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Lipophilic Calix[4]arene Ester and Amide Derivatives as Neutral Carriers for Sodium Ion-Selective Electrodes

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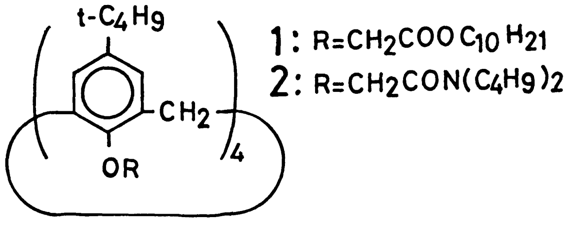
Lipophilic calix[4]arenes bearing ester and amide linkages were synthesized and tested for their usefulness as neutral carriers of Na^+-selective electrodes. The resulted poly(vinyl chloride) (PVC) membrane electrodes based on the calixarene derivatives were found to be highly selective for Na^+.

Calixarenes, cyclic oligomers of phenol-formaldehyde condensates, are promising rigid components for synthetic ionophores.[1-4] Calixarenes incorporating ether, ester, and amide linkages at the phenolic oxygen atoms seem to possess complexing abilities towards alkali and alkaline-earth metal ions.[1-3] The modified calixarene derivatives can be candidates for neutral carriers of ion-selective membrane electrodes.[5] We report here highly Na^+-selective electrodes based on lipophilic calix[4]arene derivatives.

The neutral carriers employed here were calix[4]arene ester and amide derivatives, **1** and **2**. In the calixarene derivatives, long aliphatic chains, four decyl and eight butyl groups, were incorporated to promote the lipophilicity, which is an important factor for the properties of the resulting membrane electrodes, such as EMF stability and electrode duration. Calixarene derivatives **1** and **2** were synthesized by the reaction of p-(t-butyl)-calix[4]arene with a large excess of decyl bromoacetate and N,N-dibutyl chloroacetamide, respectively (NaH, in DMF/THF(1/1), reflux, for 3 h). The PVC membranes were prepared as reported previously[6] and consisted of 9.7% (in weight) neutral carrier, 65.5% membrane solvent (plasticizer), 24.3% PVC, and 0.5% dipicrylamine sodium salt. The EMF measurements were carried out at 25 °C with an electrochemical cell of Ag-AgCl/1 x 10^{-3} M(1 M = 1 mol dm^{-3}) NaCl/PVC membrane/sample solution/0.1 M NH_4NO_3/4 M KCl/ AgCl-Ag. The selectivity coefficients were determined by a mixed solution method (FIM) with background concentrations of 0.05 M for alkali metal ions and H^+ and 0.5 M for alkaline-earth metal ions and NH_4^+.



Selectivity coefficients for the Na^+-selective electrodes based on the calixarene derivatives were determined under membrane conditions with different solvents. In the **1**-based electrodes, high dielectric-constant solvents such as o-fluorophenyl o-nitrophenyl ether(FPNPE), o-nitrophenyl phenyl ether(NPPE), o-nitrophenyl octyl ether(NPOE), and tris(2-ethylhexyl) phosphate(TEHP) gave better results than low dielectric-constant solvents such as bis(2-ethylhexyl) sebacate (DOS) and dipentyl phthalate(DPP) in the electrode selectivity, especially in the k_{NaK}^{Pot} value. The selectivity tendency derived from the membrane solvents, however, was reversed in the **2**-based electrode. The selectivity coefficient values under the optimized membrane conditions are listed in Table 1. The Na^+ selectivities are quite high in the ion-selective electrode of calixarene derivatives, especially of **1**, of which electrode possesses an excellent k_{NaK}^{Pot} value of 4×10^{-3}. The **1**-based electrode is comparable or even superior to previous neutral carrier-type Na^+-selective electrodes in the ion selectivities.$^{7,8)}$ Both of the **1**- and **2**-based membrane electrodes exhibited Nernstian response (59 mV $decade^{-1}$) in the Na^+ activity range of 1×10^{-4} - 1 M, although the electrode sensitivity was diminished in the **2**-based electrodes with the phenyl ether-type membrane solvents. Thus, the calix[4]arene derivatives, which are also highly lipophilic and easy to prepare, are great alternatives to the previous Na^+ neutral carriers for the ion-selective electrodes. Further study is now under way regarding practical applications of the calixarene-based Na^+ electrodes.

Table 1. Selectivity coefficients for calixarene-based Na^+-selective electrodes$^{a)}$

Neutral carrier	$-\log k_{NaM}^{Pot}$									
	Li^+	K^+	Rb^+	Cs^+	NH_4^+	H^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
1	3.0	2.4	3.1	3.5	4.2	1.9	4.0	3.8	4.0	3.2
2	2.4	2.1	3.2	3.9	4.3	2.5	4.7	2.8	2.9	3.1

a) Membrane solvent: FPNPE for **1**-electrode and DOS for **2**-electrode.

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