sodium salt, because the deprotonation of thiol could be easily done with NaOH. The crude products containing many by-products were purified by silica gel chromatography to prevent decomposition of the resulted thiacrown ethers by distillation. Some of these purified products had to be kept under a nitrogen atmosphere, because they were unstable under ambient atmosphere. Isolation of Ag^+-thiacrown ether complexes as crystals was possible in the case of only (**8**), (**9**) and (**10**). The another Ag^+ complexes were not able to be isolated as crystals, so the extract obtained by the solvent extraction(see the experimental section) was used without further purification. The Ag^+-thiacrown ether complexes were found to possess 1:1 stoichiometry by elemental analysis.

Electrode Response

Silver ion-selective electrodes of liquid membrane type using thiacrown ether derivatives reported so far did not exhibit sufficient electrode response and reproducibility.[6] On the contrary, ion-selective electrodes based on lipophilic crown ethers for alkali and alkaline-earth metal ions often showed an ideal Nernstian response. High solubility of the lipophilic neutral carriers in the electrode membranes may bring about the efficient electrode response.[11] In this study, therefore,

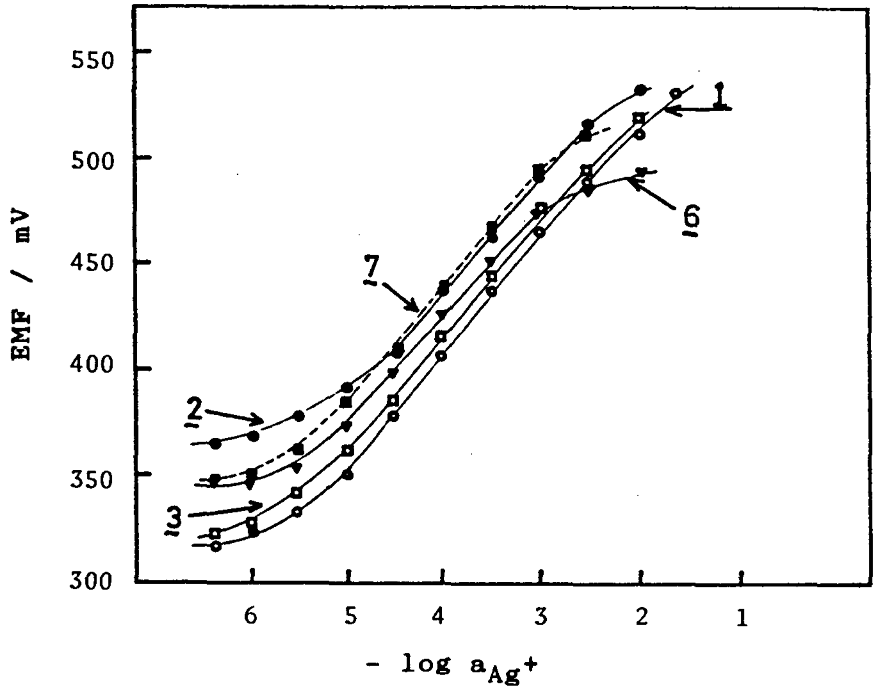


Figure IV-1. Electrode response of Ag^+-selective electrodes based on Ag^+ complexes of thiacrown ethers (1-7).

lipophilic-thiacrown ether derivatives were applied to the neutral carrier of the Ag^+-selective electrode. Electrode responses for Ag^+-selective electrodes based on the Ag^+ complexes of thiacrown ethers, (1-7), are shown in Figure IV-1. Any of the Ag^+-selective electrodes based on the thiacrown ethers exhibited Nernstian response to Ag^+ activity change in the range of 10^{-2} - 10^{-5} M. The increased lipophilicity of the dodecyl-thiacrown ethers seems to allow the neutral carriers to stay stably in the membrane. In the PVC-matrix membrane without any lipophilic salt, the slope for calibration curve showed only about 45 mV/decade, though the theoretical value for Ag^+ selective electrode is 59 mV/decade(Figure IV-2-b). The poor sensitivity in the high Ag^+ activity is partly due to an anion response.

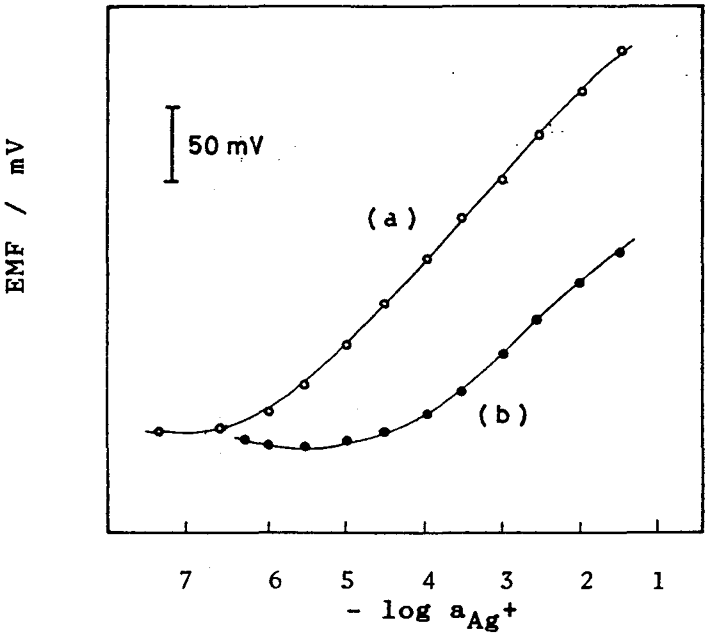


Figure IV-2. Calibration plots of pure $AgNO_3$ solution with Ag^+ electrode based on (1)-DOP-PVC membrane. With(a) and without(b) 0.3 wt% $[(NO_2)_3C_6H_2]_2NNa$.

Lipophilic salts such as dipicrylamine sodium salt (DPASS) were added as a membrane component of the Ag^+ electrode, resulting in an ideal Nernstian slope (59 mV/decade) in the Ag^+ activity range of 10^{-5} - 10^{-2} M (Figure IV-2-a). Even after the conditioning of (1)-membrane, which does not contain the Ag^+ complex initially, the potential response was still slow and unstable at several-time measurements. The Ag^+ electrode using Ag^+-(1) complex instead of (1), however, gave much better electrode response and stability. The response time for the Ag^+- selective electrode based on the Ag^+-(1) complex was within 30 sec.

Silver Ion Selectivities

In the case of Ag^+-selective electrodes based on the thiacrown ethers, the selectivity coefficients for Ag^+ were improved gradually with repeated measurements. With the electrode conditioning period, the selectivity coefficients were changed, especially with respect to Hg^{2+}. As a result, the longer conditioning times allowed the higher Ag^+ selectivities with respect to Hg^{2+}. This is probably because, to making the electrode conditioning, complexation of the lipophilic thiacrown ether in the membrane with Ag^+ proceeds quite slowly. On the other hand, a PVC-membrane containing the Ag^+ complex of the neutral carrier instead of the uncomplexed one showed very stable emf readings on the Ag^+ activity measurements even when the membrane was conditioned for a very short time. Selectivity coefficients for Ag^+ with respect to other cations in the Ag^+ electrodes are summarized in Figure IV-3. The both Ag^+ electrodes of the mono- and dithiacrown ethers are highly Ag^+ selective. Hg^{2+} interferes with the Ag^+ electrode response most seriously of all, but the selectivity coefficients (k_{AgM}^{Pot}) for Ag^+ with respect to Hg^{2+} still range from 6.5×10^{-3} to 3.4×10^{-2} in the thiacrown ether-based electrodes. The selectivity coefficients for Ag^+ with respect to the heavy and transition metal ions are less than 10^{-3}. Also, the selectivity coefficients for Ag^+ with respect to alkali and alkaline-earth metal ions are below 10^{-4}, their interference being negligible. Interestingly, the selectivities in the Ag^+ electrodes of the thiacrown ether are the quite similar to each other in spite of difference in the number and displacement of sulfur atoms among the thiacrown ether derivatives. Most of the thiacrown-based Ag^+-selective electrodes are superior to the conventional Ag_2S-based Ag^+-

electrodes in the selectivity, being quite promising for practical use.

In the PVC membrane of Ag^+-(1) complex, the effect of membrane solvents was investigated on the selectivity coefficients, k^{Pot}_{AgM} with respect to alkali, alkaline-earth, and heavy metal ions, NH_4^+, and H^+ (Figure IV-4). The selectivity coefficients do not depend on the kind of membrane solvents. The interference by the metal ions except for Hg^{2+} is negligible in any of the membranes with different membrane solvents. However, in the membrane of TEHP, the electrode response was interfered with by H^+, of which the selectivity coefficient was even larger than that of Hg^{2+}. Generally, the selectivity coefficient

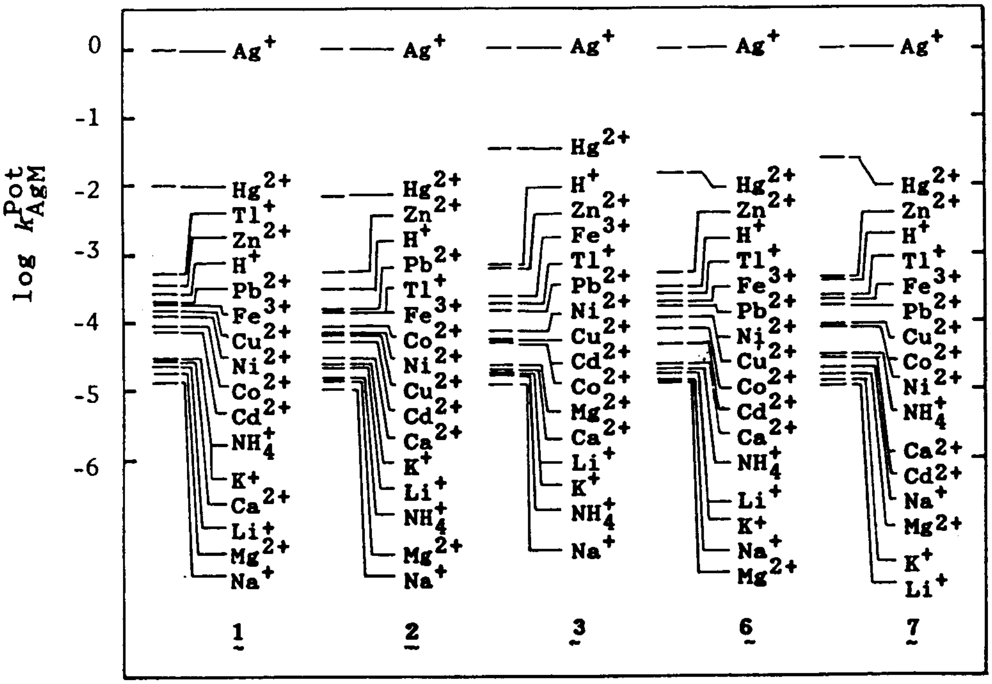


Figure IV-3. Selectivity coefficients for Ag^+ with respect to other cations in thiacrown-based electrodes.

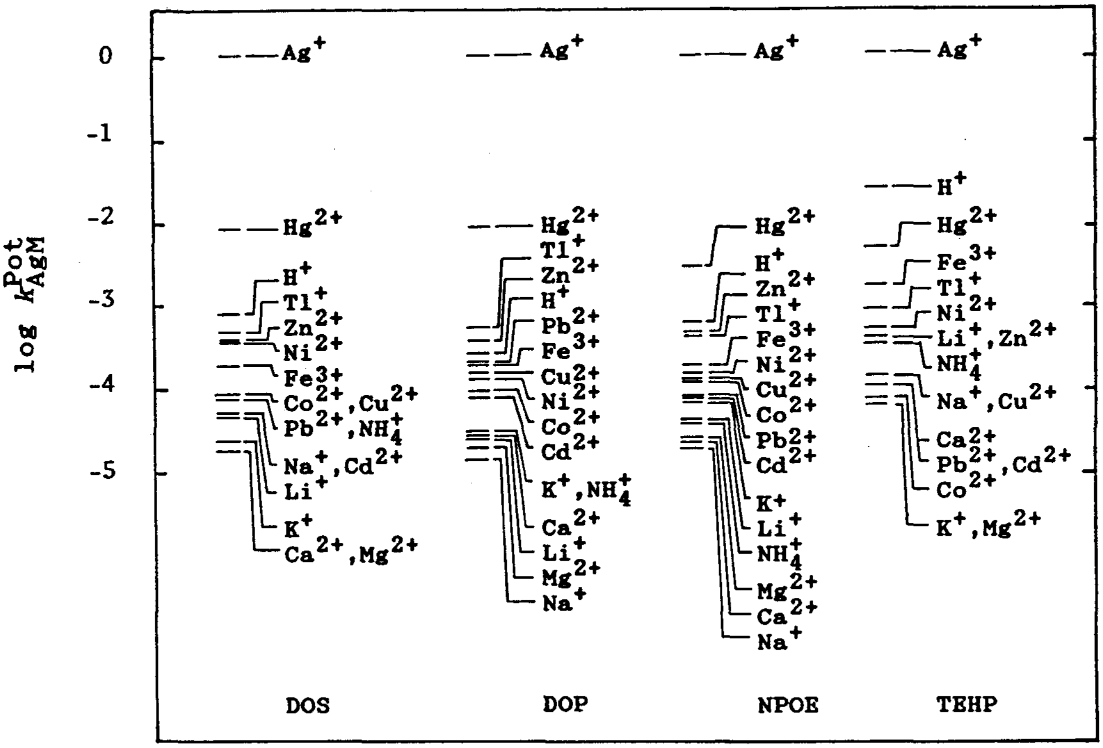


Figure IV-4. Effect of membrane solvent on selectivity coefficients.

of Hg^{2+} for the NPOE membrane system was superior to those for the other membrane solvent systems, although the electrode sensitivity for the NPOE system was not very good at high Ag^+ concentration range (log $a_{Ag^+} > -2.5$). Similar tendency for the selectivity coefficients was observed in the DOP and DOS membrane systems, which showed the theoretical Nernstian behavior at wide Ag^+ activity ranges. DOP, which was superior to DOS in the Ag^+ selectivity, was employed here as the best plasticizer. Ag^+-electrodes reported so far, which were conventional Ag_2S-based solid membrane type or neutral carrier-based liquid membrane type, were severely interfered with by Hg^{2+}.[6,16] This Ag^+-electrode based on the Ag^+-(1) complex, however, possesses much higher selectivity against Hg^{2+} than those of the above electrodes.

Effect of pH

The pH dependence of emf reading for the Ag^+-selective electrode based on the Ag^+-(1) complex is shown in Figure IV-5. The pH values in the sample solutions were adjusted by HNO_3 and NaOH. The suitable pH range for the emf measurements lies in the region from neutral to acid (pH 2). High pH values (pH > 7.5) in the sample caused some emf decrease probably because of Ag_2O precipitation with OH^-. On the other hand, at low pH ranges (pH < 2) emf values also decreased. Lai et al.[6] have reported that the emf decrease below pH 2 might be derived from protonation of the thiacrown ether, which in turn causes loss of

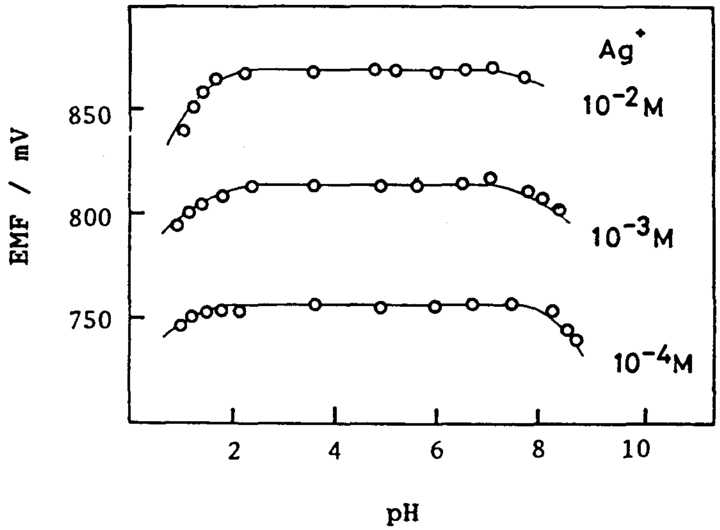


Figure IV-5. Effect of pH in sample solutions on potential responses of Ag^+-selective electrode based on Ag^+-(1) complex.

cation-complexing ability. The Ag^+-(1) complex would dissociate by H^+, with which Ag^+ sites of Ag^+-(1) complex would be partly replaced. The suitable pH ranges for the practical measurements in the Ag^+ electrode based on Ag^+-(1) complex were evidently wide compared to those for previously reported Ag^+ electrodes.[6] Furthermore, the stability of emf readings for the present Ag^+ electrode was predominant in the measuring pH ranges.

Silver Ion Determination

Attempts were made to determine Ag^+ in artificial aqueous samples by using the Ag^+-selective electrode based on Ag^+-(1) complex. Quantitative analyses were carried out by potentiometric titrations of halogen ions with Ag^+, and that of Ag^+ with halogen ions(Figure IV-6). The titration curves showed ideal S-shape in which the emf changed clearly around the end point. Another application of silver ion determination by a standard addition method, called Gran's plot method, was investigated with the Ag^+-selective electrode. The Ag^+ concentrations for the sample ranged from 5×10^{-4} M to 2.5×10^{-3} M. The results are summarized in Table IV-1. The relative standard deviation exhibited low dispersion, and the errors were also small for 7.5×10^{-4} M, 1×10^{-3} M, and 2.5×10^{-3} M Ag^+. These results indicate clearly that the Ag^+-selective electrode based on the Ag^+-(1) complex is evidently promising for the application of silver ion determinations. Also, this Ag^+ electrode based on the Ag^+-(1) complex is quite different from conventional Ag_2S-based electrodes in that coexistence of Hg^{2+} in samples can be permitted on the potentiometry in the former electrode.

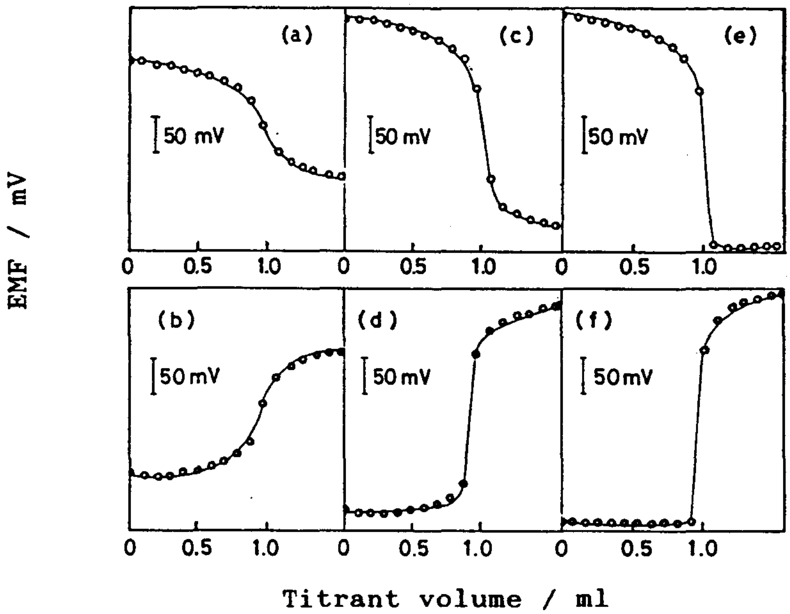


Figure IV-6. Potentiometric titrations of Ag^+ and halogen ions in artificial samples with Ag^+-selective electrode based on Ag^+-(1) complex.

Titrations of Ag^+(10^{-3} M) with (a)Cl^-(10^{-2} M), (c)Br^- (10^{-2} M), and (e)I^-(10^{-2} M); and titrations of (b)Cl^- (10^{-3} M), (d)Br^-(10^{-3} M), and (f)I^-(10^{-3} M) with Ag^+ (10^{-2} M).

TABLE IV-1

Silver ion determination in artificial samples by Gran's plot method using Ag^+ ISE based on Ag^+-(1) complex

Sample No.	Ag^+ concentration (M)		Relative standard deviation (%)	Error (%)
	Actual	Found[a]		
1	5.0×10^{-4}	5.58×10^{-4}	2.26	11.50
2	7.5×10^{-4}	7.38×10^{-4}	3.01	1.67
3	1.0×10^{-3}	1.01×10^{-3}	1.14	1.00
4	2.5×10^{-3}	2.49×10^{-3}	1.70	0.40

[a] The value was obtained as the average value on 4-time measurements.

Summary

Dodecyl-monothia-16-crown-5, which contains one sulfur and four oxygen atoms, was synthesized and tested for its usefulness as a neutral carrier for Ag^+-selective polymeric membrane electrodes. Employment of the Ag^+-complex of the thiacrown ether as the membrane active material instead of the thiacrown ether itself allowed a better potential response. The resulted ion-selective electrodes exhibited Nernstian response to Ag^+ in a wide activity range. The ion selectivities against alkali, alkaline-earth, and heavy metal ions, NH_4^+, and H^+ were quite excellent. Silver ion in artificial samples was successfully determined by Ag^+ potentiometric titration and Gran's plot method with the Ag^+ electrode. Moreover, lipophilic dithiacrown ethers were also synthesized and their ion selectivities were evaluated as neutral carriers of polymeric membrane Ag^+-selective electrodes. High Ag^+-selectivities and excellent electrode properties were realized with the monothiacrown ethers as well.

References

1. R. M. Izatt, G. C. LindH, R. L. Bruening, P. Huszthy, C. W. McDaniel, J. S. Bradshaw, and J. J. Christensen, *Anal. Chem.*, 60, 1694(1988).
2. K. Kimura, T. Maeda, H. Tamura, and T. Shono, *J. Electroanal. Chem. Interfacial Electrochem.*, 95, 91(1979).

3. T. Shono, M. Okahara, I. Ikeda, K. Kimura, and H. Tamura, *J. Electroanal. Chem. Interfacial Electrochem.*, **132**, 99(1982).
4. S. Kitazawa, K. Kimura, H. Yano, and T. Shono, *J. Am. Chem. Soc.*, **106**, 6978(1984).
5. S. Kamata, M. Higo, T. Kamibeppu, and I. Tanaka, *Chem. Lett.*, **1982**, 287.
6. M. T. Lai and J. S. Shih, *Analyst(London)*, **111**, 891(1986).
7. C. F. H. Allen and J. W. Gates; "Organic Syntheses"; Wiley: New York, 1955; Coll. Vol. III, P 140.
8. G. R. Dutton and C. R. Noller; "Organic Syntheses"; Wiley: New York, 1950; Coll. Vol. II, P 109.
9. D. Ammann, R. Bissig, M. Guggi, E. Pretsch, and W. Simon, *Helv. Chim. Acta*, **58**, 1535(1975).
10. H. Sakamoto, K. Kimura, Y. Koseki, M. Matsuo, and T. Shono, *J. Org. Chem.*, **51**, 4974(1986).
11. K. Kimura, S. Kitazawa, and T. Shono, *Chem. Lett.*, **1984**, 639.
12. "Recommendations for Nomenclature of Ion-Selective Electrodes"; *Pure Appl. Chem.*, **48**, 127(1976).
13. G. Gran, *Analyst(London)*, **77**, 661(1952).
14. J. Buter, and R. M. Kellogg, *J. Org. Chem.*, **46**, 4481(1981).
15. A. Anantanarayan, P. J. Dutton, T. M. Fyles, and M. J. Pitre, *J. Org. Chem.*, **51**, 752(1986).
16. S. Wakida and Y. Ujihira, *Anal. Sci.*, **2**, 231(1986).

CONCLUSION

The aim of this study was designing of mixed-donor thiacrown compounds and their analytical applications. The conclusions of this study are as follows:

(1) Poly- and bis(benzothiacrown ether) derivatives containing monocyclic thiacrown ethers with two oxygen and three or four sulfur atoms were synthesized. The thiacrown ether derivatives were found to complex Ag^+ or Hg^{2+} more powerfully than alkali and alkaline-earth metal ions, and they showed greater affinity for Ag^+ and Hg^{2+} than the corresponding monomeric analogs. Silver ion extraction from solutions of mixtures of silver, heavy and transition metal ions were successful with the poly- and bis(benzothiacrown ether)s, so far as the solutions do not contain much mercury(II) ion. Stoichiometries of Ag^+/crown ether were 1:1 for the monomeric analogs and bis(benzothiacrown ether)s with four sulfur atoms in the ring, and 1:2 for the bis(benzothiacrown ether)s with three sulfur atoms.

(2) The silver ion extraction from a copper ore sample was possible at ca. 80% recovery by using poly- and bis-(benzothiacrown ether)s as the extractant.

(3) Spectrofluorimetric determination of silver ion by ion-pair extraction with benzothiacrown ether - silver ion - eosin systems was carried out and the detection ranges were 2-10 p.p.b. of silver ion. The interferences of alkali, alkaline-earth and heavy metal ions except mercury(II) ion were scarcely observed

in the extraction-spectrofluorimetric determination. Trace amounts of silver ion in a river water sample were determined by this spectrofluorimetric method with ion-pair extraction. In contrast, atomic absorption spectrometry did not allow to determine such low Ag^+ concentrations.

(4) Monothiacrown ether having lipophilic group, dodecyl-monothia-16-crown-5, was synthesized and used as a neutral carrier of Ag^+-selective electrode. The resulted ion-selective electrode exhibited good Nernstian response in a wide Ag^+ activity range. The Ag^+ selectivities of the electrode against other metal ions were excellent. Also, a series of lipophilic dithiacrown ether derivatives were synthesized and proved to be excellent neutral carriers for Ag^+-selective electrodes like the monothiacrown ether.

ACKNOWLEDGMENT

The author is sincerely grateful to Professor Toshiyuki Shono, Osaka University, for his constant guidance and encouragement throughout this work.

The author is particularly indebted to Associate Professor Keiichi Kimura, Osaka University, for his continuous advices and valuable discussions.

Grateful acknowledgment is also given to Associate Professors Minoru Tanaka and Takayuki Matsushita, Osaka University, Professor Sanae Ikeda, Tokushima University, and Professor Akira Ishigaki, Nara National College of Technology, for their helpful suggestions.

The author would like to thank Professor Hiroshi Sakurai, President of Nara National College of Technology, for giving chance to studying this work.

The author further wishes to thank Dr. Takumi Maeda, Dr. Hidefumi Sakamoto, Mr. Yousuke Matsui, and Mr. Kazuhiro Akama, for their helpful discussions and experimental assistances.

The author also wishes to thank all the members of the Shono Laboratory, Osaka University, for their friendships.

Finally, the author would like to thank his parents, Yukio Oue and Kiyoko Oue, and his wife, Yukiko Oue, for their heartful encouragement.