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Effect of π Electrons on the Detection of Silver Ions by Ion-selective Electrodes Containing Tripodal Broom Molecules as an Ionophore

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Tripodal "broom" molecule derivatives containing π electrons were used as ionophores of silver ion-selective electrodes. The ability of the electrodes to detect silver ions was evaluated using the Nernst equation. When allyl- and propargyl-type tripodal broom molecules, and a propargyl-type monopodal analog were used in the electrode, Nernstian responses for silver ions were observed, indicating that π electrons play an important role in the detection of silver ions. In the presence of interfering metal ions, the selectivity for silver ions was affected by the number and density of π electrons in the ionophore. The electrode containing the allyl-type tripodal broom molecule was used to accurately determine the concentration of glucosamine hydrochloride in a real sample.

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Introduction

The microanalysis of metal ions in environmental samples, such as industrial wastewater and river, sea, and rain waters, has been developed due to current interest in ambient pollution. Accuracy, sensitivity, specificity, usability, rapid response, and automatization are required for analysis of the metal concentration, to identify the generation source, flow route, and effect of a target metal ion. In addition, the microanalysis of metal ions is important in biochemistry and pharmacy because trace amounts of metal ions contribute to the activity and stability of enzymes and drugs.

The microanalysis of metal ions using ion-selective electrodes is one of the favored methods, because it does not require any pretreatment, and allows a quick, simple, and selective determination of the quantity of a target metal ion. The detection ability of an ion-selective electrode depends on the structures of the incorporated ionophores, in particular, the coordination groups in the ionophores. For example, ionophores containing nitrogen or sulfur atoms, which are soft ligands according to the "hard and soft acids and bases" theory, have been utilized to prepare ion-selective electrodes because of their high affinity for soft metals, such as silver, thallium and mercury ions, and so on.[1-7] However, ionophores containing nitrogen or sulfur atoms tend to be influenced by the pH. Moreover, the strong affinity of nitrogen and sulfur atoms for soft metal ions at the interface of membranes causes low selectivity, slow response, and weak sensitivity.

It has recently been shown that ionophores containing π electrons with weak affinity improve the selectivity, response, and sensitivity for detecting certain metal ions. For instance, Bobacka *et al.* reported that spherical hydrocarbons, known as cyclophanes, are effective ionophores in silver and mercury ion-selective electrodes, owing to the relatively weak interaction of the π coordinated benzene rings in cyclophane with soft metal ions, and also with soft organic cations, like pyridinium and tetramethylammonium ions.[8,9] Allyl-type calix[4]arenes have also been used as ionophores in soft metal ion-selective electrodes, which exhibited excellent selectivity for soft metal ions over sodium ions.[10-13] We prepared a methyl ketonic calix[4]arene derivative to evaluate the potential response for silver ions.[14] This derivative may provide a π interaction with not so strong, but selective, affinity for soft metal ions.

Tripodal "broom" molecules are trimethylol-based compounds. They have a long alkenyl (or alkyl) branch, and provide a relatively narrow and rigid recognition site for metal ion with possible C_3 symmetry. These features endow the molecules with a relatively high lipophilicity, and a preorganized coordination space, respectively. This means that the tripodal "broom" molecule has a potential to be a candidate of scaffolds for metal discrimination.

In the present study, for the molecular evaluation of novel tripodal framework, "broom" molecules containing π electrons as a coordination group have been synthesized to evaluate the effects of the number and density of π electrons on the potential response of silver ion-selective electrodes containing the molecules, *i.e.* trifunctional ionophores, of allyl, propargyl, and propyl type, and their monopodal analogs, *i.e.* monofunctional ionophores, as shown in Fig. 1. As an application, the content of glucosamine hydrochloride in supplements was indirectly determined by potentiometric titration to confirm the practical performance of the silver ion-selective electrode.

Experimental

Reagents and materials

Polyvinyl chloride (PVC) with an average polymerization degree of 1100 was purchased from Katayama Chemical Co., Japan. Potassium tetrakis(*p*-chlorophenyl) borate (KT*p*ClPB)

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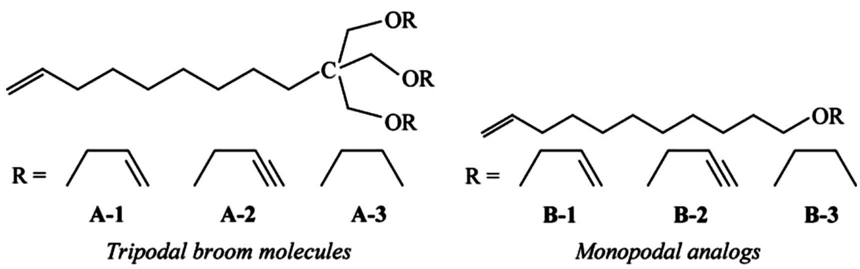

Fig. 1 Chemical structures of ionophores for silver: **A-1**, allyl-type tripodal broom molecule; **A-2**, propargyl-type tripodal broom molecule; **A-3**, propyl-type tripodal broom molecule: **B-1**, allyl-type monofunctional analog; **B-2**, propargyl-type monofunctional analog; **B-3**, propyl-type monofunctional analog.

was used as a anion excluder, and was supplied by Tokyo Chemical Industry, Japan. *o*-Nitrophenyl phenyl ether (NPPE, Wako Chemical Industries, Japan) was used as a plasticizer for PVC. A commercially available supplement containing glucosamine hydrochloride purchased from DHC Co., Japan was used to indirectly determine the effectiveness of the electrode. Ion-selective electrodes (No. 7900), a double-junction type reference electrode (No. 4083), and a potentiometer (PHL-40 pH meter) were purchased from DKK-TOA Co., Japan.

Synthesis of ionophores for silver ions

The starting material for the tripodal broom molecule derivatives, 1,1,1-tris(hydroxymethyl)-9-decene (**A-0**), was synthesized using a similar method as that in previous literature.[15] To introduce allyl, propargyl, or propyl groups into the tripodal broom compounds, sodium hydride (60% in oil) was added to a solution of **A-0** in dry dimethylformamide (DMF, 100 cm^3) under a nitrogen atmosphere. The corresponding bromide reactant was added dropwise to the mixture over 30 min, and then the resulting mixture was stirred for 24 h at room temperature. After the deactivation of sodium hydride by the addition of methanol, water and chloroform were added, and then the product was extracted into the organic layer. The organic layer was washed with 1 M (M = mol dm^{-3}) HCl and saturated NaCl solutions (3 times each), dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. Allyl-, propargyl-, and propyl-type monopodal analogs were synthesized by the same procedure using 10-undecenol (**B-0**) as the starting material. Proton nuclear magnetic resonance (^1H NMR) spectra were measured using an NMR spectrometer (Jeol, JNM-AL300) at 300 MHz at room temperature. Elemental analyses were performed on a Yanaco CHN Corder MT-6 analyzer (Yanagimoto Mfg. Co., Ltd.) at the Center of Elementary Analysis of Kyushu University.

1,1,1-Tris(allyloxymethyl)-9-decene (**A-1**); **A-0** (0.98 g, 4.26 mmol), allyl bromide (5.55 g, 45.9 mmol, 10.8 eq.), sodium hydride (0.88 g, 22.0 mmol, 5.16 eq.), TLC: $CHCl_3$ (R_f = 0.80). Yield: yellow viscous liquid (1.39 g, 92.6%). ^1H NMR: ($CDCl_3$, 300 MHz, TMS) δ 1.27 - 1.56 (m, 12H, $-(C\underline{H_2})_6-$), δ 2.04 (q, 2H, $CH_2{=}CH{-}C\underline{H_2}{-}(CH_2)_6-$), δ 3.23 (s, 6H, $O{-}C\underline{H_2}{-}CH{=}CH_2$), δ 3.96 (d, 6H, J = 5.7 Hz, $-C{-}C\underline{H_2}{-}O-$), δ 4.90 - 5.02 (m, 2H, $C\underline{H_2}{=}CH-$ in alkenyl moiety), δ 5.11 - 5.28 (m, 6H, $-CH{=}C\underline{H_2}$ in allyl moiety), δ 5.74 - 5.95 (m, 4H, $C\underline{H_2}{=}CH-$ in alkenyl moiety and $-CH{=}CH_2$ in allyl moiety). *Anal.* calcd. for $C_{22}H_{38}O_3$ $0.2C_3H_7NO$ (DMF): C 74.33, H 10.93. Found: C 74.21, H 10.68.

1,1,1-Tris(propargyloxymethyl)-9-decene (**A-2**); **A-0** (3.10 g, 13.5 mmol), propargyl bromide (9.61 g, 80.8 mmol, 5.99 eq.), sodium hydride (2.37 g, 59.2 mmol, 4.39 eq.), TLC: $CHCl_3$ (R_f = 0.65). Yield: brownish-red viscous liquid (2.70 g, 58.3%). ^1H NMR: ($CDCl_3$, 300 MHz, TMS) δ 1.28 - 1.34 (m, 12H, $-(C\underline{H_2})_6-$), δ 2.09 (q, 2H, $CH_2{=}CH{-}C\underline{H_2}{-}(CH_2)_7-$), δ 2.39 (s, 3H, J = 2.4 Hz, $-C{\equiv}C\underline{H}$), δ 3.41 (s, 6H, $-C{-}C\underline{H_2}{-}O-$), δ 4.11 (d, 6H, J = 2.4 Hz, $-O{-}C\underline{H_2}{-}C{\equiv}CH$), δ 4.90 - 5.02 (m, 2H, $C\underline{H_2}{=}CH-$), δ 5.74 - 5.86 (m, 1H, $CH_2{=}C\underline{H}-$). *Anal.* calcd. for $C_{22}H_{32}O_3$ $0.2C_3H_7NO$ (DMF): C 75.59, H 9.38. Found: C 75.59, H 9.53.

1,1,1-Tris(propoxymethyl)-9-decene (**A-3**); **A-0** (3.10 g, 13.5 mmol), propyl bromide (9.98 g, 81.1 mmol, 6.01 eq.), sodium hydride (4.72 g, 118 mmol, 8.74 eq.), TLC: $CHCl_3$ (R_f = 0.67). Yield: colorless viscous liquid (4.12 g, 85.3%). ^1H NMR: ($CDCl_3$, 300 MHz, TMS) δ 0.89 (t, 9H, J = 7.2 Hz, $-CH_2{-}C\underline{H_3}$), δ 1.28 (m, 12H, J = 2.4 Hz, $-(C\underline{H_2})_6-$), δ 1.54 (m, 6H, $-O{-}CH_2{-}C\underline{H_2}{-}CH_3$), δ 2.02 (q, 2H, $CH_2{=}CH{-}C\underline{H_2}{-}(CH_2)_6-$), δ 3.23 (t, 6H, J = 6.6 Hz, $-O{-}C\underline{H_2}{-}CH_2{-}CH_3$), δ 3.27 (s, 6H, $-C{-}C\underline{H_2}{-}O-$), δ 4.89 - 5.02 (m, 2H, $C\underline{H_2}{=}CH-$), δ 5.74 - 5.88 (m, ^1H, $CH_2{=}C\underline{H}-$).

Allyloxy-1-undecene (**B-1**); **B-0** (3.21 g, 13.5 mmol), allyl bromide (6.25 g, 51.7 mmol, 3.83 eq.), sodium hydride (3.58 g, 89.5 mmol, 6.63 eq.), TLC: $CHCl_3$ (R_f = 0.80). Yield: colorless viscous liquid (3.52 g, 88.4%). ^1H NMR: ($CDCl_3$, 300 MHz, TMS) δ 1.26 - 1.53 (m, 12H, $-(C\underline{H_2})_6-$), δ 1.56 (m, 2H, $-(CH_2)_6{-}C\underline{H_2}{-}CH_2{-}O$), δ 2.00 (q, 2H, $CH_2{=}CH{-}C\underline{H_2}{-}(CH_2)_6-$), δ 3.39 (t, 2H, J = 6.6 Hz, $-CH_2{-}C\underline{H_2}{-}O-$), δ 3.94 (d, 2H, $-O{-}C\underline{H_2}{-}CH{=}CH_2$), δ 4.89 - 5.02 (m, 2H, $-CH{=}C\underline{H_2}$ in allyl moiety), δ 5.13 - 5.30 (m, 2H, $C\underline{H_2}{=}CH-$ in alkenyl moiety), δ 5.76 - 5.98 (m, 2H, $CH_2{=}C\underline{H}-$ in alkenyl moiety and $-C\underline{H}{=}CH_2$ in allyl moiety).

Propargyloxy-1-undecene (**B-2**); **B-0** (3.11 g, 18.3 mmol), propargyl bromide (6.48 g, 54.5 mmol, 2.97 eq.), sodium hydride (3.56 g, 89.0 mmol, 4.86 eq.), TLC: $CHCl_3$ (R_f = 0.78). Yield: brownish-red viscous liquid (1.61 g, 42.1%). ^1H NMR: ($CDCl_3$, 300 MHz, TMS) δ 1.28 - 1.37 (m, 12H, $-(C\underline{H_2})_6-$), δ 1.57 (m, 2H, $-(CH_2)_6{-}C\underline{H_2}{-}CH_2{-}O$), δ 2.03 (q, 2H, $CH_2{=}CH{-}C\underline{H_2}{-}(CH_2)_6-$), δ 2.41 (t, 1H, J = 2.4 Hz, $-C{\equiv}C\underline{H}$), δ 3.51 (t, 2H, J = 6.6 Hz, $-CH_2{-}C\underline{H_2}{-}O-$), δ 4.13 (d, 2H, $-O{-}C\underline{H_2}{-}C{\equiv}CH$), δ 4.90 - 5.02 (m, 2H, $C\underline{H_2}{=}CH-$), δ 5.74 - 5.88 (m, 1H, $CH_2{=}C\underline{H}-$).

Propoxy-1-undecene (**B-3**); **B-0** (3.34 g, 19.6 mmol), propyl bromide (6.58 g, 53.5 mmol, 2.73 eq.), sodium hydride (3.66 g, 91.5 mmol, 4.67 eq.), TLC: $CHCl_3$ (R_f = 0.82). Yield: colorless viscous liquid (1.75 g, 42.1%). ^1H NMR: ($CDCl_3$, 300 MHz, TMS) δ 0.89 (t, 3H, $-CH_2{-}C\underline{H_3}$), δ 1.26 (m, 14H, $-(C\underline{H_2})_7-$), δ 1.54 (m, 2H, $-O{-}CH_2{-}C\underline{H_2}{-}CH_3$), δ 2.02 (q, 2H, $CH_2{=}CH{-}C\underline{H_2}{-}(CH_2)_7-$), δ 3.71 (m, 4H, $-C\underline{H_2}{-}O{-}C\underline{H_2}-$), δ 4.89 - 5.02 (m, 2H, $C\underline{H_2}{=}CH-$), δ 5.74 - 5.88 (m, 1H, $CH_2{=}C\underline{H}-$).

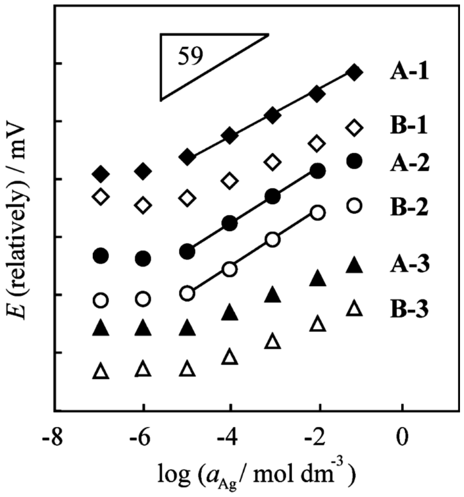

Fig. 2 Potential responses for silver ions using ion-selective electrodes containing various ionophores.

Preparation of electrode membranes

The ionophores (5 mg) in Fig. 1, KT*p*ClPB (1 mg) as the anion excluder, NPPE (100 mg) as the plasticizer, and PVC (50 mg) as the matrix were dissolved in dry tetrahydrofuran (1.5 cm^3). The mixture was added dropwise onto a chip with a membrane filter (polytetrafluoroethylene; diameter, 6 mm), and then dried in air. This procedure was repeated ten times. After drying in air for 24 h, the chip was conditioned by soaking in a 1 mM $AgNO_3$ solution in an incubator at 25°C overnight.

Potentiometric measurement of ion-selective electrodes containing ionophores for silver

The inside of a conditioned chip was suffused with a $AgNO_3$ solution (1 mM), and connected to the tip of an ion-selective electrode. An ion-selective electrode containing an ionophore and a double-junction type reference electrode were immersed in a Ag^+ sample solution (10^{-7} - 10^{-1} M), and the difference in potential was determined using a potentiometer. The electrochemical cell was consisted of a Ag-AgCl/1 mM $AgNO_3$/PVC membrane/sample solution/0.1 M NH_4NO_3/3 M KCl/Ag-AgCl. The potential response was evaluated using the Nernst equation,

$$E = E_0 + \frac{2.303RT}{nF}\log a \tag{1}$$

where E, E_0, R, T, F, n and a are the electrical potential (mV), standard potential (mV), gas constant (8.314 J K^{-1} mol^{-1}), measurement temperature (298 K), Faraday constant, valency of the metal ion, and activity of the metal ion, respectively.

Determination of the potential response for silver ion as a coexistent system

To investigate the selectivity of ion-selective electrodes containing ionophores for silver, the difference in the potential responses obtained by the electrode in silver sample solutions (10^{-7} - 10^{-1} M) was determined by a potentiometer in the presence of various metal ions, such as lithium, sodium, potassium, thallium, calcium, and cadmium ions (10^{-3} M). The selectivity coefficient of the ionophores for silver ions against other metal ions ($K^{\mathrm{pot}}_{\mathrm{Ag,M}}$) was estimated by the following equation using the value for the detection limit according to the Nernst equation:

$$K^{\mathrm{pot}}_{\mathrm{Ag,M}} = \frac{a_{\mathrm{Ag}^+}}{a_{\mathrm{M}^{n+}}}, \tag{2}$$

where a_{Ag^+} and $a_{\mathrm{M}^{n+}}$ are the activities of silver ion at the detection limit and the activities of coexisting metal ions.

^{1}H NMR measurement of an allyl-type tripodal broom molecule-silver complex

The coordination of silver at the binding site in the ionophore **A-1** was clarified by ^{1}H NMR measurements. Organic and aqueous phases were prepared by dissolving the ionophore **A-1** (5 mM) in chloroform and silver nitrate (100 mM) in 6 M nitric acid, respectively. The organic and aqueous phases were mixed with a ratio of 1:5, and then shaken at 303 K for 72 h. ^{1}H NMR spectra of the organic phase were measured to confirm any chemical shifts before and after complexation with silver ions.

Determination of the concentration of glucosamine hydrochloride in real sample

The silver ion-selective electrode containing the ionophore **A-1** was applied to measure the concentration of glucosamine hydrochloride in a real sample. An aqueous solution of glucosamine hydrochloride was prepared from a commercially available supplement, consisting of glucosamine hydrochloride, crystalline cellulose, glycerin fatty acid ester, and silica. Six tablets of supplement (*ca.* 2.61 g) were ground in a mortar, and then glucosamine hydrochloride was extracted into 100 cm^3 of distilled water by stirring at 40°C for 2.5 h. After removal of insoluble components by filtration, an aqueous solution of glucosamine hydrochloride was obtained. The silver ion-selective electrode containing the tripodal broom molecule **A-1** was immersed in this solution. $AgNO_3$ solution (10 mM) was titrated to the solution, and then the potential response was determined. The equivalence point of the titration was estimated using Gran's plot method. The content of glucosamine determined from the titration using the silver ion-selective electrode containing tripodal broom molecule **A-1** was compared with those determined by the Elson–Morgan method[16] and the Somogyi–Nelson method[17,18] using glucosamine hydrochloride as a standard, together with the labelled content guaranteed by the manufacturer.

Results and Discussion

Potential responses of ion-selective electrodes for silver

The potential responses of ion-selective electrodes containing allyl-type ionophores (**A-1** and **B-1**), propargyl-type ionophores (**A-2** and **B-2**), and propyl-type ionophores (**A-3** and **B-3**) for silver ions in the concentration range from 10^{-7} to 10^{-1} M were measured, as shown in Fig. 2. The slopes of the lines and detection limits obtained from the results in Fig. 2 are summarized in Table 1. The Nernstian responses (slope of approximately 59 mV decade^{-1}) were observed from the electrodes containing the ionophores **A-1**, **A-2**, and **B-2**, while no Nernstian response was observed from electrodes containing the ionophores **A-3** and **B-3**, which have propyl groups, indicating that π electrons are necessary for the detection of silver ions. The electrode containing ionophore **B-1** did not exhibit a Nernstian response, even though **B-1** possesses π electrons. This is attributed to the multidentate effect of the functional group in the tripodal broom molecule on detecting silver ion. Focusing on the propargyl-type ionophores (**A-2** and

Table 1 Potential response properties of silver ion-selective electrodes containing various ionophores

Ionophore	Slope/mV decade^{-1}	Detection limit/M
◆ **A-1**	57.3	1.89×10^{-7}
◇ **B-1**	48.3	—
● **A-2**	64.4	2.67×10^{-6}
○ **B-2**	58.4	7.64×10^{-6}
▲ **A-3**	48.9	—
△ **B-3**	42.5	—

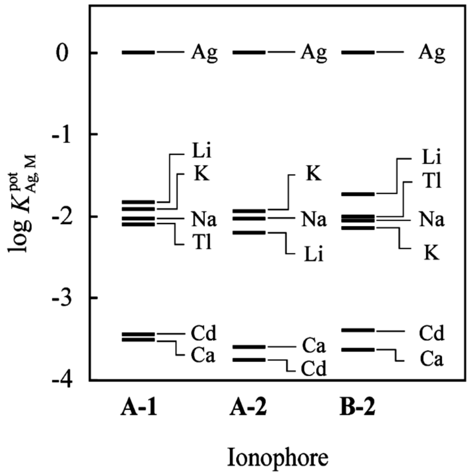

Fig. 3 Selectivity coefficients for silver ion against various metal ions using silver ion-selective electrodes containing ionophores **A-1**, **A-2**, and **B-2**.

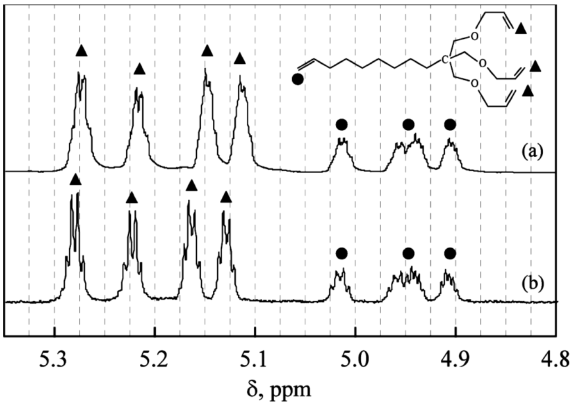

Fig. 4 Chemical shifts for terminals of allyl group and alkenyl chain in ionophore **A-1**; (a) before and (b) after complexation with silver ion.

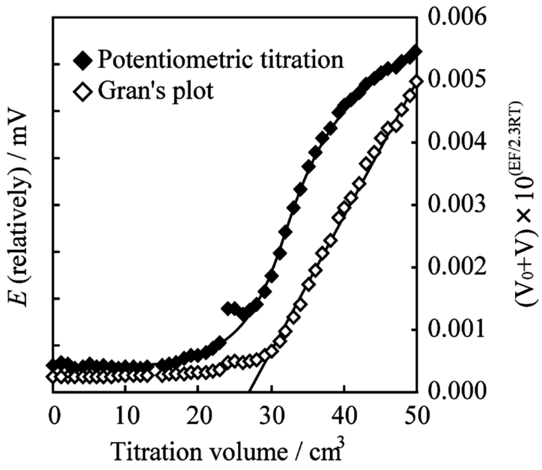

Fig. 5 Potentiometric titration and Gran's plot of glucosamine hydrochloride solution with silver nitrate solution using silver ion-selective electrode containing ionophore **A-1**.

B-2), both ionophores gave a Nernstian response to silver ions because of a significant affinity between the propargyl groups and silver ions, compared with the allyl groups. However, the detection limit ranges for **A-2** and **B-2** were narrower than that for **A-1**. This may have been caused by some interfering factors, such as a stronger affinity between the propargyl group and silver ion compared with the allyl group.

Estimation of selectivity coefficients for silver ion against other metal ions

The potential responses for silver ions of ionophores exhibiting Nernstian response were investigated in the presence of various coexisting metal ions. The selectivity coefficients for silver against other metals using ionophores **A-1**, **A-2**, and **B-2** are shown in Fig. 3. Commonly, the selectivity for silver against alkali metals was poor; the values of log $K^{\mathrm{pot}}_{\mathrm{Ag,M}}$ against alkali metal ions are *ca.* –2. These selectivities limit the conditions in which the silver ion-selective electrode can be applied, because such alkali metals exist widely in many environments. It is presumed that the low values of log $K^{\mathrm{pot}}_{\mathrm{Ag,M}}$ can be attributable to the coordination of alkali metals with oxygen atoms in the ionophores. Compared with cadmium and calcium ions, silver ions were selectively detected by the ionophores, so the presence of soft divalent ions was negligible during the determination of silver using ion-selective electrodes. In thallium ion-coexistent system, the potential response for silver was affected by the structures of the ionophores. Thallium ion is a soft monovalent ion, like silver ion; however, it has a larger ionic radius than silver ion. Ionophores **A-1** and **B-2** responded to silver rather than thallium, while no detection of silver was observed using the silver ion-selective electrode containing ionophore **A-2**. From the additional results of the potential responses, even **B-2** with a single propagyl group responded to thallium ion. This possibly means that **A-2** does not coordinate by the intramolecular site consisting of three propagyl groups, but by a single or two propagyl groups outside of the molecule.

*Identification of the silver coordination site in ionophore **A-1***

The coordination site of silver in the ionophore **A-1** was estimated from peak shifts in the ^{1}H NMR spectra before and after complexation with silver ions, as shown in Fig. 4. No shift upon complexation was observed for the peak attributed to the double bond in the alkenyl chain. In contrast, the peak corresponding to the terminal of the allyl group was shifted to a low magnetic field upon complexation, indicating that silver coordinates with π electrons in three of the allyl groups. Furthermore, preorganization of the coordination site by the multiple π electrons is important for complexation of **A-1** with silver ions.

Table 2 Comparison of the contents of glucosamine hydrochloride in supplement determined by various methods

Determination method	Content of glucosamine hydrochioride per 1 g of supplement/mg g^{-1}
Potentiometric titration	624.4 ± 14.4
Elson–Morgan	635.5 ± 67.3
Somogyi–Nelson	587.1 ± 24.4
Labelled content	712.6

Analytical application of silver ion-selective electrode for detection of glucosamine hydrochloride

The concentration of glucosamine hydrochloride in a real sample was determined using a silver ion-selective electrode containing the tripodal broom molecule **A-1**. The potentiometric titration curves and Gran's plot are shown in Fig. 5. The equivalence point of the potentiometric titration was observed at 28.6 cm^3 in the Gran's plot. The content of glucosamine hydrochloride determined by potentiometric titration using the silver ion-selective electrode containing **A-1** is compared with those determined by colorimetric methods, together with the labelled content in Table 2. The contents of glucosamine hydrochloride determined by the quantitative methods were lower than the labelled content, indicating that glucosamine hydrochloride may not have been completely extracted from the supplement. The content of glucosamine hydrochloride determined by the potentiometric titration corresponded with those by Elson–Morgan and Somogyi–Nelson methods, which determine the concentration of amino sugars and reducing sugars, respectively. The coloring reaction in the Somogyi–Nelson method is inhibited by concentrated metal salts.[19] Therefore, the potentiometric titration method using the silver ion-selective electrode containing **A-1** was used successful for an indirect determination of the concentration of a chloride salt in an actual sample, without inhibition by interfering metal ions and organic compounds.

Conclusions

Silver ion-selective electrodes containing tripodal broom molecules with π electrons have been prepared, and their ability to detect silver ions was investigated. The number and density of π electrons in the ionophores were important factors affecting the potential response, detection limit, and selectivity for silver ions. The most efficient ionophore for silver ions was found to be the allyl-type tripodal broom molecule. The ionophores should be designed so that π electrons are multi-functionally introduced in tripodal broom molecule, and that oxygen atoms are eliminated from tripodal broom molecule derivatives, so as to improve the response, sensitivity and selectivity of silver ion-selective electrodes.

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