

Highly selective methylammonium-selective membrane electrode made by the modification of the upper rim of calix[6]arene derivatives

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Abstract

The upper rim of calix[6]arene-hexaacetic acid hexaethyl esters was modified with various alkyl substituents to develop ionophores for constructing organic ammonium ion-selective membrane electrodes. We found that the substitution of bulkier alkyl groups enabled a more effective discrimination of simple aliphatic ammonium ions such as methylammonium and ethylammonium. In particular, an electrode based on *p*-1,1,3,3-tetramethylbutylcalix[6]arene-hexaacetic acid hexaethyl ester showed the highest response to methylammonium among various organic ammonium ions and inorganic cations, giving the following selectivity coefficients; $\log k_{\text{CH}_3\text{NH}_3^+, X}^{\text{Pot}}$: $\text{C}_2\text{H}_5\text{NH}_3^+$, -0.2 ; $\text{C}_3\text{H}_7\text{NH}_3^+$, -1.4 ; $\text{C}_4\text{H}_9\text{NH}_3^+$, -1.9 ; $\text{C}_6\text{H}_{13}\text{NH}_3^+$, -1.6 ; phenethylammonium, -1.9 ; Na^+ , -2.8 ; K^+ , -1.8 ; Rb^+ , -1.6 ; Cs^+ , -0.2 ; NH_4^+ , -2.8 . The electrode exhibited a near Nernstian response to methylammonium in the concentration range of 1×10^{-5} to 1×10^{-2} M with a slope of 58.5 mV per concentration decade in 0.1 M MgCl_2 . The limit of detection was 3×10^{-6} M. The electrode could be used over a pH range of 2–10. Formation of a 1:1 complex between *p*-1,1,3,3-tetramethylbutylcalix[6]arene-hexaacetic acid hexaethyl ester and methylammonium was confirmed by electrospray ionization mass spectrometry. The response characteristics of the methylammonium-selective electrode were compared with those of NH_4^+ -selective electrodes so far developed.

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1. Introduction

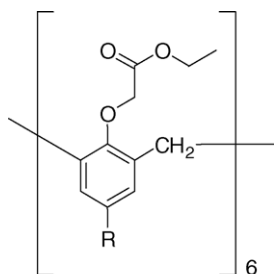
One of the most pressing challenges in sensor research is the construction of highly selective receptors for molecular recognition. Calixarene derivatives are one candidate for molecular receptors for the selective recognition of primary organic ammonium ions and have been used to construct various types of molecular sensors including

ion-selective electrodes [1,2]. Among various calixarene derivatives, calix[6]arene-hexaacetic acid hexaethyl ester (**1**) (see the structure in Fig. 1) was an excellent ionophore (or more generally a molecular receptor) for making a hexylammonium-selective electrode [3]; this ionophore, named amine ionophore I, soon became commercially available from Fluka [4]. Later, it was found to induce a strong response to methylammonium [5,6]. However, there was extensive interference by Cs^+ , consistent with the fact that this ionophore also acts as a cesium ionophore [4,7,8]. Recently, the corresponding *p*-*tert*-butylcarix[6]arene derivative (**4**), shown in Fig. 1, was found to respond to ethylammonium with remarkably less interference from Cs^+ [9]. This ionophore also became commercially available

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- 1 : R=H
 2 : R=Me
 3 : R=*i*-Pr
 4 : R=*t*-Bu
 5 : R = $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ | \quad | \\ -\text{C}-\text{CH}_2-\text{C}-\text{CH}_3 \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$

Fig. 1. Chemical structures of calix[6]arene derivatives tested.

from Fluka; however, the name given to it was cesium ionophore II, although the response to ethylammonium was much stronger than that to Cs^+ as mentioned above.

We were particularly interested in the marked decrease in interference by Cs^+ when a *tert*-butyl group was introduced at the upper rim of calix[6]arene. It is tempting to speculate that the introduction of an appropriate alkyl substituent covering the calix[6]arene cavity would lead to a stricter inclusion of the hydrophobic part of organic ammonium ions, thus making it possible to construct more specific organic ammonium ion-selective electrodes. To test this speculation, we investigated the effect of the substitution in calix[6]arene on the response to organic ammonium ions systematically in the present study. It was found that a much bulkier substituent covering the calix[6]arene cavity enhanced the recognition of methylammonium or ethylammonium with remarkable suppression from interference by inorganic cations. Notably, the introduction of a 1,1,3,3-tetramethylbutyl group (5) gave the highest selectivity toward methylammonium among various organic ammonium ions and inorganic cations.

2. Experimental

2.1. Reagents

p-1,1,3,3-Tetramethylbutylcalix[6]arene-hexaacetic acid hexaethyl ester (5), *p*-*tert*-butylcalix[6]arene-hexaacetic acid hexaethyl ester (4), *p*-isopropylcalix[6]arene-hexaacetic acid hexaethyl ester (3) and *p*-methylcalix[6]arene-hexaacetic acid hexaethyl ester (2) were synthesized according to procedures similar to ones described previously [10–13]. Methylammonium trifluoromethanesulfonate was synthesized as reported previously [14]. Other chemicals were obtained from commercial sources: amine ionophore I (1) and bis(2-ethylhexyl) sebacate were from Fluka (Buchs, Switzerland); potassium tetrakis

(*p*-chlorophenyl)borate (KTpCIPB) and 2,6,13,16,23,26-tetraoxaheptacyclo[25.4.4.4^{7,12}.4^{17,22}.0^{1,17}.0^{7,12}.0^{17,22}]tritetracontane (TD19C6) were from Dojindo Laboratories (Kumamoto, Japan); nonactin was from Sigma (St. Louis, MO, USA); and poly(vinyl chloride) (PVC) (degree of polymerization, 1020) was from Nacalai Tesque (Kyoto, Japan). All other chemicals were of analytical reagent grade.

2.2. Electrode system

A methylammonium-selective electrode was constructed using PVC-based membranes, as reported previously [9,15,16]. The PVC membranes had the following composition: 1 mg of ionophore, 20 mol% of KTpCIPB relative to the ionophore, 60 μl (55 mg) of bis(2-ethylhexyl) sebacate and 30 mg of PVC. The materials were dissolved in tetrahydrofuran (about 1 ml) and poured into a flat Petri dish (28 mm in diameter). The solvent was then evaporated off at room temperature. The resulting membrane was excised and attached to a PVC tube (4 mm o.d., 3 mm i.d.) with tetrahydrofuran adhesive. The sensor membranes were conditioned overnight in a solution of 10 mM methylamine hydrochloride. The electrochemical cell arrangement was Ag, AgCl/internal solution/sensor membrane/sample solution/1 M NH_4NO_3 (salt bridge)/10 mM KCl/Ag, AgCl. The internal solution was the same as that used to condition the membrane. For comparison, NH_4^+ -selective electrodes were similarly prepared using nonactin or TD19C6 as an ionophore. In this case, the internal solution was 10 mM NH_4Cl . Potential measurements were made with a voltmeter produced by a field-effect transistor operational amplifier (LF356; National Semiconductor, Sunnyvale, CA, USA; input resistance $>10^{12} \Omega$) connected to a recorder. To examine the pH-dependence of the electrode, a miniature pH glass electrode (1826A-06T; Horiba, Kyoto, Japan), together with test and reference electrodes, was immersed in each sample solution to simultaneously measure the solution pH. The volume of the sample solution was 1 ml, because our electrode system was compact, as described previously [16,17].

2.3. Evaluation of the electrode performance

The detection limit was defined as the intersection of the extrapolated linear regions of the calibration graph [9,15,16,18]. The selectivity coefficients of the electrode ($k_{i,j}^{\text{Pot}}$) were determined by a separate solution method [9,15,16,18,19] using respective chloride salts. The values were calculated from the equation,

$$\log k_{i,j}^{\text{Pot}} = \frac{(E_j - E_i)}{S} + \log c_i - \log c_j^{1/z_j}$$

where E_i and E_j represent the emf readings measured for methylammonium and the interfering ion, respectively, S the theoretical slope of the electrode for methylammonium (59.2 mV at 25 °C), c_i and c_j the concentrations of methylammonium and the interfering ion, respectively, and z_j the charge

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