# Polymeric Membrane Sodium-Selective Electrodes Based on Calix[4]arene Ionophores *

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**Abstract.** Six kinds of tetra alkylester type calix[4]arene derivatives, ($R_1 = R_2 = CH_3$: **1**, $C_2H_5$: **2**, $C_3H_7$: **3**, $n$-$C_4H_9$: **4**, $t$-$C_4H_9$: **5**, $n$-$C_{10}H_{21}$: **6**), a diethyl-didecyl mixed ester type ($R_1 = C_2H_5$, $R_2 = C_{10}H_{21}$: **7**), and three kinds of lower rim bridged types ($R_1 = C_2H_5$, $R_2$—$R_2 =$ —$(CH_2)_{10}$—: **8**, —$(CH_2)_{12}$—: **9**, —$(CH_2)_2(OCH_2CH_2)_3$—: **10**) were characterized by electrochemical measurement to elucidate the effect of the length of the alkyl group of alkoxycarbonyl substituents on $Na^+$ selectivity. To obtain excellent $Na^+$ selective ionophores, introduction of short chain alkyl groups rather than long chain ones, such as a decyl group, and maintenance of sufficient solubility of the calix[4]arene derivatives in the membrane solvent are required concurrently. Among the calix[4]arenes tested, 25,26,27,28-tetrakis[(ethoxycarbonyl)methoxy]-*p-tert*-butylcalix[4]arene **2**, and the diethyl-didecyl mixed ester type derivative **7** are the best ionophores for a $Na^+$ selective electrode. On the other hand, sodium selectivity of the bridged type derivative **9** is comparable or even superior to that of the known bis(12-crown-4).

**Key words:** Calix[4]arene, $Na^+$ selective ionophore, lower rim bridged calix[4]arene.

## 1. Introduction

The cyclic tetramer of *p-tert*-butylphenol-formaldehyde condensates which maintains a cone-type conformation called a calix[4]arene from its cuplike shape, similar to that of a Greek crater vase, tends to complex with small organic compounds or metal ions. Further, incorporation of carbonyl groups such as ester, amide and ketone linkages into the phenolic oxygen atoms of the calixarene makes it function as an ionophore [1].

Previously, we have reported that the bulkier decyl ester type calix[4]arene derivative **6** [2] is available a sodium selective ionophore for polymeric membrane electrodes, independently of Diamond's work [3]. Selectivity coefficients for $Na^+$ with respect to other alkali and alkaline-earth metal ions, $NH_4^+$, and $H^+$ on the

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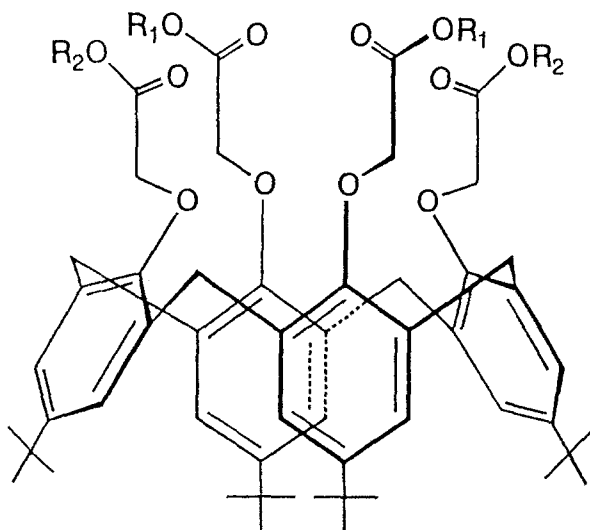
Tetra ester type              Diester-diester type

(1) $R_1 = R_2$ : -$CH_3$          (7) $R_1$ : -$C_2H_5$ , $R_2$ : -$C_{10}H_{21}$

(2) $R_1 = R_2$ : -$C_2H_5$        Bridged type

(3) $R_1 = R_2$ : -$C_3H_7$            $R_1$ : -$C_2H_5$

(4) $R_1 = R_2$ : -$n$-$C_4H_9$     (8)[ $R_2$—$R_2$ ] : -$(CH_2)_{10}$-

(5) $R_1 = R_2$ : -$t$-$C_4H_9$     (9)[ $R_2$—$R_2$ ] : -$(CH_2)_{12}$-

(6) $R_1 = R_2$ : -$C_{10}H_{21}$   (10)[ $R_2$—$R_2$ ] : -$(CH_2)_2$-$(OCH_2CH_2)_3$ -

Fig. 1.   Structural scheme of derived calix[4]arenes.

electrode based on derivative **6** are superior to $Na^+$ selective electrodes based on the known bis(12-crown-4) compound [4]. On the other hand, valuable membrane electrodes based on various calix[4]arene derivatives have also been reported [5–10]. In these cases, the sodium ion is encapsulated in the cavity of the calix[4]arene, interacting with the four carbonyl and four phenolic oxygen atoms as shown in Figure 1. The most important factor governing the selectivity characteristics of a calix[4]arene derivative is the spatial arrangement of the polar binding groups in a rigid conformation with optimum dimensions for sodium ions as the target ion. It is worthwhile to make a judicious choice of the substituents, $R_1$ or $R_2$, introduced onto the phenolic oxygen residues of the calix[4]arene with the intention of obtaining an excellent sodium ion selective ionophore.

In the present work, the effect of the length of the alkyl group of the alkoxycarbonyl substituents on sodium ion-selectivity is established by comparison of the electrochemical properties of the PVC membrane electrodes based on six kinds of tetra ester types, ($R_1 = R_2 = CH_3$; **1**, $C_2H_5$; **2**, $C_3H_7$; **3**, $n$-$C_4H_9$; **4**, $t$-$C_4H_9$; **5**, $n$-$C_{10}H_{21}$; **6**), one diester-diester mixed type ($R_1 = C_2H_5$, $R_2 = C_{10}H_{21}$; **7**) and

three kinds of bridged type ($R_1$ = $C_2H_5$; $R_2$—$R_2$ = —$(CH_2)_{10}$—; **8**, —$(CH_2)_{12}$—; **9**, —$(CH_2)_2$—$(OCH2CH_2)_3$—; **10**) calix[4]arene derivatives.

## 2. Experimental

### 2.1. SYNTHESIS OF CALIX[4]ARENE DERIVATIVES

*p-tert*-Butylcalix[4]arene was prepared according to the Gutsche method [11]. The tetra ester type derivatives, **1–6**, and the diethyl-didecyl mixed ester type, **7** [12], were prepared by the Williamson reaction with the corresponding alkyl bromoac-etates according to the literature methods [2, 3, 5, 13, 14]. Decyl $\alpha$-bromoacetate was obtained by esterification of bromoacetic acid with decylalcohol in benzene in the presence of $H_2SO_4$. Methyl, ethyl, propyl and *tert*-butyl-$\alpha$-bromoacetate were reagent grade and were used without further purification. Bridged type derivatives **8–10**, were synthesized by the subsequent reaction of calix[4]aryl diethyl ester [15, 16] with the corresponding alkyl bisbromoacetate according to the literature methods [17–19].

To *p-tert*-butylcalix[4]arene diethyl ester (1.36 mmol) dissolved in dry acetone (100 mL) was added $K_2CO_3$ (2.76 mmol) and a small amount of KI followed by alkyl bisbromoacetate (1.08 mmol) in dry acetone (50 mL). The mixture was refluxed for 75 h. After the reaction, the solvent was evaporated off and then water was added to the residue. The mixture was extracted with chloroform and the organic layer was dried over $MgSO_4$. The chloroform and excess alkyl bromoac-etate were removed under reduced pressure. The resulting residue was dissolved in chloroform and methanol was added to obtain needle-like crystals or colorless oil as crude product. The crude product was dissolved in chloroform and chro-matographed on a 2 × 25 cm column of ODS, using chloroform : acetonitrile (30 : 55) as an eluent. Identification of the synthesized calix[4]arene derivatives has been done by MS (Nippon Denshi JMW-AX506W), NMR (Varian unity 300) and elemental analysis.

### 2.1.1. *Mixed Ester Type Calix[4]arene Derivatives*

*Diethyl didecyl ester derivative* **7**. Colorless oil; MS (FAB): 1216 ($M^+$), 1239 ($M^+$+Na); $^1$H-NMR (CDCl$_3$) $\delta$ 0.86 (6H, s, $CH_3$(CH$_2$)$_7$), 1.05 and 1.08 (18H each, s each, ($CH_3$)$_3$C), 1.25 (28H, m, ($CH_2$)$_7$CH$_3$), 1.27 (6H, t, CH$_2$$CH_3$), 1.61 (4H, m, CH$_2$$CH_2$(CH$_2$)$_7$), 3.15 and 4.82 (8H each, d each, Ar$CH_2$Ar), 4.10 and 4.18 (4H each, q each, CO$CH_2$), 4.76 and 4.81 (4H each, s each, O$CH_2$CO), 6.74 and 6.77 (4H each, s each, *ArH*); *Anal. Calcd.* for C$_{76}$H$_{112}$O$_{12}$: C, 74.96; H, 9.27. *Found*: C, 74.91; H, 9.13.

*Bridged type derivative* **8**. Colorless oil; MS (FAB): 1076 ($M^+$), 1099 ($M^+$+Na); $^1$H-NMR (CDCl$_3$): $\delta$ 0.91 and 1.23 (18H each, s each, ($CH_3$)$_3$C), 1.04 (12H, m, ($CH_2$)$_6$), 1.27 (6H, t, CH$_2$$CH_3$), 1.64 (4H, m, $CH_2$(CH$_2$)$_6$$CH_2$), 3.17 and 4.84 (4H

each, d each, Ar$CH_2$Ar), 4.11 (4H, s, O$CH_2$CH$_3$), 4.20 (4H, s, O$CH_2$CH$_2$), 4.61 (4H, s, O$CH_2$CO), 5.02 (4H, s, (CH$_2$)$_{10}$O$CH_2$CO), 6.57 and 6.98 (4H each, s each, Ar$H$). *Anal. Calcd.* for $C_{66}H_{90}O_{12}$: C, 73.15; H, 8.44. *Found*: C, 73.71; H, 8.41.

*Bridged type derivative* **9**. Pale yellow crystals; m.p. 103–105°C, MS (FAB): 1102; $^1$H-NMR (CDCl$_3$) $\delta$ 1.07 (16H, m, $(CH_2)_8$), 1.14 and 1.29 (18H each, s each, $(CH_3)_3$C), 1.41 (6H, t, CH$_2$C$H_3$), 1.80 (4H, m, $CH_2$(CH$_2$)$_8$C$H_2$), 3.38 and 4.82 (4H each, d each, Ar$CH_2$Ar), 4.13 and 4.27 (4H each, q each, CO$CH_2$), 4.47 and 4.49 (4H each, s each, O$CH_2$CO), 7.12 (s, 8H, Ar$H$). *Anal. Calcd.* for $C_{68}H_{94}O_{12}$: C, 74.01; H, 8.59. *Found*: C, 73.95; H, 8.48.

*Bridged type derivative* **10**. White crystals; m.p. 127–129°C, MS (FAB): 1094; $^1$H-NMR (CDCl$_3$) $\delta$ 0.84 and 1.31 (18H each, s each, $(CH_3)_3$C), 1.33 (t, 6H, CH$_2$C$H_3$), 3.18 and 4.87 (8H each, d each, Ar$CH_2$Ar), 3.77 and 4.25 (18H each, m each, O$CH_2$), 4.51 and 5.15 (4H each, s each, O$CH_2$CO), 6.47 and 7.09 (4H each, s each, Ar$H$). *Anal. Calcd.* for $C_{64}H_{86}O_{15}$: C, 70.17; H, 7.91. *Found*: C, 70.88; H, 8.05.

## 2.2. OTHER CHEMICALS

Poly(vinyl chloride) (PVC) with an average polymerization degree of 1100 was purified by reprecipitation from THF in methanol. The plasticizers or membrane solvents, di-$n$-octylphthalate (DOP), $o$-nitrophenyl octyl ether (NPOE), and 2-fluorophenyl-2-nitrophenyl ether (FPNPE) were obtained from Dojindo Laboratories. The lipophilic salt, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaTFPB), was obtained from Tokyo Chemical Industry Co., Ltd. and Dojindo Laboratories.

## 2.3. ELECTRODE FABRICATION AND EMF MEASUREMENT

The preparation of the electrode membranes was as described previously [2], i.e., PVC (25 mg), a plasticizer or membrane solvent (67.5 mg), the calix[4]arene neutral carrier (10–30 mg) and lipophilic salt (0.5 mg) were dissolved in THF. The solution was poured into a Petri dish (21 mm i.d.). THF was evaporated slowly to yield the membrane with 0.1–0.2 mm thickness.

The emf measurements were carried out at $25 \pm 0.1$°C using a pH/mV meter (Tokyo Chemical Laboratories Co., Ltd., TP-1000GP) equipped with a double-junction type Ag–AgCl reference electrode. The representative electrochemical cell for emf measurements was an Ag–AgCl | internal solution ($1 \times 10^{-3}$ M NaCl) | PVC membrane | measured solution | 0.1 M NH$_4$NO$_3$ | 4 M NaCl | AgCl–Ag. The selective coefficients, $k_{\mathrm{NaM}}^{\mathrm{Pot}}$, were determined using a fixed interference method (FIM) with background concentrations of 0.05 M for alkali metal and H$^+$ ion and 0.5 M for alkaline-earth metal ions and NH$_4^+$ ion.

TABLE I. Effect of membrane solvent on $Na^+$ selectivity of the **2**-based PVC membrane electrodes.

| Cation | $-\log k_{NaM}^{Pot}$ | | |
|--------|------|------|-------|
| | DOP | NPOE | FPNPE |
| $K^+$ | 2.56 | 2.51 | 2.57 |
| $Li^+$ | 3.44 | 2.98 | 3.39 |
| $H^+$ | 3.49 | 3.10 | 2.49 |
| $NH_4^+$ | 4.42 | 4.03 | 4.18 |
| $Mg^{2+}$ | 4.64 | 4.39 | 4.62 |
| $Ca^{2+}$ | 4.09 | 3.98 | 4.11 |

## 3. Results and Discussion

### 3.1. TETRAESTER TYPE CALIX[4]ARENE

The capability of neutral-carrier-type ion selective electrodes is considered to be dependent on its functional characteristics as an ionophore of the neutral carrier itself and on the compatibility of the carrier into the PVC membrane containing membrane solvent and lipophilic salt. At first, effects of membrane solvents on the sensitivity and selectivity of the $Na^+$ selective electrodes based on six of the calix[4]arene derivatives **1-6**, were determined. The membrane solvents tested were NPOE and FPNPE as the phenyl ether type solvents and DOP as the diester type one. Selectivity coefficients for $Na^+$ ion with respect to other alkali and alkaline-earth metal ions, $NH_4^+$ and $H^+$ on the electrodes based on derivative **2** are summarized in Table I.

Each membrane solvent, DOP and NPOE, gave good results with a Nernstian response, 58–59 mV/decade, in accordance with the wide $Na^+$ activity change in the activity range of $1.0 \times 10^{-5} - 1$ M and the $Na^+$ selectivity with respect to $K^+$, $-\log k_{NaK}^{Pot}$ are 2.56 and 2.51, respectively. Although the FPNPE solvent leads to a value of 2.57, it allowed not only a poor response of 50 mV/decade to the $Na^+$ activity changes but also a poor $Na^+$ selectivity against hydrogen ion ($-\log k_{NaH}^{Pot}$ = 2.49). Such reduced sensitivity and $Na^+$ selectivity tendencies derived from the use of FPNPE as a membrane solvent were also observed for the other tetra ester type derivatives, **1** and **3** to **6**. That is, as a membrane solvent, a low dielectric constant solvent such as DOP gave better results compared to the high dielectric solvents such as NPOE and FPNPE.

A comparison of the selectivity coefficients for the tetra ester type calix[4]arene derivatives–DOP system electrodes is depicted in Table II.

As summarized in Table II, although the **6**-based electrode presents a better $Na^+$ selectivity with respect to $K^+$, the selectivity coefficient $-\log k_{NaK}^{Pot}$ being 2.17 compared with the bis(12-crown-4) based electrode, the selectivity is inferior to the electrodes based on the other tetra ester type derivatives having a shorter alkyl

TABLE II. Selectivity comparison among $Na^+$ selective electrodes based on tetra ester type calix[4]arenes 1 to 6 and known bis(12-crown-4) type PVC membrane $Na^+$ electrodes.

| Cation | $- \log k_{NaM}^{Pot}$ | | | | | | |
| | 1 | 2 | 3 | 4 | 5 | 6 | A–NPOE |
|---|---|---|---|---|---|---|---|
| $K^+$ | 2.25 | 2.56 | 2.51 | 2.49 | 1.70 | 2.17 | 2.05 |
| $Li^+$ | | 3.44 | 3.40 | 3.36 | | 2.81 | 3.50 |
| $H^+$ | 3.18 | 3.49 | 3.75 | 3.55 | 3.40 | 3.53 | 4.44 |
| $NH_4^+$ | | 4.42 | 4.26 | 4.20 | | 3.34 | 3.55 |
| $Mg^{2+}$ | | 4.64 | 4.62 | 4.69 | | 4.39 | 4.00 |
| $Ca^{2+}$ | | 4.09 | 4.10 | 4.06 | | 3.94 | 3.93 |

Membrane solvent for derivative 1 to 6: DOP.
A: dibenzyl-bis(12-crown-4) [4].

chain except for derivative 5. On the other hand, derivative 1 and 5 based electrodes produced unsatisfactory results such that the neutral carriers were separated out as crystals in the membrane. In the derivative 5 based electrodes, the reduced $Na^+$ selectivity, the selectivity coefficient with respect to $K^+$, $- \log k_{NaK}^{Pot}$ being 1.70 is probably a consequence of the steric hindrance provided by the bulky *tert*-butyl groups around the cavity.

These facts led us to the following concept. That is, to obtain excellent $Na^+$ selective carriers, it is necessary to introduce shorter alkyl chains rather than longer alkyl ones such as a decyl group and to retain sufficient solubility of the resulting calix[4]arene derivatives into the membrane phase. Therefore, we designed and synthesized a diethyl-didecyl mixed ester derivative, 7, and three kinds of lower rim bridged type calix[4]arenes, 8 to 10. The other objects of capping the lower rim of the calix[4]arene with a bridge of a different length methylene groups are to fix the calixarene in a rigid cone conformation and to change the cavity size.

## 3.2. LIPOPHILICITY OF CALIX[4]ARENE DERIVATIVES

The chromatographic retention character of these calix[4]arenes were determined by means of HPLC using an ODS (4.6 × 500 mm) column and chloroform : acetonitrile (30 : 55) mixed solvent as an eluent. The observed retention times for calix[4]arene derivatives are summarized in Table III. Although the retention time does not necessarily reflect the compatibility of the calix[4]arenes with an electrode membrane, its values may have a correlation to the lipophilicity and/or the solubility of the calix[4]arenes into the membranes solvent.

Derivative 6 shows the most remarkable lipophilicity among these derivatives. On the other hand, the retention times of derivatives 7, 9, and 10 are 16.28, 14.10 and 22.13 min, respectively. The lipophilicities of these derivatives are not as good as derivative 6 but remarkably improved in comparison with derivatives 1 to 5.

TABLE III. Comparison of retention times of calix[4]arene derivatives in HPLC.

| Derivative | Retention time (min) |
|---|---|
| 1 | 7.05 |
| 2 | 7.65 |
| 3 | 8.78 |
| 4 | 10.12 |
| 5 | 10.10 |
| 6 | 48.48 |
| 7 | 16.28 |
| 8 | 9.37 |
| 9 | 14.10 |
| 10 | 22.13 |

Column: 5-ODS-H 4.6 × 500
Eluent: chloroform : acetonitrile (30 : 55)
Flow rate: 1.0 ml/min.

## 3.3. MIXED ESTER TYPE CALIX[4]ARENES

### 3.3.1. Diethyl-Didecyl Mixed Ester Derivative

The selectivity coefficients of the mixed ester type derivative, 7-based $Na^+$ selective electrodes are evaluated. Table IV shows the selectivity comparison among the neutral-carrier-type $Na^+$ selective electrodes based on derivative 7 and our previously reported $Na^+$ neutral carriers which possess one of the best $Na^+$ selectivities against $K^+$. In the 7-based electrode, DOP and NPOE gave good results, allowing high $Na^+$ selectivity with respect to $K^+$, $NH_4^+$, $H^+$, $Mg^{2+}$, and $Ca^{2+}$. Particularly, the 7–DOP system electrode is superior to the known bis(12-crown-4) and tert-octyl and de-tert-butylated calix[4]aryl tetradecyl ester based PVC membrane for $Na^+$ selectivity coefficient with respect to $K^+$, $Li^+$, $NH_4^+$ and $H^+$. Furthermore, another favorable characteristic of derivative 7 is its good solubility in a low dielectric constant solvent such as DOP which effectively avoids contamination phenomena of the membrane electrode by adhering proteins in human blood sera. Also, the lifetime of the 7–DOP system electrode was studied by periodically recalibrating it in standard solution and calculating the response slope. During the 6 months or more of the observation period, the electrodes showed superior performance. These results must depend on the well-balanced lipophilicity of derivative 7. Accordingly, derivative 7 is a very promising neutral carrier for sodium ion assay.

TABLE IV. Selectivity comparison among Na$^+$ selective electrodes based on derivative 7 and previously reported calix[4]arenes.

| Cation | $-\log k_{NaM}^{Pot}$ | | | | |
|---|---|---|---|---|---|
| | 7–DOP | 7–NPOE | 7–FPNPE | B–DOP | C–FPNPE |
| K$^+$ | 2.57 | 2.38 | 2.07 | 2.34 | 2.20 |
| Li$^+$ | 3.49 | 3.40 | 3.02 | 3.21 | 2.95 |
| H$^+$ | 4.00 | 3.18 | 3.64 | 3.31 | 2.39 |
| NH$_4^+$ | 4.27 | 4.40 | 4.06 | 4.09 | 3.61 |
| Mg$^{2+}$ | 4.96 | 4.35 | 4.57 | 4.25 | 4.69 |
| Ca$^{2+}$ | 4.14 | 3.78 | 4.11 | 3.81 | 3.29 |

B: di-*tert*-butylated calix[4]aryl decyl ester [5].
C: *p-t*-octyl calix[4]aryl decyl ester [6, 21].

TABLE V. Selectivity comparison among Na$^+$ selective electrodes based on bridged type calix[4]arenes, 8 to 10.

| Cation | $-\log k_{NaM}^{Pot}$ | | | | |
|---|---|---|---|---|---|
| | 8–DOP | 8–NPOE | 8–FPNPE | 9–DOP | 10–DOP |
| K$^+$ | 1.92 | 1.85 | 1.76 | 2.20 | 1.67 |
| Li$^+$ | 3.30 | 3.08 | 2.79 | 3.15 | 3.29 |
| H$^+$ | 3.49 | 2.94 | 2.03 | 2.58 | 2.76 |
| NH$_4^+$ | 3.93 | 3.36 | 3.06 | 3.63 | |
| Mg$^{2+}$ | 4.76 | 4.10 | 3.49 | 3.82 | |
| Ca$^{2+}$ | 4.09 | 3.67 | 3.43 | 3.24 | 3.67 |

### 3.3.2. *Bridged Type Derivative*

Table V displays the sodium ion selectivity for three kinds of bridged type calix[4]arene derivatives. Since the capping of the lower rim of calix[4]arene with a bridge of different length methylene groups results in the fixation of a rigid cone conformation and the change of the cavity size, the Na$^+$ selectivity is expected to be improved.

Unfortunately, as seen in Table V, in the 8 and 10-based electrodes, the Na$^+$ selectivity coefficient with respect to K$^+$, $-\log k_{NaK}^{Pot}$ were about 1.9 and 1.7, respectively. The reduced Na$^+$ selectivity against K$^+$ in the latter case may be caused by the three active oxygen atoms derived from the —(CH$_2$)$_2$—(CH$_2$CH$_2$O)$_3$— group, because these oxygen atoms and the carbonyl ones form the crown ether ring which is favorable for K$^+$ complex formation. On the contrary, the 9-based electrode was superior to the 8 and 10-based electrodes; the Na$^+$ selectivity coefficient with respect to K$^+$, $-\log k_{NaK}^{Pot}$ being 2.2, and selectivity comparable to that of the commonly used bis(12-crown-4) ionophore was observed. These results suggest that the length of the methylene bridge moiety is effective for the improve-

ment of Na$^+$ selectivity by calixarene, while oxygen atoms containing the bridge moiety are irrelevant.

Recently, Shinkai et al. [20] studied PVC membrane electrodes based on the calix[4]arene derivative and reported that the p-tert-octyl-calix[4]aryl tetraethyl ester–FPNPE system electrode allowed high Na$^+$ selectivity. The Na$^+$ selectivity coefficient being 3.1 [20], though its value was not evaluated by a fixed interference method (FIM). Its excellent Na$^+$ selectivity compared with those of our similar derivative, p-tert-octylcalix[4]aryl tetradecyl ester [6, 21], is probably derived from the introduction of shorter alkyl groups such as the ethyl ester and tert-octyl group into the upper rim moiety to produce lipophilicity, as already mentioned.

In conclusion, the diester-diester mixed type derivative 7 and diester-bridged type 9 are promising neutral carriers for sodium ion assay. Further investigation on the electrode membrane condition such as membrane solvents and lipophilic salts for the calix[4]arene derivatives, 7–10, are currently being done in our laboratory.

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