Silver Ion-Selective Electrodes Using π -Coordinate Calix[4]arene Derivatives as Soft Neutral Carriers

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Calix[4]arene derivatives incorporating π -coordinate substituents such as allyl, benzyl, and propargyl groups were designed as soft neutral carriers for silver ion sensors. Most of all, *tert*-butylcalix[4]arene tetra(allyl ether) is an excellent neutral carrier for plasticized poly(vinyl chloride)membrane silver ion-selective electrodes. The ion sensors showed high silver ion selectivity over alkali metal ions and also good selectivity against other soft metal ions such as lead and mercury(II) ions. The electrode potential response was as rapid as that for neutral-carrier-type alkali metal ion electrodes due to the soft interaction between π -coordinate substituents and silver ion, which was elucidated by ¹H NMR spectroscopy.

A most attractive potentiometric sensor is a neutral-carriertype one that realizes excellent ion selectivities. The neutral carriers are dissolved or dispersed in the ion-sensing membranes that are generally a liquid membrane or a plasticized polymeric membrane. The original ion selectivity of the neutral carriers themselves is reflected in the resulting ion-sensing membranes and therefore the ion sensors in many cases. Naturally occurring ionophores such as valinomycin were applied as the neutral carrier for alkali-metal ion-selective electrodes in the early stages. Synthetic ionophores such as crown ether derivatives, polyetheramides, and calixarene ionophores have been so far designed as the neutral carriers. Sophisticated designing of neutral carriers can afford extremely high ion selectivities that cannot be attained in "ionic" ion-exchanger-type sensors. Since most of the neutral carriers contain oxygen or nitrogen atoms as the heteroatoms for metal-ion binding, the resulting neutral-carrier-type ion sensors are mainly for alkali and alkaline-earth metal ions.

The synthetic ionophores, when some of their oxygen atoms are replaced with sulfur atoms, exhibit high affinity toward soft metal ions such as Ag^{+, 1–5} Thus, several crown ethers containing

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sulfur atoms, so-called thiacrown ethers, were designed for neutral carriers for Ag^+ -selective electrodes. Coordination bonding of Ag^+ with the crown-ring sulfur atoms is, however, powerful, as compared with ion—dipole interaction between metal ions and oxygen atoms (high complex formation constants). This often brings about slow metal-ion exchange equilibria in the membrane interface, resulting in some disadvantage of the thiacrown etherbased ion sensors over those based on oxygen-atom-containing neutral carriers, i.e., slow sensor response and poor sensitivity. The drawback for thiacrown ether-based Ag^+ sensors may be alleviated more or less by the decreased number of the crown-ring sulfur atoms.^{5,6}

A soft acid, Ag⁺, is apt to interact with π electrons and the π coordination is quite selective and relatively weak.^{7–12} We envisage that neutral carriers incorporating π -coordinate substituents may be useful to realize quick response and high sensitivity for neutral-carrier-type Ag⁺ sensors. It occurred to us that the incorporation of π -coordinate groups such as allyl, benzyl, and propargyl groups into a rigid skeleton may afford excellent π -coordinate neutral carriers. Thus, we have synthesized calix[4]arene derivatives containing π -coordinate substituents at the lower rim.¹³ Here we report the designing of the π -coordinate calix[4]arene neutral carriers and the sensor property of plasticized-poly(vinyl chloride) (PVC) membrane Ag⁺-selective electrodes based on them.

EXPERIMENTAL SECTION

Synthesis of Calix[4]arene Neutral Carriers. The general procedure for the synthesis is as follows. *tert*-Butylcalix[4]arene (1.35 mmol) was dispersed in dry tetrahydrofuran (THF) (50 cm³) containing dry *N*,*N*-dimethylformamide (DMF) (5 cm³) and treated with NaH (25 mmol) followed by alkyl bromide (25 mmol).

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 $\begin{array}{l} 1: R_1 = t\text{-}Bu \ , R_2 = -\text{-}CH_2CH=CH_2 \\ 2: R_1 = t\text{-}Bu \ , R_2 = -\text{-}CH_2Ph \\ 3: R_1 = t\text{-}Bu \ , R_2 = -\text{-}CH_2C=CH \\ 4: R_1 = t\text{-}Bu \ , R_2 = -\text{-}CH_2CO_2CH_2CH=CH_2 \\ 5: R_1 = H \ , \ \ R_2 = -\text{-}CH_2CH_2CH_3 \end{array}$

After the reaction, the excess of NaH was treated with methanol (about 20 cm³) and the mixture was distributed to the chloroform/ diluted aqueous HCl (100/200 cm³) mixture. The chloroform extract was washed with water (about 100 cm³) and dried over MgSO₄. The chloroform evaporation afforded a crude product, which was purified by recrystallization or silica gel column chromatography.

For the synthesis of *tert*-butylcalix[4]arene tetra(allyl ether) **1**, the reaction was carried out at room temperature for 1 h to obtain a main product with cone conformation. The purification was performed by recrystallization with ethanol to yield a pure product of **1** with only cone conformation; colorless crystal; mp 213-214 °C; ¹H NMR (270 MHz, CDCl₃) δ 1.07(s, 36H, *t*-Bu), 3.12 and 4.38(d, J = 12.5 Hz, 4H, ArCH₂Ar), 4.46(d, J = 6.3 Hz, 8H, OCH₂), 5.17(d, J = 9.9 Hz, 4H, =CH₂), 5.26(d, J = 17.2 Hz, 4H,= CH₂), 6.49–6.37(m, 4H, -CH=C), 6.77(s, 8H, ArH); MS, *m/e* (% relative intensity) 808 (M⁺,100), 613 (75). Anal. Calcd for C₅₆H₇₂-O₄: C, 83.12; H, 8.97; O, 7.91. Found: C, 83.04; H, 8.94.

*t*Butylcalix[4]arene tetra(benzyl ether) **2** was prepared by refluxing for 1 h, according to a procedure in the literature.¹⁴ Similarly, *tert*-butylcalix[4]arene tetra(propargyl ether) **3** was obtained under the refluxing conditions.¹⁵ The crude product was purified by silica gel chromatography (benzene/hexane = 1:1) to afford a colorless crystal: mp 212–213 °C; ¹H NMR (270 MHz, CDCl₃) δ 1.07(s, 36H, *t*Bu), 2.48(s, 4H, C=CH), 3.16 and 4.60(d, J = 13.0 Hz, 4H, ArCH₂Ar), 4.80(d, J = 1.9 Hz, 4H, CH₂C=C), 6.79(s, 8H, ArH); MS, *m/e* (% relative intensity) 800 (M⁺, 100), 613 (45). Anal. Calcd for C₅₆H₆₄O₄: C, 83.96; H, 8.05; O, 7.99. Found: C, 83.72; H, 8.02.

tert Butylcalix[4]arene tetra(allyl ester) **4** with cone conformation was synthesized by the reaction of *t*-butylcalix[4]arene with allyl 1-bromoacetate in acetone in the presence of K_2CO_3 .¹⁶ In a similar way to **2** and **3**, calix[4]arene tetra(propyl ether) **5** was obtained.

Other Materials. PVC (an average polymerization degree of 1100) was purified by reprecipitation from THF in methanol twice. The membrane plasticizer 2-fluoro-2'-nitrodiphenyl ether (FNDPE) was purchased from Dojindo Laboratory. *o*-Nitrophenyl octyl ether (NPOE)¹⁷ and bis(2-ethylhexyl sebacate (DOS) were distilled in vacuo. Potassium tetrakis(*p*-chlorophenyl)borate (KTpClPB), which is an anion excluder, was also obtained from Dojindo Laboratory. Metal and ammonium nitrates employed were of analytical grade. Water was deionized and distilled.

Electrode Fabrication. The general procedure for casting the ion-sensing membranes is the following: PVC (50 mg), a plasticizer (125 mg), a calix[4]arene derivative (10 mg), and KTpClPB (1 mg) were dissolved in THF (3 cm³). The whole

solution was poured into a flat Petri dish with an inner diameter of 23 mm. Gradual evaporation of the THF at ambient temperature afforded an elastic, semitransparent membrane with a thickness of about 0.2 mm. The resulting PVC membranes consisted of 26.9 wt % PVC, 67.2 wt % plasticizer, 5.4 wt % neutral carrier, and 0.5 wt % KTpCIPB. A disk of 5-mm diameter was cut out from the membrane with a cork borer and was then fixed into an electrode body (DKK Corp. 7904L type) by using a drop of THF. After drying the THF for 2 h, an internal filling solution (1 × 10⁻¹ mol cm⁻³ AgNO₃ aqueous solution saturated with AgCl) was set up into the electrode. Conditioning of the thus resulting electrodes was done by soaking them in the AgNO₃ solution overnight.

 $\begin{array}{l} \label{eq:measurements} \textbf{Measurements.} \ Emf\ measurements\ were\ carried\ out\ at\ 25 \\ \pm\ 0.1\ ^{\circ}C\ by\ using\ a\ pH/mV\ meter\ (Toko\ Chemical\ Laboratory, model\ TP-1000). \ The\ outer\ reference\ electrode\ was\ a\ double-junction-type\ Ag-AgCl\ reference\ electrode. \ The\ electrochemical\ cell\ for\ the\ emf\ measurements\ was\ Ag\ |\ AgCl\ |\ 1\ \times\ 10^{-1}\ mol\ dm^{-3}\ AgNO_3\ |\ ion-sensing\ membrane\ |\ sample\ solution\ ||\ 1\ mol\ dm^{-3}\ CH_3CO_2Li\ ||\ 3\ mol\ dm^{-3}\ KCl\ |\ AgCl\ |\ Ag. \end{array}$

The selectivity coefficients for Ag⁺ with respect to interfering ions were determined by a mixed solution method, that is, the fixed interference method (FIM).¹⁸ The background concentrations of interfering ions were 5 \times 10⁻⁴ mol dm⁻³ for Hg²⁺; 1 \times 10^-3 mol dm^-3 for Tl^+; 1 \times 10^-1 mol dm^-3 for Pb^{2+} and H^+; 5 \times 10⁻¹ mol dm⁻³ for Ca²⁺, Mg²⁺, Li⁺; 1 mol dm⁻³ for Na⁺, K⁺, and NH₄⁺. The backgrounds for the *tert*-butylcalix[4]arene tetra(allyl ester) 4 system were 1 \times 10 $^{-3}$ mol dm $^{-3}$ for Na $^+$ and 1 \times 10 $^{-2}$ mol dm⁻³ for K⁺ and Tl⁺. The selectivity coefficients for Ag⁺ with respect to other cations were determined 10 times, using two different membranes for each of the neutral carriers, and the values thus obtained were averaged. The activity coefficients (γ) were calculated according to the Davies equation, $\log \gamma = -0.511$ - $(I)^{1/2}/(1 + 0.33\alpha (I)^{1/2}) - 0.10I$, using the values of ionic strength (1) and ion size parameter (α).¹⁹ For the Ag⁺ assay, model samples for aqueous solutions containing 1 mol dm⁻³ NaNO₃, 1 mol dm⁻³ NH₄NO₃, and appropriate concentrations (1 \times 10⁻³, 7.5 X 10⁻⁴, 5.0 \times 10⁻⁴, and 1 \times 10⁻⁴ mol dm⁻³) of AgNO₃ were employed. For Gran's plot method²⁰ on the Ag⁺ assay, the volume for the sample solution was 10 cm³. The volumes for added solutions were 1×10^{-2} mol dm $^{-3}$ for $1\times 10^{-3}-5\times 10^{-4}$ mol dm $^{-3}$ Ag $^+$ samples and 1×10^{-3} mol dm⁻³ for 1×10^{-4} mol dm⁻³ sample, 0.4 cm³ for 1×10^{-2} and 1×10^{-3} mol dm⁻³ Ag⁺ samples, and 0.2 cm³ for 7.5 imes 10⁻³ and 5 imes 10⁻⁴ mol dm⁻³ samples, respectively. The addition was carried out four times for each measurement.

¹H NMR spectroscopy of the calixarene neutral carriers for the study of Ag⁺-complexing behavior of calixarene derivatives was measured in CDCl₃/CD₃OD(4/1) at room temperature, using silver trifluoromethanesulfonate as the Ag⁺ salt. The measurements in the presence of Ag⁺ were made with a metal ion/neutral carrier ratio of 1, unless otherwise stated.

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Figure 1. Potential response to Ag⁺ activity changes of Ag⁺-selective electrodes based on π -coordinate *tert*-butylcalix[4]arene neutral carriers 1–4. Neutral carrier: 1 (\oplus), 2 (\triangle), 3 (\Box), and 4 (\bigcirc).

RESULTS AND DISCUSSION

Design of π **-Coordinate Calixarene Neutral Carriers.** It is well-known that carbon–carbon double and triple bonds exhibit π -coordinate property. Appropriate assembly of π -coordinate groups can afford the coordination atmosphere for Ag⁺. Assembling the π -coordinate groups requires a rigid and stable skeleton, for which we chose *tert*-butylcalix[4]arene here.

We decided to use *tert*-butylcalix[4]arene derivatives incorporating allyl, benzyl, and propargyl groups at the lower rim. They are easily accessible from commercially available *tert*-butylcalix-[4]arene by a simple one-step reaction of *tert*-butylcalix[4]arene and alkyl bromide in the presence of NaH. In the reaction for the preparation of 1 under reflux conditions,¹⁴ mixture products of 1 with cone and partial-cone conformations were formed which were very hard to separate by simple recrystallization from ethanol. The reaction for preparation of 1 was, therefore, carried out at room temperature to obtain a pure product with cone conformation. For preparation of 2 and 3, the reflux reaction condition even afforded the predominant cone conformation.

Thus, we applied π -coordinate calix[4]arene derivatives **1**, **2**, and **3** as neutral carriers for Ag⁺-selective electrodes. For comparison, *tert*-butylcalix[4]arene tetra(allyl ester) **4** and calix-[4]arene derivative possessing propyl groups instead of allyl ones **5** were also employed. The calix[4]arene derivatives, **1**–**4**, possess only cone conformation. Calixarene derivative **5** is a mixture of its cone and partial-cone conformations⁷ that was used without time-consuming separation.

Potential Response and Selectivity of Silver Ion Selective Electrodes. The π -coordinate calixarene derivatives were applied as neutral carriers for Ag⁺-selective electrodes. Plasticized-PVC membranes were adopted as the ion-sensing membranes, and NPOE, DOS, and FNDPE were tested as the plasticizer. The solubility of π -coordinate neutral carriers **1**–**3** in plasticizer are in the order FNDPE > NPOE >> DOS. So, FNDPE was chosen as the plasticizer of Ag⁺-selective PVC membranes. Figure 1 shows typical potential responses for Ag⁺-selective PVC-membrane electrodes based on π -coordinate calix[4]arene derivatives **1**–**3**, together with that for the electrode of calix[4]arene tetra(allyl ester) **4** for comparison. The electrode of *tert*-butylcalix[4]arene tetra(allyl ether) **1** exhibited a near-Nernstian response to Ag⁺activity changes in the range of $1 \times 10^{-4} - 1 \times 10^{-1}$ mol dm⁻³

Table 1. Slopes and Linear Ranges in the Calibration Graph for Ag⁺-Selective Electrodes Based on Calixarene Neutral Carriers

neutral carrier	slope (mV decade ^{-1})	linear range (pAg)
1	58.3 ± 0.7	1-4
2	51.1 ± 1.1	1-4
3	51.8 ± 0.5	2-4
4	57.4 ± 0.5	1-4
5	57.1 ± 0.7	1-4

(Table 1). This is also the case with the electrode of *tert*-butylcalix. [4]arene tetra(allyl ester) **4**. However, the electrodes based on *tert*-butylcalix[4]arene carrying benzyl and propargyl groups at the lower rim, **2** and **3**, did not show very good sensitivity, i.e., they showed comparably low slopes of the calibration graph (51 mV decade⁻¹) and narrow linear ranges. The modest sensitivities for Ag⁺-selective electrodes of **2** and **3** are in contract to the high sensitivity for the electrode of **1**. *tert*-Butylcalix[4]arene tetra(allyl ether) **1** can probably complex Ag⁺ effectively by the cooperate π -coordination with the four allyl substituents, which is discussed later in the ¹H NMR measurements. The relatively low sensitivities in the sensor systems of **2** and **3**, on the other hand, might be attributed to the poor solubility of the neutral carriers and their Ag⁺ complexes, which in turn leads to the inefficient cation exchange in the membrane interface.

For comparison, calix[4]arene tetra(propyl ether) **5** was also tested as the Ag⁺ neutral carrier to elucidate the importance of the rigid calix[4]arene skeleton and the π -coordinate substituents. The calix[4]arene derivative without any special π -coordinate group, **5**, also works as the Ag⁺ neutral carrier with a near-Nernstian response to the Ag⁺ activity changes, although the Ag⁺ selectivity for the electrodes based on **5** is significantly different from that for the electrodes of **1**, as discussed later. It is probably because the aromatic rings themselves of the calix[4]arene skeleton for **5** can undergo π coordination toward Ag⁺, as described in the later discussion by NMR experiments.

The Ag⁺ selectivities against other interfering ions were determined in the electrode systems that afforded Nernstian or near-Nernstian responses, their selectivity coefficients being summarized in Figure 2. The electrode based on tert-butylcalix-[4] arene tetra (allyl ether) **1** is highly Ag⁺-selective against alkali and alkaline-earth metal ions, NH4+, H+, and even a soft metal ion, Hg²⁺. There is some interference by a monovalent soft metal ion, Tl⁺, in this electrode. Conventional Ag₂S-based Ag⁺-selective electrodes generally suffer from terrible interference by Hg²⁺. Definitely, the present calixarene-based Ag⁺ electrodes are superior to the Ag₂S-based electrodes from this point of view. It should be noted that the electrode based on the calix[4]arene tetra(allyl ester) 4 suffers from remarkable interference by Na⁺, though the electrode responds to Ag⁺ activity changes with a near Nernstian slope. Calix[4]arene tetraester derivatives are wellknown Na⁺ neutral carriers for the ion-selective electrodes, since their ester carbonyl groups can bind Na⁺ powerfully.^{21,22} The high affinity of tert-butylcalix[4]arene tetra(allyl ester) 4 to Na⁺ is the

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Figure 2. Selectivity comparison among Ag⁺-selective electrodes based on calix[4]arene neutral carriers 1, 4, and 5.

reason for the terrible interference by Na⁺ in the Ag⁺-selective electrode of **4**, which is a very undesirable factor on practical applications of Ag⁺ electrodes. Another noteworthy thing is the terrible Tl⁺ interference in the Ag⁺-selective electrode based on calix[4]arene tetra(propyl ether) **5** (Figure 2). The high Tl⁺ interference in the electrode of **5** cannot be neglected on the Ag⁺ assay using the ion electrode, if the sample solutions contain even a small quantity of Tl⁺. This implies that the π -coordinate cavity formed by the aromatic rings in the calix[4]arene skeleton of **5** is more suitable for complexing Tl⁺ than Ag⁺.

¹H NMR Study for Silver Ion Complexing Behavior. ¹H NMR spectroscopy affords important information about the Ag⁺complexing behavior of the present calix[4]arene neutral carriers, i.e., how they undergo π -coordination toward the metal ion. This helps us to understand the difference in the Ag⁺ selectivity against other metal ions, especially Na⁺ and Tl⁺, among the calix[4]arene neutral carriers. For instance, the ¹H NMR spectrum for tertbutylcalix[4] arene tetra(allyl ether) was changed by addition of an equimolar amount of Ag⁺, especially in the chemical shift for protons of the potential π -coordinate groups. Typical ¹H NMRspectral changes for the 1-Ag⁺ system were given in Figure 3, with respect to the proton peaks assigned to its allyl group and aromatic ring. The changes $(\Delta \delta)$ in the chemical shift for protons of the potential π -coordinate groups for the **1** system on the Ag⁺ addition are also listed in Table 2, together with the data for the other π -coordinate *tert*-butylcalix[4]arene neutral carriers. The allyl proton assigned to =CH₂ shifted remarkably to a higher frequency with $\Delta \delta$ values of 0.51 and 0.62, while the aromatic protons shifted slightly with a $\Delta \delta$ value of 0.18. The significant spectral changes support the much more extensive contribution of the allyl group to the Ag⁺ complexation by π coordination rather than the aromatic ring. Thus, a plausible structure of the Ag⁺ complex of **1** is as shown schematically in Scheme 1a.

In the *tert*-butylcalix[4]arene tetra(benzyl ether) **2** system, the chemical shift changes are not very remarkable in the aromatic protons, both for the benzyl and calixarene skeleton. This means that the π coordination of the benzyl group in the **2** system is not so efficient as that of the allyl group in the **1** system, probably because of the steric effect of the bulky benzyl group. A marked chemical shift change of the propargyl protons with a slight change of the skeletal aromatic protons was also found in the



Figure 3. ¹H NMR spectral changes for *tert*-butylcalix[4]arene tetra-(allyl ether) **1** solution on Ag⁺ addition. (a) 2.5×10^{-3} mol dm⁻³ **1**; (b) 2.5×10^{-3} mol dm⁻³ **1** and Ag⁺ in CDCl₃/CD₃OD (4/1).

Table 2. ¹H NMR Chemical Shift Changes ($\Delta\delta$) for Protons Assigned to Possible π -Coordinate Groups of *tert*-Butylcalix[4]arene Neutral Carriers 1–4 on Addition of Equimolar Ag⁺

	$\Delta\delta$ (ppm) ^a		
calixarene	skeletal aromatic ring	π -coordinate group	
1	0.18	0.62 and 0.51 (=CH ₂) 0.26 (CH=)	
2	0.17	0.05 and 0.12 (C ₆ H ₅ for benzyl)	
3	0.08	0.42 (≡CH)	
4	0.40	0.11 and 0.12 (=CH ₂)	
	0.14	(CH=)	
$^{a}\Delta\delta(\mathrm{ppn}%)=\left(\Delta\delta(\mathrm{ppn})^{a}\Delta\delta(ppn$	h) = δ (with an equimol	ar amount of Ag+) $-\delta$ (without	

the metal ion).

system of *tert*-butylcalix[4]arene tetra(propargyl ether) **3** in the presence of Ag⁺.¹⁵ The propargyl-group-containing calixarene derivative, **3**, must be a powerful π -coordinate ligand for Ag⁺. This is also supported by the fact that the addition of an excess amount (10 times) of Ag⁺ to the **3** solution for the NMR measurement results in significant precipitation of its Ag⁺ complexes. The easy precipitate formation of Ag⁺ electrode. In the electrode based on **3**, a severe drift was observed on the emf measurements, which is definitely derived from some precipitate formation of the neutral carrier–Ag⁺ complexes in the interface between the ion-sensing membrane and aqueous sample phase.



It is of much interest to compare the Ag⁺-complexing behavior between tert-butylcalix[4]arene tetra(allyl ether) 1 and its corresponding allyl-ester derivative 4. In contrast with the significant chemical shift change of the allyl proton in the 1 system, the change is considerably small in the 4 system. The chemical-shift change for the skeletal aromatic proton is, on the other hand, very remarkable. This suggests that the contribution of the allyl group of **4** to its Ag^+ complexation is not so great as that of **1**. On such a conformation of **1**, the allyl groups may be a little too far from the rigid calixarene skeleton to assemble the four allyl groups effectively for the metal-ion complexation in tert-butylcalix-[4] arene tetra(allyl ester) 4. Scheme 1b presents a plausible structure of the Ag^+ complex with 4, in which Ag^+ is located differently from the way it is located in the 1 complex. The Na⁺ interference in the Ag⁺ electrode based on **4** might be ascribable not only to the powerful Na⁺ binding of the carbonyl groups but also to the comparatively inefficient π interaction of the allyl groups with Ag⁺.

Since there are tiny but clear chemical-shift changes in the skeletal aromatic protons in the system of the π -coordinate tertbutylcalix [4] arene neutral carriers, 1-4, the skeletal aromatic rings conceivably contribute to their Ag⁺ complexation to some extent. This is evidenced by the fact that the calix[4]arene derivatives not possessing any special π -coordinate group, 5, works as the neutral carrier for Ag+-selective electrodes. The 1H NMR data for the systems of 5 was a little difficult to interpret due to their mixtures of cone and partial-cone conformations. However, in the calix[4]arene derivatives not possessing any special π -coordinate group, there seems to be some peak shift (0.2-0.3 ppm) of the skeletal aromatic protons to a higher frequency on the Ag^+ addition. It is probable in the case of 5 that the calixarene derivative accommodates Ag⁺ in the center of a cylindrical cavity made from the calix[4]arene skeleton (Scheme 1c).⁷ The Tl⁺ selectivity over Ag⁺ in the electrode based on **5** may also suggest that Tl⁺ can fit into the cylindrical cavity of the calix[4]arene tetra(propyl ether) 5 more suitably than Ag⁺ can.²³

Application of Calixarene-Based Silver-Ion Electrodes. The Ag⁺-selective electrode based on *tert*-butylcalix[4]arene tetra-(ally ether) **1** is an excellent Ag⁺ sensor with high sensitivity and selectivity. The response time (t_{90}) for the electrode was several

 Table 3. Silver-Ion Assay in Model Samples for Waste

 Fixing Solutions for Photography^a

Ag^+ concn (mol dm ⁻³)		coefficient of
actual value	obtained value	variation (%)
$1.0 imes10^{-3}$	$1.0 imes10^{-3}$	4.9
$7.5 imes10^{-4}$	$7.5 imes10^{-4}$	6.5
$5.0 imes10^{-4}$	$4.8 imes10^{-4}$	26.6
$1.0 imes 10^{-4}$	$1.1 imes10^{-4}$	29.2

^{*a*} The measurement was made 10 times by Gran's plot method. See the Experimental Section for the details.

seconds on the Ag+ activity change from 1 \times 10 $^{-3}$ to 3 \times 10 $^{-3}$ mol dm⁻³. The potential response, which is similar to that for popular neutral-carrier-based alkali metal ion electrodes, is faster than that for the Ag+-selective electrodes based on thiacrown ether derivatives.⁵ Ag⁺ assay in aqueous sample solutions with high background concentrations of Na⁺ and NH₄⁺ was carried out with the electrode based on *tert*-butylcalix[4]arene tetra(allyl ether) 1, to check a possibility for Ag⁺ assay with the ion-selective electrodes in waste fixing solutions for silver photography. The results are summarized in Table 3. The values for coefficient of variation depend on the Ag⁺ concentrations. In the Ag⁺ concentration of 7.5 \times $10^{-4}~mol~dm^{-3}$ or higher, the metal ion can be determined within several percentage points of the coefficient of variation even in the presence of 1 mol dm^{-3} of Na⁺ and NH₄⁺. Such a Ag⁺ assay by the electrodes based on *tert*-butylcalix[4]arene tetra(ally ester) 4, of course, is almost impossible due to the terrible Na⁺ interference.

In conclusion, the present Ag^+ -selective electrode based on *tert*-butylcalix[4]arene tetra(ally ether) **1** showed high sensitivity and selectivity and fast potential response. The present ion sensors may therefore be promising for applications such as a Ag^+ assay in sample solutions containing high backgrounds of alkali-metal ions.

ACKNOWLEDGMENT

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture.

Received for review April 28, 2000. Accepted August 7, 2000.

AC000490D

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