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

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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 a Ag^+ -complex of the thiacycrown ether as the membrane active material instead of the thiacycrown ether itself allowed the 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.

Keywords Ion selective electrode, silver ion, complex-carrier, dodecyl-monothia-16-crown-5

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 were carried out, because of their expected applications to clinical and environmental analyses.¹⁻³ On the contrary, few studies concerning heavy metal-ISEs based on thiacycrown ether derivatives have been reported because of their poor solubilities and sluggish cation-complexing equilibrium. Kamata *et al.*⁴ have fabricated a Cu^{2+} -selective electrode based on 13,14-benzo-1,4,8,11-tetrathiacyclopentadecane. Recently, Lai *et al.*⁵ 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 the 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.

We have attempted to design highly soluble thiacycrown 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.⁶

This paper describes 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.

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 twice by reprecipitation from tetrahydrofuran (THF) in methanol. All of the metal salts employed here were nitrates of analytical grade and were purchased from Wako Pure Chemicals. Water was deionized and distilled.

The monothiacrown ether, 6-dodecyl-1,4,8,11-tetraoxa-14-thiacyclohexadecane 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) dis-

solved 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/hexane=1/10, $R_f=0.3$); white crystals; yield 25%; mp 37.5°C ; IR(KBr) 2920 and 2850 (C-H), 1120 (C-O), 725 cm^{-1} (C-S); $^1\text{H-NMR}(\text{CCl}_4)$ $\delta=0.88$ (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, $\text{OCH}_2\text{CH}(\text{C}_{12}\text{H}_{25})\text{CH}_2\text{O}$), 3.50–3.70 (12H, m, OCH_2); MS, (m/z) 418 (M^+). Anal. Calcd for $\text{C}_{23}\text{H}_{46}\text{O}_4\text{S}$: C, 65.99%; H, 11.08%; S, 7.66%. Found: C, 65.85%; H, 11.06%; S, 7.37%.

The Ag^+ -1(1:1) complex was prepared as follows. Equal volumes (4 ml) of dodecyl-monothia-16-crown-5 (16 mg/0.0382 mmol) chloroform solution and 1 M AgNO_3 aqueous solution were taken into a stoppered test tube. After the solution was stirred in the 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; yield 44%; mp $104\text{--}105^\circ\text{C}$; IR(KBr) 2920, 2850 (C-H), 1360 (NO_3), 1120, 1100 cm^{-1} (C-O-C); Anal. Calcd for $\text{C}_{23}\text{H}_{46}\text{O}_4\text{S}$. AgNO_3 : C, 46.94%; H, 7.88%; N, 2.38%. Found: C, 46.68%; H, 7.90%; N, 2.39%.

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^+ -1 complex, 68.9 wt% membrane solvent (plasticizer), and 0.3 wt% lipophilic salt (0.1 mol% to the Ag^+ -1 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 1×10^{-3} M (or 1×10^{-1} M) AgNO_3 aqueous solution. The electrodes were conditioned by soaking in 1×10^{-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°C . The electrochemical cell was $\text{Ag-AgCl}/10^{-3}\text{ M AgNO}_3/\text{membrane/measured solution}/0.1\text{ M NH}_4\text{NO}_3/4\text{ M KCl}/\text{Ag-Cl-Ag}$.

The potentiometric selectivity coefficients, $k_{\text{AgM}}^{\text{Pot}}$, 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} , 1×10^{-3} 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 Ag^+ 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: 1×10^{-2} M NaCl , KBr and KI aqueous solutions.

Results and Discussion

Electrode response

Silver ion selective electrodes of liquid membrane type using thiacycrown ether derivatives reported so far did not exhibit sufficient electrode response and reproducibility.⁵ Ion selective electrodes based on lipophilic crown ethers for alkali and alkaline-earth metal ions often showed 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, dodecyl-thiacrown ether 1 was applied to the neutral carrier of the Ag^+ -selective electrode. 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/

Fig. 1 Calibration plots of pure AgNO_3 solution with Ag^+ electrode based on 1-DOP-PVC membrane. With (a) and without (b) 0.3 wt% dipicrylamine sodium salt.

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decade, though the theoretical value for Ag^+ selective electrode is 59 mV/decade (Fig. 1(b)). The poor sensitivity in the high Ag^+ activity is partly due to an anion response. Lipophilic salts such as dipicrylamine sodium salt 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 (Fig. 1(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 s.

Selectivities

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, by making the electrode conditioning, complexation of 1 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. In the PVC membrane of Ag^+ -1 complex, the effect of membrane solvents was investigated on the selectivity coefficients, $k_{\text{AgM}}^{\text{Pot}}$ with respect to alkali, alkaline-earth, and heavy metal ions, NH_4^+ , and H^+ (Fig. 2). 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 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 ($\log a_{\text{Ag}} > -2.5$). Similar tendency for the selectivity coefficients was observed in the DOP and DOS membrane systems, which showed the theoretical Nernstian behaviors at wide Ag^+ activity

Fig. 2 Effect of membrane solvent on selectivity coefficients.

Fig. 3 Effect of pH in sample solutions on potential responses of Ag^+ -selective electrode based on Ag^+ -1 complex.

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+} .^{5,14} This Ag^+ -electrode based on the Ag^+ -1 complex, however, possesses much higher selectivities against Hg^{2+} .

Effect of pH

The pH dependence of emf reading for the Ag^+ -selective electrode is shown in Fig. 3. The pH values in the sample solutions were adjusted by HNO_3 and NaOH . The suitable pH range for the emf measurements ranges from neutral to acid (pH 2). High pH values ($\text{pH} > 7.5$) in the sample caused some emf decrease probably because of Ag_2O precipitation with OH^- . On the other hand, at low pH ranges ($\text{pH} < 2$) emf values also decreased. Lai *et al.*⁵ have reported that the emf decrease below pH 2 might be derived from protonation of the thiocrown ether, which in turn causes loss of 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.⁵ 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 (Fig. 4). The titration curves revealed ideal S-shape in which the emf changed drastically around the end point.

Another application of silver ion determination by a standard addition method, called Gran's plot method,

Fig. 4 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 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.

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 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 Ag^+ -1 complex is evidently promising for the application of silver ion determinations. Also, this Ag^+ electrode based on 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.

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(Received December 24, 1988)

(Accepted January 17, 1989)