



## **PREPARATION OF THIOESTER TYPE OF BROOM EXTRACTANT WITH SILVER SELECTIVITY**

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### **ABSTRACT**

A novel tripodal thioester type of broom extractant has been synthesized to investigate selectivity for soft metal ions. Broom extractant exhibited high extractability for silver ion compared with monopodal compound. The complexation ratio of the broom extractant and silver ion was found to be 1:1 from the result of extractant concentration dependency. For stripping of loaded silver ion, complete stripping was achieved with both 1 mol dm<sup>-3</sup> thiourea and high concentration of acidic solutions. As an application, electrode response of silver ion was observed at concentration range of 10<sup>-3</sup> to 10<sup>-6</sup> M silver nitrate using broom extractant as an ionophore.

Keywords: Broom type extractant, Tripodal compound, Silver ion, Extraction, Ion selectivity electrode

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### **INTRODUCTION**

Silver is one of typical precious metal and is used for various purposes including adornment. Quantitative analysis of silver ion is useful in mixed solution of precious metals. Recently, development of silver ion selective electrodes has been carried out by using clathrates such as crown ethers and calixarenes [1-6].

Lately, extractants, which were soft ligands containing nitrogen and sulfur atoms were used for mutual separation of precious metals [7-11]. Although the studies on complexation of metal and tripodal compound have

been reported, these compounds were not suitable as the extractants due to their poor lipophilicity [12-16]. Broom extractants bear some characteristics consisting of long chain alkyl group (as hydrophobic groups) and a tripod-like branched structure for metal recognition site (as a hydrophilic group). The structure of original broom type compound (trimethylol compound) is shown in Fig.1. The present extractant has alkenyl hydrophobic group. It would provide more lipophilicity and be polymerized to use as an ion-exchange resin by double bond for the future work. Metal recognition site provides rigid  $C_3$  symmetry based on a  $sp^3$  carbon for high recognition ability of particular metal ion. Functional group has been introduced at particular position and selective metal extraction due to preorganization would be expected. In addition various functional groups can be introduced. In the previous work, broom extractant introducing phthalamic acid was prepared to investigate separation of rare earth metal ions [17].

In the present work, we have prepared thioester type of broom extractant to investigate silver ion extraction and stripping compared with mono compound. The structures of the present extractants are also shown in Fig.1. Complexation ratios of metal to the broom extractant and the monopodal compound have been also determined. In an application, the broom extractant has been also used as an ionophore for silver ion selective electrode.

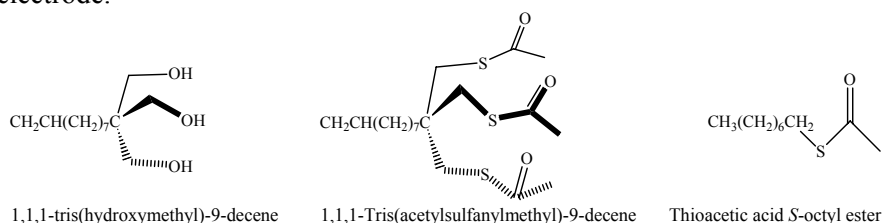


Fig. 1. Chemical structures of the original broom compound (1,1,1-tris(hydroxymethyl)-9-decene) and the present extractants.

## MATERIALS/METHODS/PROCEDURES

### Reagents

Tribromo compound, 1,1,1-tris(bromomethyl)-9-decene was synthesized from the corresponding aldehyde by the same procedure reported in the previous paper [17,18]. Synthetic route of the tripod extractant is shown in Fig.2, together with the monopodal extractant. That is, at first, 10-undecenyl aldehyde and formaldehyde with calcium hydroxide were reacted in methanol to obtain 1,1,1-tris(hydroxymethyl)-9-decene. The triol compound and *p*-toluene sulfonylchloride were reacted in pyridine to obtain 1,1,1-tris(*p*-toluene sulfonylmethyl)-9-decene. The tritosyl compound and lithium bromide were reacted in MIBK to obtain 1,1,1-tris(bromomethyl)-9-decene.

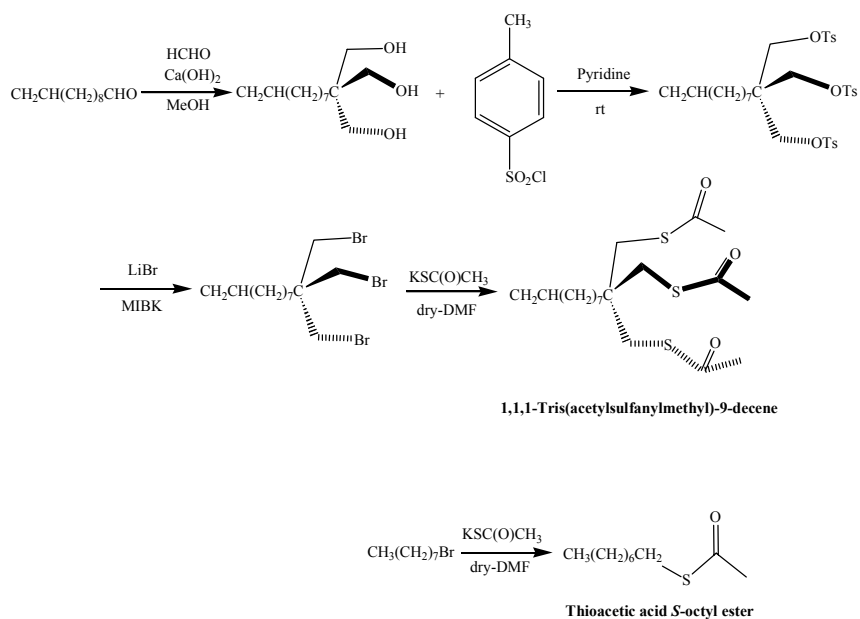


Fig. 2. Synthetic routes for the tripodal broom and monopodal compounds.

### 1,1,1-Tris(acetylsulfanylmethyl)-9-decene [18]

Under a nitrogen stream, 1,1,1-tris(bromomethyl)-9-decene (6.21 g, 14.8 mmol), dry-DMF 200 cm<sup>3</sup>, and potassium thioacetate (15.21 g, 129.8 mmol) were mixed and stirred at 323 K for 42 h. Water (100 cm<sup>3</sup>) was added and the desired compound was extracted with CHCl<sub>3</sub> (75 cm<sup>3</sup> × 3). Combined organic layer was washed with 1 M (M = mol dm<sup>-3</sup>) HCl (50 cm<sup>3</sup> × 3) and water (50 cm<sup>3</sup> × 2). Organic layer was dried over anhydrous MgSO<sub>4</sub>, and evaporated under a reduced pressure to give yellow viscous liquid. Yield 87.7%, TLC (SiO<sub>2</sub>, ethyl acetate : hexane = 1:1 v/v) R<sub>f</sub> = 0.51. FT-IR (neat)  $\nu_{C-H}$  2963 cm<sup>-1</sup>,  $\nu_{C=O}$  1698 cm<sup>-1</sup>,  $\nu_{C=C}$  1639 cm<sup>-1</sup>,  $\nu_{C-(C=O)}$  1422 cm<sup>-1</sup>,  $\nu_{C-S}$  627 cm<sup>-1</sup>; <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, TMS, 303 K)  $\delta$  1.32 (12H, m, CH<sub>2</sub>CH(CH<sub>2</sub>)<sub>6</sub>), 2.00 (2H, m, CH<sub>2</sub>CHCH<sub>2</sub>CH<sub>2</sub>), 2.35 (9H, s, SC(O)CH<sub>3</sub>), 2.99 (6H, s, CH<sub>2</sub>SC(O)), 4.97 (2H, m, CH<sub>2</sub>CH), 5.80 (1H, m, CH<sub>2</sub>CH); E.A. Found : C, 54.72 ; H, 7.64, N, 0.02%, Calcd. For C<sub>19</sub>H<sub>32</sub>O<sub>3</sub>S<sub>3</sub> : C, 56.39, H, 7.97, N, 0.00%, Calcd. For C<sub>19</sub>H<sub>32</sub>O<sub>3</sub>S<sub>3</sub> in +0.04 CHCl<sub>3</sub> : C, 54.72, H, 7.71, N, 0.00%.

### Thioacetic acid S-octyl ester

Under a nitrogen stream, 1-bromooctane (5.26 g, 27.2 mmol), dry-DMF 200 cm<sup>3</sup>, and potassium thioacetate (6.00 g, 52.5 mmol) were added and stirred at 323 K for 42 h. Water (100 cm<sup>3</sup>) was added and the desired compound was extracted with CHCl<sub>3</sub> (60 cm<sup>3</sup> × 3). Organic layer was washed with 1 M HCl (50 cm<sup>3</sup> × 3) and water (50 cm<sup>3</sup> × 2). Combined

organic layer was dried over anhydrous  $\text{MgSO}_4$ , and evaporated under a reduced pressure to give yellow viscous liquid. Yield 97.3%, TLC ( $\text{SiO}_2$ , chloroform : hexane = 1 : 4 v/v)  $R_f = 0.32$ . FT-IR (neat)  $\nu_{\text{C-H}}$  2925  $\text{cm}^{-1}$ ,  $\nu_{\text{C=O}}$  1695  $\text{cm}^{-1}$ ,  $\nu_{\text{C-(C=O)}}$  1464  $\text{cm}^{-1}$ ,  $\nu_{\text{C-S}}$  626  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ , TMS, 303 K)  $\delta$  0.88 (3H, t,  $\text{CH}_2\text{CH}_3$ ), 1.27 (10H, m,  $\text{CH}_3(\text{CH}_2)_5$ ), 1.56 (2H, m,  $\text{CH}_2\text{CH}_2\text{SC(O)CH}_3$ ), 2.32 (3H, s,  $\text{SC(O)CH}_3$ ), 2.87 (2H, t,  $\text{CH}_2\text{SC(O)CH}_3$ ).

### EXTRACTION TESTS FOR METAL IONS

Extraction tests were carried out by the conventional batch method. As an organic phase, the extractant was dissolved to prescribed concentration in chloroform. As an aqueous phase, metal salts were dissolved to prescribed concentration in 0.1 M HEPES solution and 0.1 M nitric acid solution to desired pH. Equal volumes of both phases were mixed and stirred for 9 h. After phase separation, the pH value and metal concentration in aqueous solution were measured by a pH meter (Orion,  $\phi$ -720A), and atomic absorption spectrophotometer (abbreviated as AAS, Shimadzu, AA-6650) and inductively coupled plasma atomic emission spectrophotometer (abbreviated as ICP-AES, Shimadzu, ICPS-8100), respectively. Extraction percentage was calculated by equation (1). where  $[\text{M}]_{\text{ini}}$  and  $[\text{M}]_{\text{eq}}$  represent the initial and equilibrium metal ion concentrations in the aqueous solution, respectively.

$$\%E = \frac{[\text{M}]_{\text{ini}} - [\text{M}]_{\text{eq}}}{[\text{M}]_{\text{ini}}} \times 100 \quad (1)$$

### Stripping test of silver ion

An organic solution containing broom extractant was contacted with the above-mentioned aqueous solution to extract silver ion completely so as to prepare the test solution; the percentage extraction of silver ion was 100%. The loaded organic solutions were contacted with equal volume of various aqueous solutions containing stripping reagents for 9 h. The silver concentrations of stripped aqueous solution were measured by AAS, and stripping percentage was calculated by equation (2) [19]. Where,  $[\text{Ag}]_{\text{s. aq.}}$  is stripping concentration of silver ion in the stripping aqueous solution.

$$\%S = \frac{[\text{Ag}]_{\text{s. aq.}}}{[\text{Ag}]_{\text{org.}}} \times 100 \quad (2)$$

### Application of silver ion selective electrode

Electrode membrane was prepared by composition ratio listed in Table 1 by using broom extractant for an ionophore [20]. Electric potentials from  $10^{-7}$  to  $10^{-1}$  M silver nitrate solution were measured by using the prepared membrane.

Electrochemical cell is Ag-AgCl /  $10^{-3}$  M AgNO<sub>3</sub> / PVC membrane / sample solution / 1.0 M KNO<sub>3</sub> / 3 M KCl / Ag-AgCl.

Table 1. Composition of electrode membrane

Extractant/mg	KTpClPB/mg	PVC/mg	NPOE/mg	THF/ml
7.79	2.28	49.6	90.7	1.50

## RESULTS AND DISCUSSION

### Extraction test of various metal ions

Extraction pH dependencies of various metal ions with broom extractant and monopodal compound are shown in Figs.3 (a) and (b). Broom extractant showed high extractability for silver ion compared with monopodal compound. Broom extractant has three functional groups and provides the preorganized structure in the molecule. At the coordination site of the broom extractant, silver and sulfur stably exist and consequently extraction is enhanced. In the palladium extraction, precipitation generated. It would be attributed to poor solubility of palladium complex into organic phase.

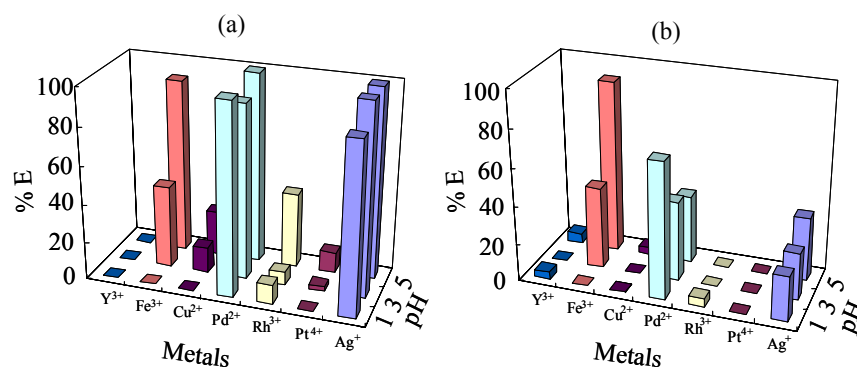


Fig. 3. Extraction behavior of various metal ions with broom extractant (a) and monopodal compound (b). Broom extractant : 5 mM, monopodal compound : 15 mM, Metal ion : 0.1 mM.

The effects of extractant concentration on distribution ratio  $D$  are shown in Figs.4 (a) and (b). The  $D$  is calculated by equation (3), where  $[Ag]_{org}$  is silver ion in the organic phase calculated from the difference of the silver concentration in aqueous solution before and after equilibration. In the case of broom extractant, the slope of the concentration dependency was 1. On the other hand, that of monopodal one was 2. The extraction equation of silver ion by the extractant is defined by equation (4), where  $n$  is number of the extractant.  $L$  represents ligand, the extractant. The equilibrium constant ( $K_{ex}$ ) was calculated from equation (4), and taking

logarithm gives the equation (5). Equation (5) corresponds to Fig. 4,  $n$  reveals the slope in Fig.4. In the case of broom extractant, the slope was 1, it supports that the complexing ratio between broom extractant and silver ion is 1:1 (broom extractant : silver ion).

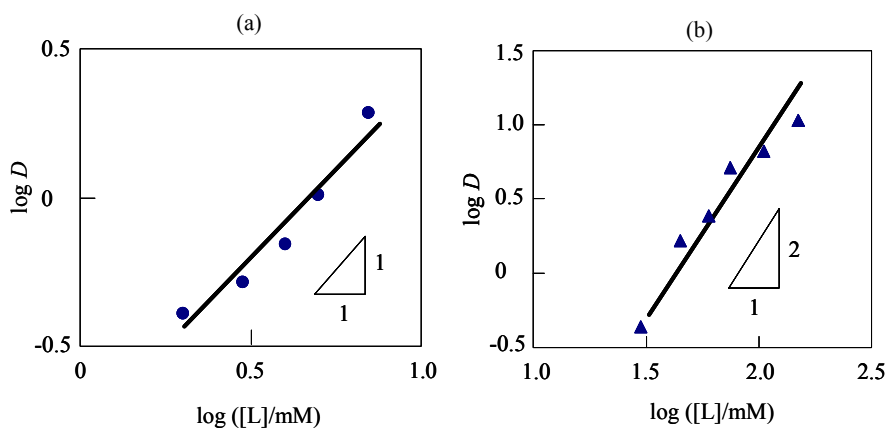
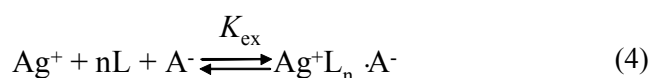


Fig. 4. Effect of extractant concentration on distribution ratio  $D$ , (a): broom extractant, (b): monopodal compound, silver ion: 0.1 mM at pH 1.

It means that the broom extractant makes intramolecular complex with silver ion. On the other hand, in the case of monopodal compound, the slope was 2, it supports that the complexing ratio between monopodal compound and silver ion is 2 : 1 (monopodal compound : silver ion).

$$D = \frac{[Ag]_{org.}}{[Ag]_{eq.}} \quad (3)$$



$$\log D = n \log [L] + \log K_{ex} + \log [A^-] \quad (5)$$

#### Stripping test of the silver ion

Result for stripping of the loaded silver is shown in Fig.5. For stripping test of silver ion, although neutral salt, basic, and dilute acidic eluents were not effective due to high affinity of silver and the extractant, quantitative stripping was achieved with 1 M thiourea and high concentration of acidic solution.

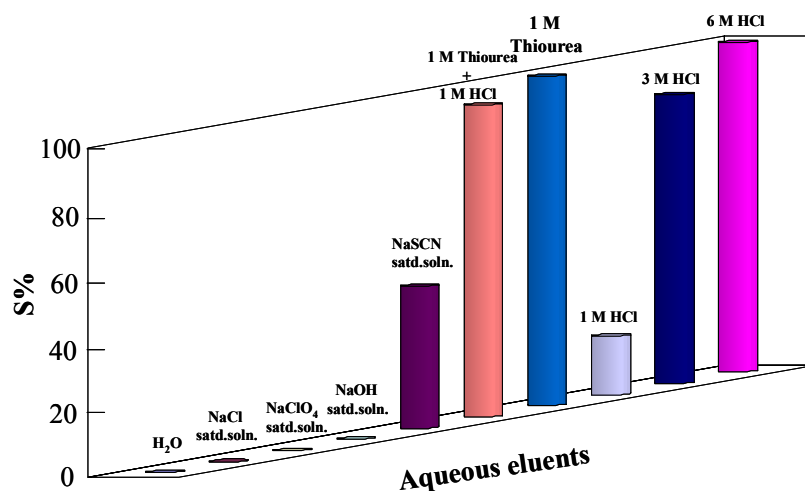


Fig. 5. Result for silver stripping with various aqueous solution.

#### Application of silver ion selective electrode

Nernstian equation is defined by Eq. (6), where  $E$  and  $E^0$  represent measured potential and standard oxidation-reduction potential, respectively.  $R$ ,  $T$  and  $F$  represent gas constant, absolute temperature (K), and Faraday constant, respectively. The  $a$  symbol represents the activity of silver ion. For a monovalent metal ion, the Nernstian slope would be nearly  $59 \text{ mV decade}^{-1}$ . Figure 6 showed electrode responses of silver ion with membrane containing broom extractant as an ionophore. In Fig.6 the Nernstian slope was observed at the concentration range of  $10^{-3}$  to  $10^{-6}$  M silver nitrate. It suggested to apply as an silver ion selective electrode.

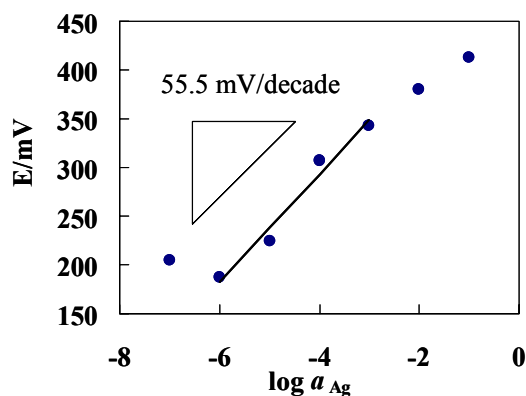


Fig. 6. Electrode responses of silver ion with membrane containing broom extractant as an ionophore.

Nernstian equation

$$E = E^0 + \frac{2.30 RT}{nF} \log a \quad (6)$$

### CONCLUSION

A novel tripodal thioester type of broom extractant has been synthesized to investigate selective extraction for soft metal ions. Broom extractant showed high extractability for silver ion compared with monopodal compound. The stoichiometry of the broom extractant and silver ion was found to be 1 : 1 (extractant : silver ion) from effect of extractant concentration on percentage extraction of soft metal ions. For stripping test of silver ion, quantitative stripping was achieved with 1 M thiourea and high concentration of acidic solution. In the application, electrode responses of silver ion was observed at the concentration range of  $10^{-3}$  to  $10^{-6}$  M silver nitrate by using broom extractant as an ionophore.

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