

## Liquid Membrane Type-Silver Ion-Selective electrode based on Silicone-rubber Membrane Modified Chemically by Monothiacrown Ether

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6-(3'-Triethoxysilylpropyl)-, 6-(4'-Triethoxysilylbutyl)-, and 6-(11'-Triethoxysilylundecyl)-1,4,8,11-tetraoxa-14-thiacyclohexadecane were immobilized on silicone-rubber membranes and silicone-rubber membrane chemically modified with monothia-16-crown-5, monothiacrown ether tried to use as a neutral carrier for  $\text{Ag}^+$ -selective polymeric membrane electrodes.  $\text{Ag}^+$ -complex effects were recognized to determination  $\text{Ag}^+$  activity concentration regions. The  $\text{Ag}^+$ -selective electrodes based on silicone-rubber membrane by covalent bonding exhibited a Nernstian response in the  $\text{Ag}^+$  activity range of  $10^{-5}$ --- $10^{-2}$  M with a response time of less than 60 sec. The ion selectivities against alkali, an alkaline-earth and heavy metal ions,  $\text{NH}_4^+$ , and  $\text{H}^+$  were quite excellent.

**Keywords**  $\text{Ag}^+$ -selective electrode, neutral carrier, monothiacrown ether, silicone-rubber membrane

Since the 1967 there have been many reports of the crown ether concerning with metal ions. New method of metal ion determination as the crown ether-metal ion complex has been studied at the new chemistry to the complex between crown-ligand and metal. It was easy to use crown ether, in which possessing donor atoms such as oxygen, likely to neutral carriers owing to its characteristics as for the alkali and alkaline-earth metal ions.

The most important process in the ion-selective electrode for the liquid membrane type is to make the superior selectivity improved by the neutral carriers. If one of the metal ions was able to complex with the finest couple for the neutral carrier one, that carrier will let the best couple select the one of the metal ion in the solution. Liquid membrane type-ion-selective electrode for their selective and precise detection of ions with operated simply determination, have been widely used to the clinical or environmental analyses with simply, safety, and speedy.

The natural neutral carrier is the valinomycin, used as the neutral carrier of a  $\text{K}^+$ -selective electrode.<sup>1</sup> Crown ethers in which donor oxygen atoms in the ring have the similar structure to valinomycin,

which connect with amide group.<sup>2-5</sup> Crown ethers also plays a significant role of neutral carriers for the alkali, and alkaline-earth metal ions.

In order to analyze the heavy and transition metal ions, our research has been studied thiacycrocrown ethers, which compound possessing a part of all of oxygen atoms in crown rings are replaced by sulfur atoms, and readily forms complexes with heavy or transition metal ions. And then thiacycrocrown ether derivatives have also been reported as the neutral carriers for heavy metal ions.<sup>6</sup> Dithia-15-crown-5, in which two sulfur atoms strongly complexed with heavy metal ions has been tested for  $\text{Hg}^{2+}$ - and  $\text{Ag}^+$ -selective electrodes.<sup>7</sup> The  $\text{Ag}^+$ -selective electrodes based on dithiacrown ether as the neutral carrier have revealed a small incline of 40 mV/decade for the calibration curves, and the interferences of  $\text{Hg}^{2+}$  and  $\text{Fe}^{3+}$  have been severe.

We have found that the thiacycrocrown ethers containing both oxygen and sulfur donor atoms in their rings have extracted  $\text{Ag}^+$  selectively. The similar type compounds of thiacycrocrown ether derivatives have been studied as the neutral carriers of  $\text{Ag}^+$ -selective electrodes.<sup>8-10</sup> In order to design highly-soluble and

highly-selective thiacycrown ethers, a lipophilic dodecyl group has been introduced into the thiacycrown ethers. This modification has made it possible to determine  $\text{Ag}^+$  by using a small quantity of the neutral carrier in the membrane. Moreover, we have not recognized differences in calibration plots and selectivity coefficients between monothiacycrown ether-based  $\text{Ag}^+$ -selective electrodes and dithiacycrown ether-based ones. As the result, monothiacycrown ether derivatives have been preferably employed for their easy syntheses. The  $\text{Ag}^+$ -selective electrode based on lipophilic monothiacycrown ether has proved to possess high ion selectivities, emf stability, electrode durability, and reproducibility.<sup>9</sup>

Recently Kaur et al have been reported PVC membrane electrode for silver ion has been shown using *p-tert*-butyl calix [4] arene derivatives to the other neutral carriers for  $\text{Ag}^+$ .<sup>10, 11</sup> This method to  $\text{Ag}^+$  determination is severe at the point of pH range, because of this electrode only to use pH range from 1.0 to 5.6. Simon et al have been already reported using silicone-rubber membrane electrodes which are superior to selectivities comparing with those of corresponding PVC membrane.<sup>12</sup> Silicone-rubber membranes are the better permeability to gas phase molecules than PVC membranes. Dipping the liquid membrane type- $\text{Ag}^+$ -selective electrode based on PVC membrane in the measuring solutions, the neutral carrier tends to dissolve in the solution from the membrane. It must be prevented to use clinical organism and ecology measurement in the condition of "*in vivo*" or "*in vitro*". The best way to avoid dissolving reagent from membrane is to make neutral carrier modify membrane, such as silicone-rubber membrane chemically.

This paper describes the effects of the connection chain length,  $-(\text{CH}_2)_n-$  [ $n = 3, 4, 11$ ], with methylene between monothiacycrown ether and silicone-rubber, and the thickness of the silicone-rubber membrane based on the monothiacycrown ether as neutral carriers for the  $\text{Ag}^+$ -selective electrodes as for the determination of the  $\text{Ag}^+$  to the response and response time, and the selectivities against for the alkali, alkaline-earth, and heavy metal ions.

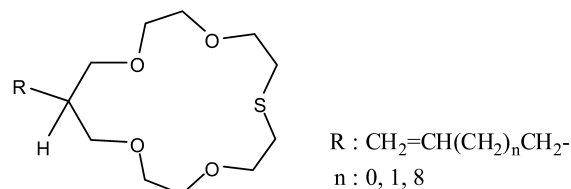
## Experimental

### Chemicals

All of the reagents were purchased from Aldrich and purified by distillation or recrystallization before use. All of the metal salts employed were as described previously.<sup>9</sup> Silicone rubber, one component RTV (Room Temperature Vulcanizable) rubber KE47T (dealcohol type) was purchased from Shin-Etsu Chemical Industry Co., Ltd. Thiacycrown ether derivatives employed here as neutral carriers have already been mentioned.<sup>9, 10</sup> Water was deionized and distilled.

### Synthesis

6-(2'-propen)-, 6-(3'-buten)-, and 6-(10'-undecen)-1,4,8,11-tetraoxa-14-thiacyclohexadecane, which are shown in Scheme 1 were synthesized in a similar way to described previously.<sup>8,10,11</sup>



Scheme 1

#### Synthesis of 10-undecenyl-1-bromide

Into a 2 liters of 4 necked round bottom flask fitted with  $\text{CaCl}_2$  tube, refluxed condenser, argon inlet, and dropped funnel, dry benzene (52 ml) and  $\text{PBr}_3$  (53.0 g/0.196 mol) were added, and after the flask was cooled in a ice bath, dry pyridine (15.6 g/0.197 mol) was dropped into it for 15 minutes. And then dry pyridine solution (5.2 g/0.066 mol) of 10-undecenyl-1-ol (100.0 g/0.581 mol) was dropped carefully over 1 hour. After added alcohol, the solution was stirred for one hour at 0 °C and for 46 hours at room temperature. The precipitation was separated and the solvent was removed in vacuum. Crude was gained 170.2 g. The crude was purified by silica gel (n-hexane,  $R_f = 0.71$ ). The yield of this compound was 103.4 g, 76%, liquid.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ) : 1.29-1.54 (12H, m,  $(\text{CH}_2)_6\text{CH}_2\text{CH}_2\text{Br}$ ), 1.80-1.90 (2H, m,  $\text{CH}_2=\text{CHCH}_2$ ), 2.00-2.01 (2H, m,  $\text{CH}_2\text{CH}_2\text{Br}$ ), 3.40 (2H, t,  $\text{CH}_2\text{Br}$ ), 4.90-5.03

(2H, m,  $\text{CH}_2=\text{CH}$ ), 5.73-5.88 (1H, m,  $\text{CH}_2=\text{CH}$ ).

#### Synthesis of diethyl 2-(10'-undecenyl) malonate, 2

Into a 2 liters of 4 necked round bottom flask fitted with  $\text{CaCl}_2$  tube, refluxed condenser, argon inlet, and dropped funnel, dry alcohol (500 ml) was added and then Na (13.4 g/0.568 g-atom) was added carefully at 0 °C. Sodium was dissolved perfectly, to this solution diethyl malonate (90.9 g/0.568 mol) was dropped. After the addition, the solution was refluxed for 1 hour and 10-undecenyl-1-bromide (133.0 g/0.568 mol) was dropped. After that the solution was refluxed for 35 hours and the solvent was removed in vacuum. The residue was purified by silica gel (ethyl acetate: n-hexane = 1:6,  $R_f$  = 0.51). The yield was 82.8 g, 47%, liquid.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ) : 1.21-1.36 (20H, m,  $(\text{CH}_2)_7\text{CH}_2\text{C}$   $\text{H}_2$ ,  $\text{OCH}_2\text{CH}_3$ ), 1.87-1.90 (2H, m,  $\text{CH}_2=\text{CHCH}_2$ ), 2.02- 2.07 (2H, m,  $\text{CH}_2\text{CH}$ ), 3.31 (1H, t,  $\text{CH}_2\text{CH}$ ), 4.15-4.23 (4H, m,  $\text{OCH}_2\text{CH}_3$ ), 4.90-5.03 (2H, m,  $\text{CH}_2=\text{CH}$ ), 5.76- 5.88 (1H, m,  $\text{CH}_2=\text{CH}$ ).

Following procedure to synthesize the compounds, they were almost the same way except for the purification by silica gel because of heating accelerate polymerization to compounds by double bond reaction. As a result, purification was occurred by silica gel column chromatography.

All of the compounds which were synthesized were identified by  $^1\text{H-NMR}$  spectrum using Nippon Denshi Co., Ltd, model JOEL-EX270-NMR.

#### Fabrication of electrodes

The ratio silicone rubber to neutral carrier was 9:1 (weight rate). Lipophilic salt, dipicryl-amine sodium salt was added into silicone-rubber membrane. The silicone-rubber membranes containing the neutral carrier were casted from the THF solutions according to the previous procedure.<sup>13</sup> The electrode body of a Philips IS-561 was equipped with a 7 mm diameter disc of the silicone-rubber membrane. The internal filling solution was a  $1 \times 10^{-1}$  M  $\text{AgNO}_3$  aqueous solution. The electrodes were conditioned by soaking in a  $1 \times 10^{-3}$  M  $\text{AgNO}_3$  solution overnight.

#### Measurements of emf

The emf were measured with a pH/mV meter of DKK corporation model PHL-20, Denki Kagaku Keiki

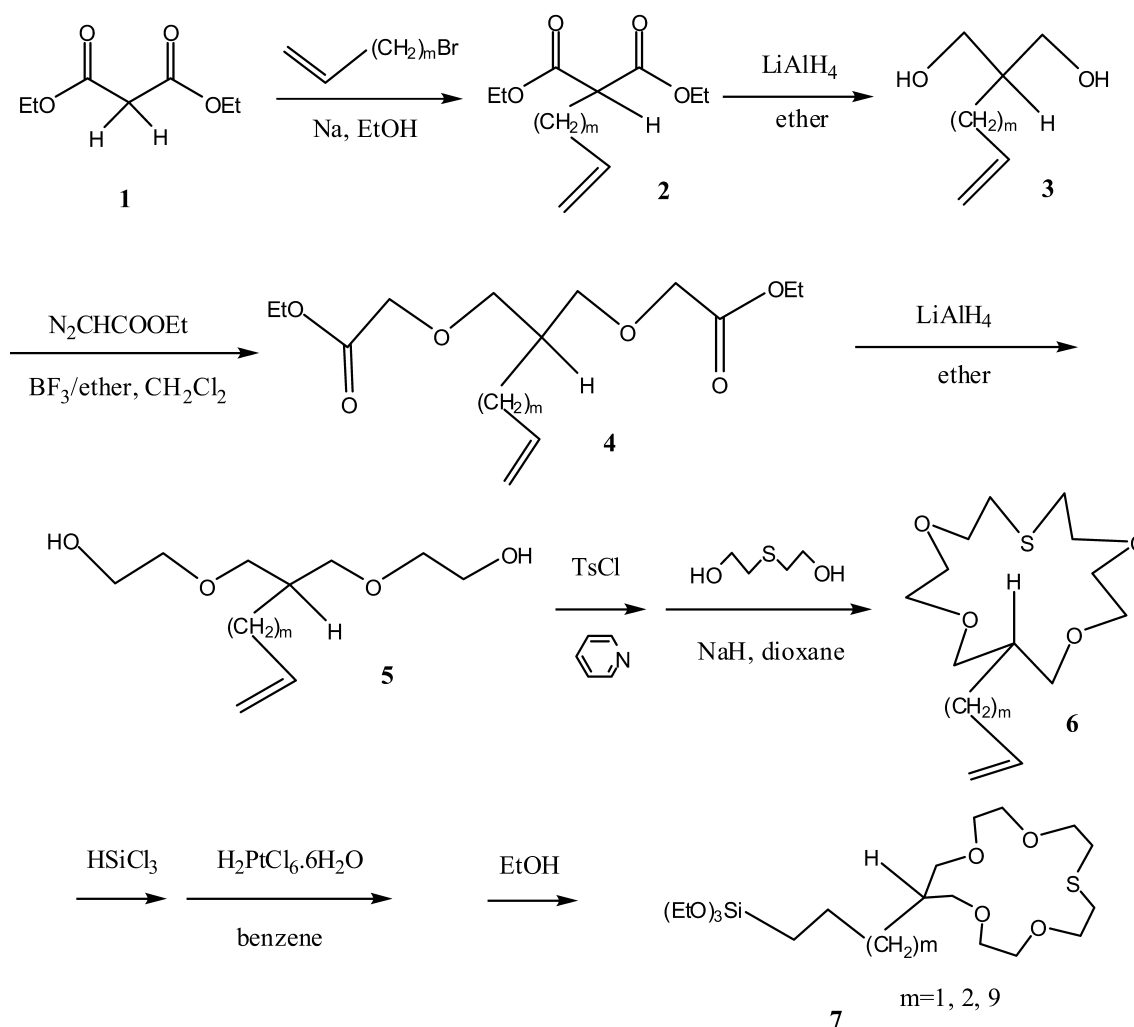
Co., Ltd, at  $25.0 \pm 0.1^\circ\text{C}$ . The electrochemical cell was  $\text{Ag-AgCl}/10^{-3}$  M  $\text{AgNO}_3$ / membrane/ measured solution/ 0.1 M  $\text{NH}_4\text{NO}_3$ / 4 M  $\text{KCl}$ /  $\text{AgCl-Ag}$ .

The potentiometric selectivity coefficients were determined by a mixed solution method (fixed interference method) according to the IUPAC recommendations.<sup>14</sup> The constant background concentrations were  $5 \times 10^{-1}$  M for alkali and alkaline-earth metal ions and  $\text{NH}_4^+$ ,  $5 \times 10^{-2}$  M for  $\text{H}^+$  and heavy metal ions, and  $5 \times 10^{-5}$  M for  $\text{Hg}^{2+}$ .

## Results and Discussion

### Synthesis

The total reaction was shown in Scheme 2. The synthesis of dodecyl monothia-16-crown-5 was reacted with halogenated dodecyl and diethyl malonate. On the other hand, to bond neutral carrier with silicone rubber, halogenated compound, which possessed double bond in the end of chain,  $\text{CH}_2=\text{CH}(\text{CH}_2)_{n-2}\text{Br}$ , was reacted with diethyl malonate. The reduction of ester by  $\text{LiAlH}_4$  was yielded to alcohol without vanishing double bond. However, the purification to each step, which was gained synthesis compounds, was difficult to polymerized the double bond by the heating distillation. The OH group was tosylated by tosyl chloride, and then the cyclic compound was yielded by the reaction of tosylation compound and  $\beta$ -thio diglycol with NaH, dioxane.  $\text{CH}_2=\text{CH}(\text{CH}_2)_{n-2}$ -monothia-16-crown-5 was hydrosilylation to yield (triethoxy silyl)-(CH<sub>2</sub>)<sub>n</sub>-monothia-16-crown-5. The process of the hydrosilylation was checked on confirmed the disappearance of the double bond proton signals,  $\delta$  = (4.90-5.09, 2H,  $\text{CH}_2=\text{CH}$ ; 5.60-6.04, 1H,  $\text{CH}_2=\text{CH}$ ), for viewing  $^1\text{H-NMR}$  spectrum survey. The synthesis compounds were purified by the octadecyl silica gel (reversed phase, RP) and plain silica gel (normal-phase, NP) column chromatography with an appropriate eluent, mostly ethyl acetate, or n-hexane. Silicone-rubber membrane chemically modified with synthesized monothia-16-crown-5 was synthesized. The total yield was lower than 50%, so totally getting higher yield in ordinary, nevertheless purification means the amount of crude obviously decreased, it was necessary to purify synthesis compounds on each step.



### Electrode Response

The membranes conditioning, which have to be dipped to the measurement solution for an overnight might be necessary, because of the new membrane surface not to make coordinate with metal ions sufficient. Also the electrode response for a virgin membrane of  $\text{Ag}^+$ -selective electrode, which was soaked for only a few hours showed about a half slope value of theoretical Nernstian response, 59 mV/decade, but dipped the membrane into measuring metal ion solution for a long time, the slope of calibration curve increased over a half slope and reached 59 mV/decade for the response time within 60 sec. The typical calibration curves for liquid membrane type- $\text{Ag}^+$ -ion selective electrodes to silicone-rubber membrane are shown in Figure 1. The  $n$  shows  $(m + 2)$  in the Scheme 2, " $m$ " = 1, 2, 9 are " $n$ " = 3, 4, 11.

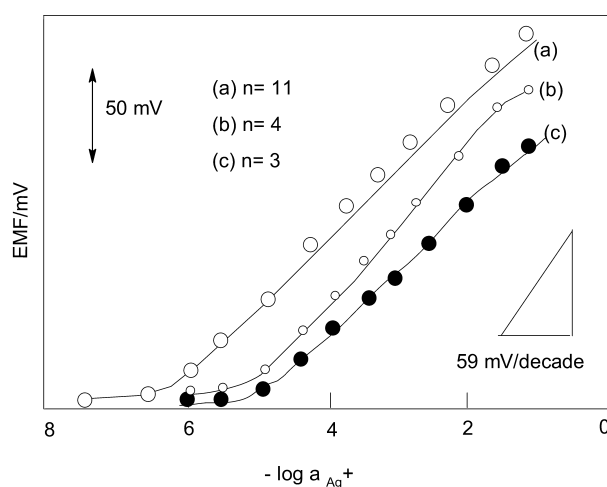


Fig.1 The electrode response of liquid membrane type- $\text{Ag}^+$ -selective electrodes based on silicone-rubber membrane constructed by monothia crown ethers as neutral carrier for the influence of methylene chain length by the space of membrane and neutral carriers.

Steric effect of a number of lipophilic groups in the lipophilic crown ethers as neutral carriers for  $\text{Li}^+$ -selective electrodes has been observed.<sup>15, 16</sup> Longest chain length of the methylene,  $n = 11$ , undecanylene shows that electrode response is the similar to dodecyl-monothiacrown ether at  $10^{-6} - 10^{-2} \text{ M Ag}^+$  activity ranges. The another methylene chain length,  $n = 3, 4$  is not useful for determination  $\text{Ag}^+$  concentrations, because of  $10^{-5} - 10^{-2} \text{ M Ag}^+$  activity ranges.

It was difficult to measure  $\text{Ag}^+$  concentration by the only constructed membrane and neutral carriers, silicone rubber and chemically modified neutral carriers. These silicone-membranes chemically modified neutral carriers- $\text{Ag}^+$ -selective electrode was intended to response for the anion,  $\text{NO}_3^-$  (Fig. 2), which is much more large anion in the volume than chlorine. As the result, addition of the lipophilic salt, dipicryl-amine made the calibration curves and determining  $\text{Ag}^+$  activity regions improve. This slope showed almost the same as to determine the  $\text{Ag}^+$  at the first time to measurement by using virgin membrane. Usage of silicone-membrane chemically modified neutral carriers- $\text{Ag}^+$ -selective electrode depended on number of times getting better the slope to measure, and the silicone membranes turned to brown to black on the surface of membrane with silver ion after 1 week later, using several times/day (Fig. 3). The reliability and durability of emf readings on the electrode response continued for a few weeks.

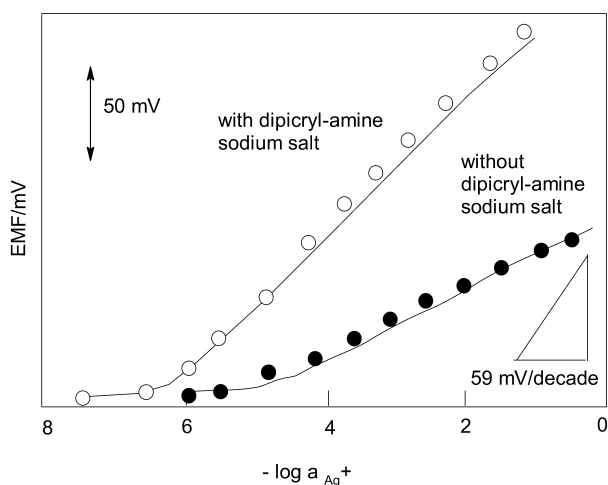


Fig. 2 The electrode response on the effect of lipophilic salt to silicone-membrane chemically modified neutral carrier- $\text{Ag}^+$  selective electrode.

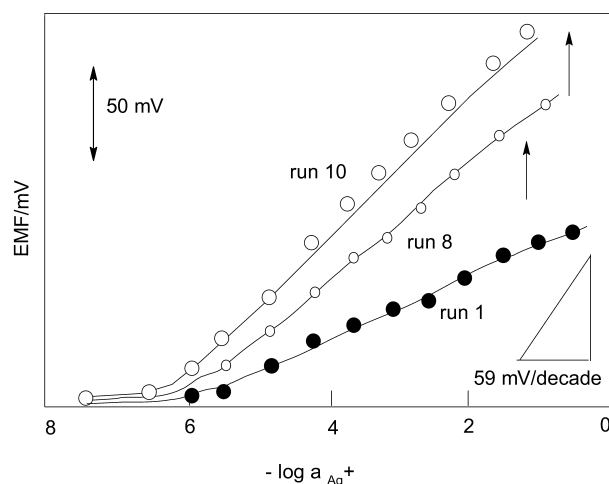


Fig. 3 The electrode response tendency on the virgin silicone-membrane chemically modified neutral carriers to being old one to measuring  $\text{Ag}^+$ .

Run 1: first time to  $\text{Ag}^+$  measurement usage,

run 8: 8 times usage, run 10: times usage

The thickness of silicone-membrane chemically modified neutral carrier- $\text{Ag}^+$ -selective electrode was changed within 1mm, but the electrode response was not improved drastically being at the thin film than thick on the slope and response times.

### Selectivities

Ordinary liquid membrane type- $\text{Ag}^+$ -selective electrode has the outstanding selectivity coefficients, which for  $\text{Ag}^+$  on the silicone-rubber membrane chemically modified neutral carriers- $\text{Ag}^+$ -selective electrode were also evidently superior to those for  $\text{Ag}_2\text{S}$  electrodes, because coexistence of  $\text{Hg}^{2+}$ ,  $\text{Cu}^{2+}$  or another heavy and transition metal ions in the sample solutions did not interfere with the measurements severely. Looking at the chain length of methylene between silicone-rubber and the monothiacrown ether, the selectivity coefficients,  $k_{\text{AgM}}^{\text{Pot}}$  with respect to alkali, alkaline-earth and heavy metal ions,  $\text{NH}_4^+$ , and  $\text{H}^+$  was evidently improved high selectivity better than solid  $\text{Ag}_2\text{S}$ - $\text{Ag}^+$ -selective electrode (Fig. 4). Some of the difference at the chain length,  $n = 3$  or 4 and 11, in the selectivity coefficients are shown in Figure 4. The electrode response except for  $n = 11$  methylene chain length was some difference to measure  $\text{Ag}^+$  activity ranges, however, the few kinds of

methylene chain length effect of these on the selectivity coefficients did not appear drastically, and on looking at Fig. 4 they did not affected the selectivity coefficients widely. The interference of the metal ions except for  $\text{Hg}^{2+}$  was also negligible being likely in the case of dodecyl monothiacrown ether, which is the best neutral carrier to  $\text{Ag}^+$  determination.

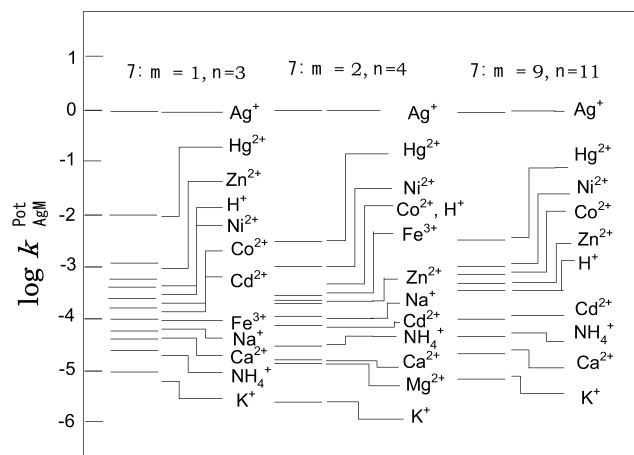


Fig. 4 Selectivity coefficients for  $\text{Ag}^+$  with respect to various kinds of cations in silicone-rubber membrane chemically modified monothiacrown ethers- $\text{Ag}^+$ -selective electrodes.

Both of "m" and "n" are the carbon number at methylene chain, so "m" is equal to (n - 2), double bond having in the molecule, "n" is methylene chain.

Though the silicone-rubber membrane chemically modified monothia-16-crown-5  $\text{Ag}^+$ -selective electrode is very simple and useful  $\text{Ag}^+$  measurement instrument by the method of electrochemistry, lately furthermore the investigation of carriers, neutral carriers are needed to respond target ions precisely like a biosensors for biological organism. It is strange that the animals feel to all the sensors in bodies themselves, sour, smell, and so on. More development of neutral carriers concerning to respond metal ions, organic materials, electron, photo, or color has to be elucidated more chemically.

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