

Polymeric Membrane Sodium Ion-Selective Electrodes Based on Calix[4]arene Triesters

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New lipophilic triesters of calix[4]arene and calix[4]quinone are investigated as sodium ion-selective ionophores in poly(vinyl chloride) membrane electrodes. For an ion selective electrode based on calix[4]arene triester **I**, the linear response is $1 \times 10^{-3.5}$ to 1×10^{-1} M of Na^+ concentrations. The selectivity coefficients for sodium ion over alkali metal and ammonium ions are determined. The detection limit ($\log a_{\text{Na}^+} = -4.50$) and the selectivity coefficient ($\log K_{\text{Na}^+, \text{K}^+}^{\text{pot}} = -1.86$) are obtained for polymeric membrane electrode containing calix[4]arene triester **I**.

Keywords : Calix[4]arene, Calix[4]quinone, PVC membrane electrode, Ion selective electrode, Sodium ion.

Introduction

Calixarenes have received considerable attention as an interesting class of ionic and molecular binding hosts.^{1,2} The synthesis, structures and cation-binding properties of calixarene derivatives as a new class of macrocyclic molecular receptors have been reviewed.³⁻⁶ Calixarene esters have appeared the unusual ionophoric properties toward the alkali metal ions such as sodium and cesium ion.⁷ Recently there has been increasing interest in the development of neutral carrier-based sodium ion-selective electrodes as alternatives of sodium ion-selective glass electrode. Analytical methods for determining the alkali metal ions have been extensively studied due to the importance of sodium,⁷⁻¹⁰ potassium^{11,12} and lithium¹³ in biological processes. The ISE dynamic response is generated by selective complexation of the target ion by ionophores dispersed in a poly(vinyl chloride) (PVC) matrix. Polymeric membrane ISEs provide one of the most powerful sensing methods because it is possible to select various sensory elements according to the charge and size of the target ion in clinical and environmental assays.⁷⁻¹⁴ Based on the recent advance of host-guest chemistry, polymeric membrane ISEs for sodium ion have been extensively developed by the use of crown ethers and related macrocyclic hosts as well as acyclic ligands.¹⁵⁻¹⁸ Many of these ISEs exhibit excellent selectivity for sodium ion as a guest and are now commercially available.¹⁹⁻²¹ We have synthesized calix[4]arene triesters and their corresponding quinones as sodium ion ionophores and reported their cation binding properties in extraction experiments.²² Now in this study, we describe the electrode optimization and the electrochemical properties of polymeric sodium ion-selective membranes based on calix[4]arene triesters and their corresponding quinones as sodium ion ionophores.

Experimental Section

Reagents. Calix[4]arene triesters and their corresponding

quinone tested as sodium ionophores are shown in Figure 1. They were prepared according to our literature procedure.²² High molecular weight PVC, dioctyl sebacate (DOS), 2-nitrophenyl octyl ether (*o*-NPOE), potassium tetrakis(*p*-chlorophenyl)borate (KTpCIPB) and tetrahydrofuran (THF), which were obtained from Fluka, were used to prepare the PVC membranes. Analytical grade chlorides of sodium, lithium, cesium, potassium, and ammonium were used. Doubly distilled water in a quartz apparatus was used to prepare all aqueous electrolyte solutions.

Fabrication of polymeric ion-selective electrodes. The typical composition of PVC-based sodium ion-selective

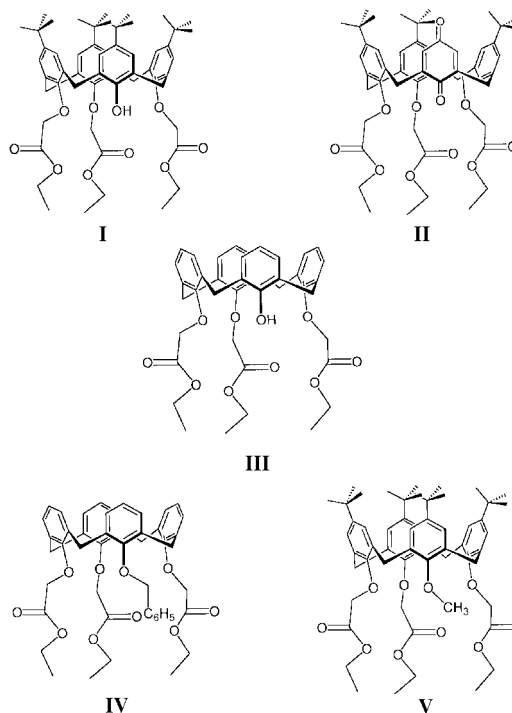


Figure 1. Five lipophilic triesters of calix[4]arene and calix[4]quinone tested as ionophores in this study.

Table 1. Composition of PVC-based Sodium Selective Membranes

Ionophore	No.	PVC	DOS	<i>o</i> -NPOE	KT <i>p</i> CIPB ^b	Ionophore
I	1	33	66		0	1
	2	33	66		50	1
	3	33		66	0	1
	4	33		66	50	1
II	5	33	66		0	1
	6	33	66		50	1
	7	33		66	0	1
	8	33		66	50	1
III	9	33	66		0	1
	10	33	66		50	1
	11	33		66	0	1
	12	33		66	50	1
IV	13	33	66		0	1
	14	33	66		50	1
	15	33		66	0	1
	16	33		66	50	1
V	17	33	66		0	1
	18	33	66		50	1
	19	33		66	0	1
	20	33		66	50	1
none	21	33	66		0	
	22	33	66		50	
	23	33		66	0	
	24	33		66	50	

^aIn wt %. ^bMol % relative to the ionophore.

electrodes was 33 mg PVC, 66 mg plasticizer, 1 mg ionophore and KT*p*CIPB (mol% of ionophore if needed). Table 1 summarizes the compositions of the sodium ion-selective membranes employed in this study. The mixture of ionophore, plasticizer and PVC were dissolved in the appropriate volume of THF and mechanically stirred. All membrane cocktails were cast in glass rings placed on glass plates for conventional ion-selective electrodes.²⁴ Solvent from PVC membrane was allowed to evaporate for at least 24 hours at room temperature.²⁴ The thickness of the resulting membrane was about 0.3 mm.

Potentiometric measurements. The electrochemical properties of the sodium ion-selective electrodes were investigated in the conventional configuration. Small disks were punched from the cast membranes and mounted in Philips electrode bodies (IS-561). For all electrodes, 0.1 M NaCl was used as an internal filling solution. The external reference electrode was an Orion sleeve-type double-junction Ag/AgCl reference electrode (Model 90-02). The electrochemical potential was measured using home-made 16-channel potentiometer coupled to a computer. The dynamic response curves were produced by adding standard solutions of cations to magnetically stirred buffer solution (0.05 M Tris-HCl, pH 7.2). The selectivity coefficients ($K_{Na^+,j}^{pot}$) were determined by the separate solution method (SSM) using 0.1 M chloride salts of the cations involved.²³ Detection limits were obtained from the intersection of two linear

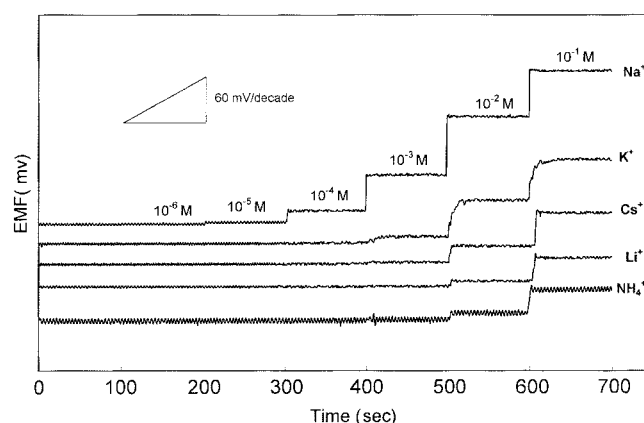


Figure 2. The dynamic response for alkali metal ions by electrode 1 based on calix[4]arene triester **I** in pH 7.2 (0.05 M Tris-HCl) buffer solutions.

lines in the plot of the concentration of Na⁺ and the potential difference.²³

Results and Discussion

New lipophilic triesters of calix[4]arene have three carbonyl oxygens, which function as well-defined convergent binding sites for the specific metal ions that sterically fit well with the pseudocavity constructed by these oxygens. In the previous studies, the calix[4]arene tetraesters have been shown to display selectivities for sodium ion in the complexation, extraction, transport, and liquid membrane experiments.¹⁹⁻²¹ The calixarene structure acted as a rigid support for the carbonyl groups that function as convergent binding sites for metal ions. Actually, calix[4]arene and calix[4]-quinone triesters have shown to display selectivities for sodium ion, in the complexation, extraction,^{21,22} and they showed ion transport ability with efficiency decreasing in the order of Na⁺ > K⁺ > Cs⁺ ~ Rb⁺ ~ Li⁺. Among them, calixarene triester **V** exhibited excellent extraction of alkali metal ions.²² The polymeric membrane ISEs are a more complicated system rather than the extraction experiments, and the conditions under which the selectivity of the ISE is examined are very different, the results of extraction experiments should be considered only as a consulted data for the ISE selectivity.

The potentiometric response properties of these polymeric membrane ISEs are examined for alkali metal and ammonium ions. Electrodes (21-21) with a membrane containing no ionophore show negligible response to all of the alkali metal and ammonium ions employed. The ion exchanger KT*p*CIPB in these experiments is known to exhibit some sensory activity for sodium ion in PVC/NPOE membrane containing no selective ionophore,³ but the sodium sensitivity with the addition of KT*p*CIPB in PVC/DOS membrane containing no ionophore is largely decreased. The polymeric membrane ISEs are investigated to measure the ability of the ionophores to act as neutral carriers in the absence of the ion exchanger. Figure 2 illustrates the dynamic response for alkali metal ions, obtained in pH 7.2 (0.05 M Tris-HCl)

buffer solutions by electrode 1 (PVC membrane containing DOS as a plasticizer) based on calix[4]arene triester **I**. The electrode 1 displays a near-Nernstian (58.3 mV/decade) response to Na⁺ in NaCl solutions over the linear range 1×10^{-3} – 1×10^{-1} M. The strongest response is observed for Na⁺ ion with a detection limit below 10^{-4} M. The response of electrode 1 is also observed for K⁺ started from *ca.* 10^{-3} M, for Cs⁺ and Li⁺ started from *ca.* 10^{-2} M. The selectivity coefficients of potentiometric responses by electrode 1 are in the order of Na⁺ > K⁺ > Cs⁺, Li⁺, and this result is identical to the extraction result which the binding efficiency is decreasing in the order Na⁺ > K⁺ > Cs⁺ > Li⁺.²² The selectivity coefficients ($K_{Na^+,j}^{pot}$) determined are summarized in Table 2. The $K_{Na^+,j}^{pot}$ values for the electrodes with a membrane containing no ionophore are also listed in Table 2. According to the results in Table 2, the PVC/DOS polymeric electrode 1 over the PVC/NPOE polymeric electrode 3 or 4 based on calix[4]arene triester **I** shows the better selective response for sodium ion. Figure 3 shows the dynamic response for Na⁺ in pH 7.2 buffer solutions by electrodes 1, 2, 9, and 10 shown in Table 1. As mentioned above, the polymeric electrode 1 in the absence of the ion exchanger based on calix[4]arene triester **I** which have para *t*-butyl substituents provides the detection limit ($\log a_{Na^+} = -4.50$) and the selectivity coefficient ($\log K_{Na^+,K^+}^{pot} = -1.86$) for Na⁺ over alkali metal and ammonium ions, and slopes in excess of 50 mV/decade change in appropriate sodium concentration. These

results are very similar to those obtained from the ISE prepared by triester monoacid derivatives of *p*-*tert*-butyl-calix[4]arene.⁶ But the polymeric electrode 9 in the absence of the ion exchanger based on the calix[4]arene triester **III** which have no para *t*-butyl substituents gives the worse detection limit and selectivity coefficient. The polymeric electrodes 2 and 10 in the presence of the ion exchanger (50 mol%) based on the calix[4]arene triesters **I** and **III** decrease the detection limit and the selectivity coefficient. Meanwhile the polymeric electrodes prepared from 30 or 70 mol% KTp-CIPB produce the similar results to that of 50 mol% KTp-CIPB, and there is no effect on the mol% of ion exchanger. The preference for Na⁺ can be reasonably explained by an excellent geometric fit with the pseudocavity constructed by the three carbonyl oxygens in calix[4]arene triester **I** which have para *t*-butyl substituents rather than calix[4]arene triester **III** which have no para *t*-butyl substituents. Although calixarene triester **V** exhibited good extraction of alkali metal ions and had also para *t*-butyl substituents, it gives the worse detection limit and selectivity coefficient. PVC membrane of calixarene triester **V** may exhibit the worst electrical properties although calixarene triester **V** showed good extraction of sodium ion in organic solution. Meanwhile, although calixarene triester **IV** have no para *t*-butyl substituents, it gives the worse detection limit and selectivity coefficient. Benzyl group in calixarene **IV** rather than hydroxyl group in calixarene **III** seems to suggest the better geometric

Table 2. Electrochemical Properties of PVC-based Sodium Selective Membrane Electrode

Ionophore	no.	slope (mV/decade)	detection limit (log a_{Na^+})	$\log k_{Na^+,j}^{pot}$			
				$j = Li^+$	$j = K^+$	$j = NH_4^+$	$j = Cs^+$
I	1	58.3	-4.50	-2.81	-1.86	-2.57	-2.42
	2	51.6	-3.95	-1.40	-0.09	-1.12	-0.71
	3	29.0	-3.02	-1.40	-1.13	-1.32	-1.62
	4	26.0	-2.56	-0.19	1.66	0.52	-0.54
II	5	57.0	-4.55	-2.54	-0.78	-2.32	-2.32
	6	56.6	-4.51	-2.23	-0.42	-2.60	-2.00
	7	31.4	-3.20	-1.13	-0.07	-1.08	-0.91
	8	39.9	-3.15	-0.98	0.86	-0.68	-0.78
III	9	54.3	-4.23	-2.51	-1.50	-2.11	-1.84
	10	48.3	-3.80	-1.52	-0.51	-1.32	-0.95
	11	17.2	-2.53	-0.88	-0.83	-0.69	-0.23
	12	36.8	-3.06	-0.44	0.99	-0.12	-0.12
IV	13	52.9	-4.09	-2.60	-1.84	-2.20	-2.32
	14	22.8	-2.63	-2.50	-1.91	-2.11	-1.88
	15	18.7	-2.56	-1.01	-0.78	-0.81	-0.12
	16	57.8	-4.34	-1.76	-1.12	-1.94	-3.16
V	17	35.7	-3.57	-2.81	-0.12	-2.10	-1.66
	18	30.0	-3.44	-1.69	-0.56	-1.57	-1.44
	19	26.2	-2.60	-0.76	0.56	-0.52	-0.15
	20	26.2	-2.42	-0.58	1.56	0.59	-0.84
none	21	30.0	-2.55	-0.74	0.73	0.30	0.64
	22		-1.95	-0.27	0.34	0.27	0.32
	23		-2.60	0.00	0.15	0.32	0.24
	24			0.00	0.20	0.14	2.57

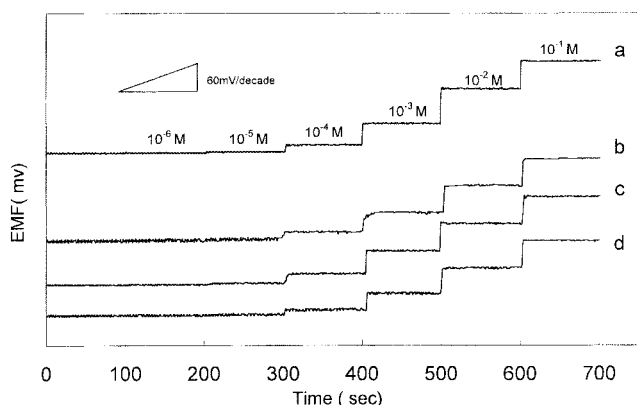


Figure 3. The dynamic response for sodium ion by electrodes (a) 1, (b) 2, (c) 9, and (d) 10 in pH 7.2 (0.05 M Tris-HCl) buffer solutions.

structure for the reception of Na^+ . Calix[4]quinone triester **II** also gives rise to the worst selectivity coefficient. Probably calix[4]quinone triester **II** produces the worse geometric structure for the reception of Na^+ in PVC membrane. At present, the mechanism of the geometric variation by the substituent in calix[4]arene triester is unclear.

According to the results in Table II, the sodium selectivity and sensitivity of calix[4]arene and calix[4]quinone triesters in polymeric electrodes are generally lowered with the addition of KTpCIPB as an additive reagent. The addition of the additive to PVC membranes containing ionophores greatly changed the selectivity of all guests employed, and the selectivity depends on the composition of polymeric electrodes. Examination of the selectivity data for the electrodes employed in this study indicates that the structure of calix[4]arene triesters as an ionophore is the major factor determining the selectivity, and the other factor determining it is the kind of plasticizer used in PVC membrane electrodes. All the electrodes responded rapidly to changes in sodium concentration with time constant of the order of a few seconds. The rate of response was only limited by the speed of stirring and the injection technique.

Conclusion

PVC-polymeric sodium ion-selective electrodes based on lipophilic triesters of calix[4]arene and calix[4]quinone have been fabricated and tested for sodium ion against alkali metal and ammonium ions. In general the polymeric electrodes combined with the calix[4]arene triesters which have para *t*-butyl substituents had superior characteristics to those combined with those which have no para *t*-butyl substituents. Among them, PVC polymeric electrode based on calix[4]arene triester **I** shows the best detection limit and the selectivity coefficient in pH 7.2 buffer solutions, and the linear response in Na^+ concentrations of $1 \times 10^{-3.5}$ – 1×10^{-1} M compared with the other electrodes prepared in this work. The sodium selectivities ($K_{\text{Na}^+,j}^{\text{pot}}$) are dependent upon ionophore as well as plasticizer used in membrane electrodes.

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