Hg(II) ion-Selective Electrodes with Neutral Carriers of Macrocycles

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New thia-and diselena-crown ethers containing two sulfer and selenium donor atoms have been prepared. And then, mercury (Hg^{2+}) ion-selective electrodes with PVC-plasticizer (STPB) based on some macrocycles as neutral carriers were also made. The electrochemical selectivities for various ions, and the effects for macrocycles, matrix of membranes, ratio of plasticizer to macrocycles, concentration and pH of test solution were investigated on the Hg^{2+} ion selective electrodes.

The 1,10-diselena-18-crown-6-PVC-STPB (sodium tetraphenylborate) exhibited good linear responses of 28.2 ± 0.6 decade^{-1} for Hg^{2+} ion in the concentration ranges of $10^{-2} \sim 10^{-6}$ M Hg^{2+} ion. This electrode exhibited comparatively good selectivities for Hg^{2+} ion in comparison with alkali and alkaline earth metal ions, some heavy metal ions and rare earth metal ion in the range of pH 2.5~6.0. In addition, this electrode was applied as a sensor in the titration of Hg^{2+} ion with I^- ion in water.

Key words : thia, diselena crown ether, Hg^{2+} ion selective electrode, PVC-plasticizer responses, neutral carriers, titration nerstian skpe.

1. Introduction

Crown compounds containing nitrogen and sulfur atoms in the ring are easier to bind heavy metal ions than alkali and alkaline earth metal ions. Thia-crown (S. Kamata ect., 1982) and azacrown ethers (US. Lai ect., 1982) can be applied as neutral carrier of Cu^{2+} and Ni^{2+} selective electrodes, respectively, although the electrode selectivities against other heavy metal ions do not seem very good. Recently, 1,4-dithio 12-crown-4 and -15-crown-5 were utilized as the neutral carrier for Hg^{2+} and Ag^+ selective electrodes. (M.T. Lai ect., 1986) These electrodes exhibited quite high selectivities for Hg^{2+} and Ag^+ with respect to alkali and alkaline earth metal ions and some other metal ions. These electrodes can be employed as sensors for Hg^{2+} and Ag^+ titrations and for the measurement of solubility product of AgCl. Employment of lipophilic thia-

crown compounds such as cyclam as the neutral carriers of Ag^+- selective electrodes seems to improve the electrode property. (M.Oue ect., 1988) The 1-dodecyl-9-thia-16- crown-5-based electrode exhibited Nernstian response for the Ag^+- activity changes in the range of $10^{-5} \sim 10^{-2}$ M. The electrode is highly Ag^+-selective aganist alkali and alkaline earth metal and heavy metal ions except Hg^{2+}, even the selectivity coefficient with respect to Hg^{2+} being close to $1.0 \sim 10^{-2}$M.

There is no commercially available mercury (II) ion selective electrode. But a few other electrodes, such as the iodide electrode ($AgI-Ag_2S$), which respond to Hg^{2+} ions have been described (ORION. 1970, Analytical. 1972) before or eleswhere. Systematic studies performed with various macrocyclic compounds in this paper showed that PVC membranes containing new macrocyclic compounds such as 1,10-diselena-18-crown-6 and derivatives of pyri-

dino-18-crown-6, diacetato 8,11-dithia-1,4-diazacyc-lodecane and 1,5,9,13-tetra thiacyclohexadecane-3, 11-diol (Figure 1) were suitable as the neutral carriers for the Hg^{2+} ion selective electrodes.

The electrochemical selectivities for various ions, the effects for kinds of macrocycles, the matrix of mambranes, ratio of plasticizer to amcrocycles concentration and pH of test solution were investigated by the Hg^{2+} ion selective electrodes. In addition, the electrode were used as a sensor of titration experiments for the determination of Hg^{2+} ion.
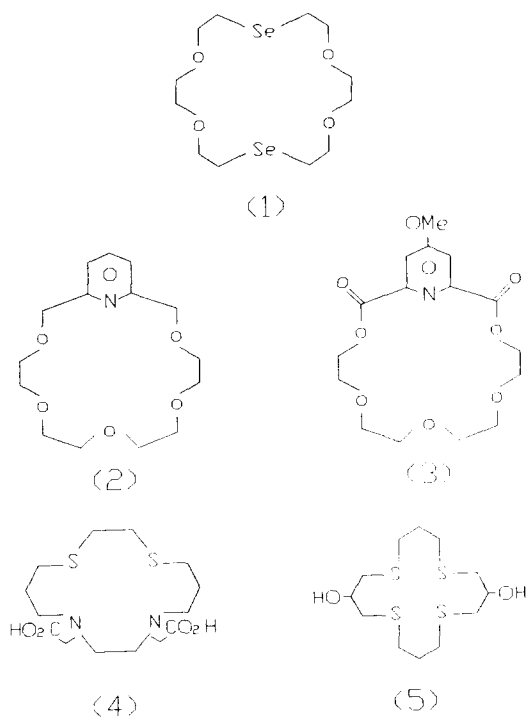

Fig. 1. Structural formulas of 1,10-diselena-18-crown-6 (1), derivatives of pyridino-18-crown-6 (2,3,) 8,11-dimethylacetato-8, 11-dithia-1,4-diazacyclodecane (4), and 1,5,9,13 tetrathiacyclohexadecane-3,11-diol (5).

2. Experimentals

Chemicals

All chemicals were analytical reagent grade. The derivatives of pyridino-18-crown-6 were obtained from Izatt's Laboratory of Brigham Young University, Provo, Utah, USA and 1,10-diselena-18-crown-6 and 8,11-dimethyl acetato-8,11-dithia-1,4-diazacyclodecane were synthesized by the methods reported in the literatures (C.W. McDaniel ect., 1989, H. D. Kim, 1993) and 1,5,9,13-tetrathiacyclodecane- 3, 11-diol was perchased from Aldrich company.

Preparation of 4,7,13,16-tetraoxa-1,10-diselena-cyclooctadecane (1,10-DISELENA-18-CROWN-6) : Gaseous hydrogen selenide was bubbled into 600 ml of ethanol, which had previously been treated with 3.8 g(0.17 mole) of sodium metal and 2.3 g of potassium chloride, (0.03 mmole), until the gas appeared in the bleach trap (the bleach solution turned red). The ethanol solution truned cloudy white. The etanol solution was heated to reflux, whereupon triethylene glycol dichloride (11.53 g, 0.062 mole) in 200 ml of ethanol was added slowly over a 15 hours period under a nitrogen purge. The resulting mixture was refluxed for 3 days under a nitrogen atmosphere and cooled. The reaction mixture was stirred with Norit and filtered through celite to give a light yellow solid, 3.35 g(27.8 %); mp 91~92°(recrystallized from ethanol); IR: 1455, 1325, 1265, 1115, 1095, 1060, 1030, 1000 cm^{-1} ; NMR (δ) 3.78 (t, 8H); 3.62 (s, 8H); 2.84 (t, 8H).

Anal. Calcd. for $C_{12}H_{24}O_4Se_2$: C, 36.93; H, 6.20; mol. wt. 392. Found: C, 37.16; H, 6.21; MS, 391, 392, 393.

Preparation of (8,11-demethylacetato-8, 11-dithia-1,4-diazacyclodecane) : The solution of 3,3'-propylenedithio dipropionic acid (12mmole), which had previously been treated with NaOH (1.60 g, 4 mmole) in water (60 ml) was obtained by the method reported in the literature (H.K. Kim, 1992).

These two-phase mixtures were stirred during the dropwise addition of a solution of 2- (chloromethyl) acetic acid (3.0 g, 20 mmol) in chloromethane (25 ml) over period of 2 hours. Stirring was continued at room temperature for 24 hours. and the organic layer was then separated. The aqueous layer was extracted with dichrolomethane (500 ml), and the combined organic layer were evaporated to give a solid which was recrystallized from methanol: yield 74% m.p. 235℃, $C_{18}H_{32}O_8N_2S_2$ (463.38).

Found: C 45.8%, H 6.92%, N 5.97%, required: C 46.1%, H 6.88%, N 5.98%, ^{1}H, at $CDCl_3$ and TMS, δ3.46 (4H, acetic group) δ3.44 (4H, acetic group), δ1.57 (2H, NH), δ1.82 (q. 4H, 2C-CH₂-C), δ2.78 (m, 8H, 2S-CH₂CH₂CH₂N), δ2.74 (S, 4H, SCH₂), δ2.88 (s, 4H, NCH₂)

Electrode Preparation

A mixture of 100 mg of PVC (M. Macini, ect., 1974, T. Maeda, ect., 1981), 30 mg of macrocyclic compounds and 50 mg of dibuthyl phthalate were dissolved in 2 mL of tetrahydrofuran (THF). In some instances, sodium tetraphenylborate (STPB) as the plasticizer was also added. The PVC-THF solution was poured into a glass dish of diameter 5 cm and the THF was evaporated at room temperature for about 24 hr. and a semi-transparent membrane about 0.03 mm thickness obtained. A good linear correlation between the thickness of the membrane and the amount of PVC was found. A piece about 12 mm in diameter was cut from the PVC membrane and attached to a polyethylene cap by wetting the membrane with the PVC-THF solution mentioned above. The diameter of the exposed membrane was about 7 mm. The polyethylene cap with the membrane was then incorportaed into an Ag-AgCl wire electrode. After filling with internal solution containing 5×10^{-4} M Hg (NO₃)₂ and 10^{-2}

M HNO₃, the electrode was conditioned by soaking in 0.1 M Hg (NO₃)₂ solution for 24 hr. A salt-bridge containing KNO₃ solution was prepared in each instance. The electrochemical system for this study was as follows:

Ag-AgCl | internal solution (5.0×10^{-4} M Hg (NO₃)₂) | | PVC-membrane | testing solution ‖ salt bridge (1M KNO₃) | SCE

The e.m.f. measurements were made with 960 autochemistry system (Orion Research, USA). The response time of these macrocyclic compounds − PVC membrane electrode was checked in short time (below one minute). In this work, the potential measurements were taken in 3 minutes after the introduction of the test solutions, which were stirred during the measurements.

Log K Determination

The metal ion binding constants with various macrocycles (Figure 1) were determined by potentiometry using the Orion-Ross double junction semi-micro combination glass electrode. The semi-micro potentiometric titrations were carried out in a sealed and thermostated vessel (5 mL 25 ± 0.1℃) under a CO₂-free nitrogen atmosphere. During each titration run, the e.m.f values of the glass electrode, which are linearly related to pH under constant ionic strength (0.1010 M Me₄NNO₃) were recorded as a function of the amount of titrant added.

Standard electrode potintial, E°(460.2 mV) and the ionic products of water (pHs'=13.70) at 0.1010 M-Me₄NNO₃ were determined by titrating a HNO₃ solution to a standardized Me4NOH solution. The log K (Table 1) values for stability constants were computed from the data obtained by titrating acidified ligand solutions with Me4NOH in the absence and presence of the metal ions. The ionic strength was maintained at 0.1010 M Me₄NNO₃ for all the
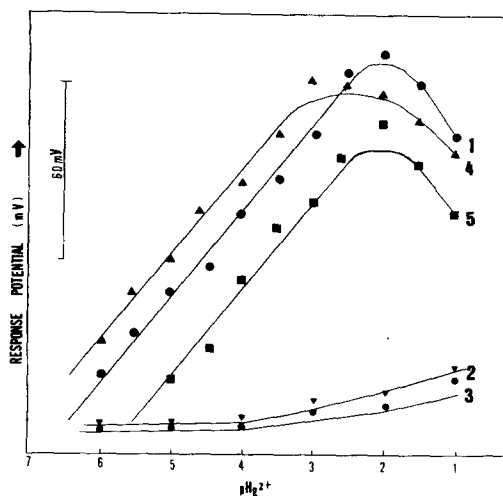
Fig. 2. **Potential responses of Hg²⁺ ion-selective electrodes base on (1) 1,10-diselena-18-crown-6, (2) 1,5,9,13-tetrathiacyclohexadecane-3,11-diol, (3) 8,11-dimethyl acetato-8,11-dithia-1,4-diazacyclodecane, (4) Py18C6 and (5) methoxy pyridine-18-crown-6 with the addition to the membranes of sodium tetraphenylborate (STPB) at an STPB to macrocycles ratio of 0.5. mercury (II) nitrate solution was used as the test solution.**

Fig. 3. **Effect of ratio of macrocycle (1) to plasticizer (STPB) in PVC-membranes on potential responses of the Hg²⁺-ion selective electrode. [A: STPB (2.5), B: STPB (1.0), C: STPB (2.0) and D: STPB (0.0)]**

titrations. The filling solution of the electrode was saturated in Me_4NNO_3 (0.8 M) solution. The program SUPERQUAD (Peter Grans, 1985) was used for all the calcurations. The selectivity coefficients for various metal ions were evaluated by using the differences of each stability constants and these values were compared to values of electrode selectivities.

Calorimetric Measurements

A Tronac Model 450 isoperibol titration calorimeter was used throughout in this study. Enthalpies for metal ion binding and protonation of ligand (Figure 1-2-3) were determined by a calorimetric titration technique described previously (O.J. Jung, 1993).
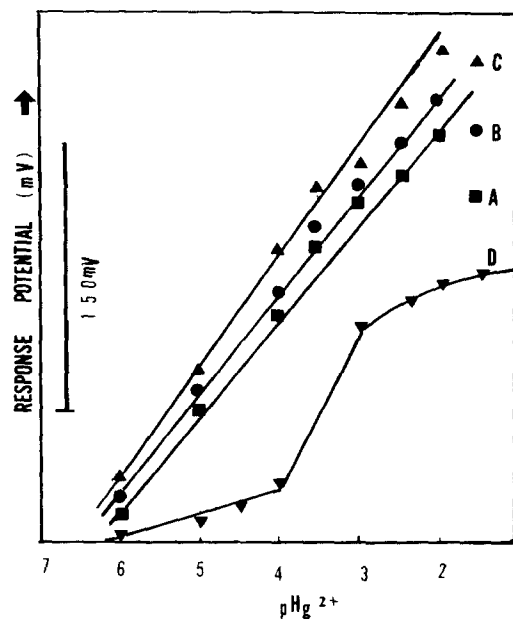
Evaluation of Electrode Selectivity

The selectivity coefficients (K_{Hg-M} ᵖᵒᵗ) for various cations were evaluated graphically by the mixed-solutions method (G. A. Rechnitz, 1972). The electrode potentials of solution of Hg²⁺ ion alone and of a mixed solution containing a fixed amount of Hg²⁺ ion ($\mathcal{A}_{Hg2+} = 1.0 \times 10^{-5}$ M) and a varying amount of the interfering ions M^{z+} ($\mathcal{A}M^{z+}$), were measured as E_1 and E_2, respectively, and can be expressed as follows:

$$K_{Hg-M} {}^{pot} \mathcal{A}_M^{z/z} = \{\exp[(E_2 - E_1)F/RT]\}\mathcal{A}_{Hg} - \mathcal{A}_{Hg} \quad (1)$$

where z is the charge of the interfering ion. K_{Hg-M} ᵖᵒᵗ can be evaluated as the slope of the graph of $\{\exp[(E_2 - E_1)F/RT]\}\mathcal{A}_{Hg} - \mathcal{A}_{Hg}$ aganist to $\mathcal{A}_M^{1/z}$. K_{Hg-M} ᵖᵒᵗ.

Table 1. Stability constants of cation complexes with macrocycles at 25°C and I=0.1010 mole · dm^{-3} (Me$_4$NNO$_3$) in methanol

cations	Log K of complexes with ligand				
	1^a	2^a	3^a	4	5
Cs$^+$	0.50	4.24	4.10	0.6	0.52
Sr^{2+}	2.40	4.32	4.98	2.43	2.13
Ba^{2+}	3.40	4.34	5.26	3.12	3.26
Nd^{3+}	3.77	3.85	3.73	3.84	3.41
Cu^{2+}	1.46	–	–	–	–
Zn^{2+}	1.37	–	–	–	–
Cd^{2+}	6.21	3.63	3.51	6.32	6.27
Pb^{2+}	5.48	2.92	2.02	5.56	5.87
Hg^{2+}	8.50	4.52	4.58	10.62	10.65

a: solution calorimetric data obtained in acetone solvent

3. Results and Discussion

The stability constants of several cation complexes with the ligands (Figure1-1~5) were presented in Table 1.

The order of stability constants of Hg^{2+}-complexes was 5>4>1>3>2 for macrocyclic ligands (1~5) and the order of stability constant of each cation complexes for various macrocycles was Hg^{2+}>Cd^{2+}>Pb^{2+}>Ba^{2+}>Sr^{2+}>Nd^{3+}>Cs^{2+}. Thus the stability constants of complexes were dependent on the size-ratio of metal ions and macrocyclic cavities because most of metal ions follow the size rule.

There has been considable interest in the design of crown compounds for the selective complexation of metal cations. Since the first oxygen, sulfur, nitrogen, phosphorus, and tin have been used to one or all of the oxygen heteroatoms. These crown ethers show selectivity for different cations based on ring size and the heteroatoms used. Substitution of either selenium or sulfur for oxygen in crown ethers greatly influences the complexation of metal cations, weakening the complexation of metal cations, weakening the complexation of alkali (Cs$^+$) and alkaline earth (Sr^{2+}, Ba^{2+}) metal ions, and
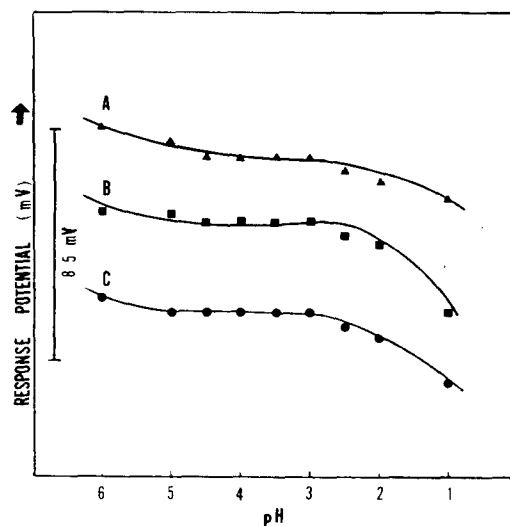

Fig. 4. Effect of pH of test solution on potential responses of an Hg^{2+} ion selective electrode based on 1,10-diselena-18-crown-6-PVC-STPV.
(A): [Hg^{2+}]=1.0×10^{-2} M (B) [Hg^{2+}]=1.0×10^{-3} M (C) [Hg^{2+}]=1.0×10^{-4} M

rare earth metal ion (Nd^{3+}) and strengthening that of soft cations such as Pb^{2+}, Cd^{2+} and Hg^{2+}. With cessium, the electrostatic forces are decreased in the diselena (1)-and thia (4,5)-crown ethers because of decreasing electronegativity of the sel-
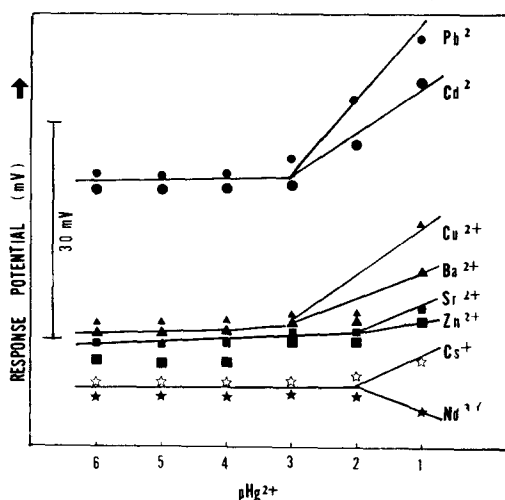
Fig. 5. Potential responses for various metal ions with Hg^{2+} ion selective electrode based on 1,10-diselana-18-crown-6. ($[Hg^{2+}]=1.0\times10^{-5}M$)

enium and sulfur atoms (H. K. Frensdoff, 1971). With mercury, lead and cadmium, the attraction by the diselena-and thia-crown ethers are enhanced by the type of covalent bonding present. Replacement of oxygen by sulfur and selenium virtually destroys the ability of crown ether to complex with other cations than those, such as Pb^{2+}, Cd^{2+} and Hg^{2+}, which show affinity for the "soft" selenium and sulfur atoms in the thia and diselena crown molecules (H. D. Lamb ect., 1981 C. W. McDaniel ect., 1989).

Especially the stability constants of Hg^{2+} complex with diselena-and thia-crown ether were higher than those of Cd^{2+} and Pb^{2+} ions because entropy effect is increased by forming the complexes.

Therefore, the selectivity of Hg^{2+} ion was the biggest as compared with the other cations when diselena-and thia-crown ethers (Figure 1) were used as ligands. And then the selectivities of mercury (II) were discussed by Hg ion selective electrodes based on the macrocycles as a neutral carriers.

Various macrocyclic compounds containing the crown ethers,1,10-diselena-18-crown-6, 1,5,9,13-tetra

thiacyclohexadecane-3,11-diol, 8,11-demethylacetato-8,11-dithia-1,4-diazacyclodecane, Py18C6, and methoxy pyridine-18-crown-6 were tried as neutral carriers for the Hg^{2+} ion selective electrodes.

The e.m.f. potential responses of Hg^{2+}-PVC electrodes based on these macrocyclic compounds were illustrated in Figure 2.

It appears that the crown ethers diselena- and dithia-crown ethers give a better potential response than the Py18C6 and methoxy pyridine-18C6, which show almost no response of the Hg^{2+} ion.

It is well known that macrocyclic cmopounds are very sensitive to the size of metal ion mentioned above. Among these macrocycles, macrocycle (1), (4) and (5) have most suitable cavity size to fit the Hg^{2+} ion. Especially, both macrocycle (4) and (5) can form stronger complexes than other crown ethers with the Hg^{2+} ion as shown in Table 1. It is reasonable to predict that both the macrocycles (4) and (5) studied here will form very strong complexes with Hg^{2+} ions, which results in a difficulty in exchanging the Hg^{2+} ions of the complexes in the PVC membrane with the Hg^{2+} ions in the test solution. Hence, the lack of response with both the macrocycle (4) and (5) can be understood. In contrast, as shown in Figure 2, the electrodes based on crown ethers (1~3) seem to exhibit a linear response to the activity of the Hg^{2+} ion. Among the macrocycles examined, 1,10-diselena-18-crown-6 (1) seems to be the best neutral carrier, exhibiting a Nernstian response with a slope of 28.2 $\pm$ 0.6 mV $\cdot$ pHg^{-1} and the widest linear range in the concentration range of $10^{-2}\sim10^{-6}$ M $Hg(NO_3)_2$. The effect of ratio of the macrocycle (1) to plasticizer (sodium tetraphenylborate, STPB) based on PVC-Hg^{2+} ion selective electrodes was discussed in Figure 3.

When the STPB as plasticizer was also added to the PVC-macrocyle (1) membranes of Hg^{2+} ion se-

lective electrodes, the response potentials were obtained linearly in the range of the concentration of $10^{-2} \sim 10^{-6}$ M-Hg $(NO_3)_2$ as shown in Figure 3-A,B and C. The addition of STPB in the macrocycle (1) results in a large improvement in the response slope. Hence the addition of STPB to a membrane can increase the electrical conductivity and the sensitivity of the electrode. Partition of cation to membrane should affect the selectivity of electrode, which depends on dielectric constant of plasticizer.

The maximum concentration (A_{max}) at the maximum response (Figure 2) is inversely proportional to the stability constant (Log K) of the complexes of the Hg^{2+} ion with the macrocycles (Table 1)(W. Shimon, 1974). Therefore, among these macrocycles, derivatires of pyridine-18-crown-6, and 1,10-diselena-18-crown-6 form the weaker complexes than thia-macrocycles for Hg^{2+} ions and the macrocycles (1), and give the largest value of A_{max} and the widest linear concentration range.

Despite the Log K values of Hg^{2+}-macrocycle (Figure 1~4 and 5) are much larger than that of Hg^{2+}-macrocycle (Figure 1-1), efficiency of the transportation of Hg^{2+} in membrane electrodes based on the PVC-macrocycle (4,5)-plasticizer was smaller than that of Hg^{2+} in those based on the PVC-macrocycle (1)-plasticizer because Log K values of Hg^{2+}-macrocycle (4,5) complexes were much larger than the value of interaction between Hg^{2+} ion and receiving species (TPB).

In addition, when the TPB⁻ anions used as plasticizers replaces NO_3^- in the membrane, because of its higher relative molecular mass, its mobility is expected to be lower than that of NO_3^- and the reduction for the mobility of the anion in the membrane can lead to an improvement of the Nernstian slope (K. Kimura ect., 1987, T. Nakamura ect., 1987). As illustrated in Figure 3C and 3B with STPB to 1,10-diselena-18-crown-6 ratios of 1.0~2.5,

the slopes are super Nernstian (>50 mV pHg⁻¹). At an STPB to crown ether ratio of 2.0 (Figure 3 C), the response slope reaches about 60 mV pHg⁻¹ which is a typical monovalent response and may be attributed to the formation of Hg(TPB)⁺ ions in the membrane. However, if the ratios of STPB to crown ethers are over 0.5 in Hg^{2+} electrode membranes, the membrane electrodes exhibited poor reproducibility and salting out occurred after about two months, whereas the membrane with an STPB to 1,10-diselena-18-crown-6 ratio of 0.5 showed good reproducibility and a Nernstian response for bivalent Hg^{2+} ion (Figure 2).

The results of this study indicate that two criteria must be met in order of the selective transportation for metal ions by neutral carriers in the Hg^{2+}-selective membrane electrode system. First, The M^{n+} ion must selectively be transported into the neutral carrier and must form its stable complex (HgL^{2+}) with the macrocycle in the eclectrode systems. In addition, the effectiveness of these transportation will be the greatest if Log K for M^{n+}-macrocycle interaction is enough large and the macrocycle is very insoluble in water. Second, the ratio of the Log K for M^{n+}-macrocycle to M^{n+}-plasticizer (TBP⁻) interaction must be enough large to ensure a quantative spripping of M^{n+} ion at a internal surface of the electrode membranes.

The effect of the pH in test solution (Hg^{2+}) on Hg^{2+} ion-selective electrode based on 1.10-diselena-18-crown-6-PVC-STPB membrane was also studied. As illustrated in Figure 4, for the Hg^{2+}-selective electrode, the potential responses of 10^{-3} and 10^{-4} M Hg^{2+} in solutions indicated no significant changes at pH>2.5 but at pH<2.5, the potential responses were drastically reduced. This could be due to protonation of the macrocycles in the membrane at pH<2.5, which results in a dissociation of metal complexes.

Table 2. Selectivity coefficients $(K_{Hg^{2+}}{}^{pot}\text{-}M^{n+})$ for various ions with a Hg^{2+} ion selective electrode base on 1,10-diselena-18-crown-6-PVC-STPB membrane

Ion	$K^{pot}_{Hg^{2+}}\text{-}M^{n+}$	Ion	$K^{pot}_{Hg^{2+}}\text{-}M^{n+}$
Cs^+	6.1×10^{-5}	Cd^{2+}	1.8×10^{-2}
Ba^{2+}	7.4×10^{-4}	Cu^{2+}	7.2×10^{-4}
Sr^{2+}	6.8×10^{-4}	Zn^{2+}	3.8×10^{-4}
Pb^{2+}	1.5×10^{-3}	Nd^{3+}	1.2×10^{-5}

The selectivities of the Hg^{2+} ion-selective membrane electrode were investigated by making the potential measurements in solutions containing a fixed amount of Hg^{2+} ion $(1.0 \times 10^{-5}$ M$)$ and varying amount of interfering ions. The interference of alkali (Cs^+) and alkaline earth metal (Sr^{2+}, Ba^{2+}), some of transition metal $(Cu^{2+}, Zn^{2+}, Cd^{2+}$ and $Pb^{2+})$ and Nd^{3+} ion were studied. As shown in Figure 5 except for Pb^{2+} and Cd^{2+}, the common transition metal ions $(M^{n+}) < 10^{-2}$ M in 10^{-5} M Hg^{2+} solution cause virtually no interference on the Hg^{2+} ion selective membrane electrode.

The selectivity coefficients $(K^{pot}_{Hg^{2+}}\text{-}M^+)$ for various ions (M^{z+}) (Jeng J. and Shin J. S. 1984) were evaluted as the slopes of the graphs of $\{\exp(E_2 - E_1) F/RT\} \mathcal{A}_{Hg} - \mathcal{A}_{Hg}$ aganist $\mathcal{A}_M{}^{z+}$ for the Hg^{2+} ion selective electrode. As shown in Table 2, the selectivity coefficients for most metal ions are fairly small $(10^{-2} \sim 10^{-5})$.

As shown in Table 1 and 2, these data are dependent on the differences of the stability constants for cation complexes with the same macrocycles. Most common ions cause only small interferences except the Cd^{2+} and Pb^{2+} ions on the Hg^{2+} ion selective electrode. The Hg^{2+} ion selective electrode was applied as a sensor in titration of Hg^{2+} ion with I^- ion and the titration curve was shown in Figure 6.

The Figure 6 exhibited the traditional potentio-titration curve of Hg^{2+} ion in the I^- ion. In titration involving $1:1$ stoichiometry of reactants, the equivalence point is the steepest point of the titration
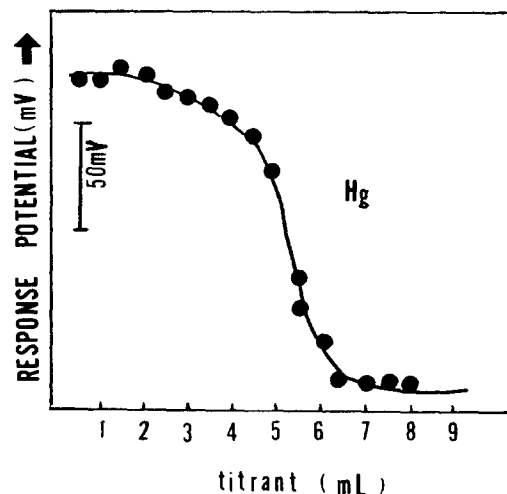
Fig. 6. Titration curve of Hg^{2+}-ion (200 mmol) with I^--ion as titrant by the Hg^{2+} ion selective electrode based on 1,10-deselena-18-crown-6-PVC-STPB membrane.

curve. For stoicheometries other than $1:1$ such as that for the reaction $Hg^{2+} + 2I^- \rightarrow HgI_2$ the curve is not symmetric near the equivalence point.

The equivalence point is not at the center of the steepest section of curve, and it is not an inflection point as shown in Figure 6.

By the experimental results, the 1,10-diselena-18-crown-6 (1)-PVC-plasticizer (STPB) membrane can be used repeatedly for at least two month, because of the low solubilities of these macrocycles in water. It can be concluded that mercury ion-selective electrodes based on the 1,10-diselena-18-crown-6-PVC-STPB membrane exhibit good sensitivities, reproductibilites, selectivities and electrical responsibilities in the wide range of concentration $(10^{-6} \sim 10^{-2}$M$)$.

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거대고리 중성운반체를 갖는 Hg(II)이온 선택성 전극

정오진

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두 개의 황과 셀렌의 주개원자를 포함한 새로운 thia 및 diselena 크라운에데르 화합물을 합성하였다. 그리고 이화합들을 중성운반체로 하고 PVC-가소제(STPB)를 포함한 Hg(II) 선택성 전극을 제작하였다. 이 전극들을 이용하여 여러 이온들의 전기화학적 선택성, 중성운반체의 종류 및 농도와 선택막의 매질에 대한 효과 그리고 실험용액의 pH변화에 대한 전극의 선택적 감응성들의 영향을 각각 검토하였다.

1,10-diselena-18-crown-6-PVC-STPB의 중성운반체의 막전극은 $10^{-2}-10$ M Hg^{2+} 이온의 농도범위에서 28.2 ± 0.6의 Nernstian 기울기를 갖는 좋은 선형적 감응성을 갖는다. 그리고 이 전극은 pH 2.5~6.0 범위에서 알칼리토 금속, 몇가지 중금속 및 희토류 금속 이온에 대하여 좋은 선택성을 갖는다. 특히 이 전극은 수용액 중에서 I^- 이온으로 Hg^{2+} 이온을 전위차 적정할 수 있는 센서로서 응용할 수 있다.