Polysiloxane based CHEMFETs for selective detection of Ca^{2+} ions

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Abstract

Different siloxane copolymers have been used as membrane materials for Ca^{2+} selective chemically modified field effect transistors (CHEMFETs). CHEMFETs with 3-benzoylaminopropyl-functionalized polysiloxane membranes and 1 wt% borate anions are intrinsically selective for Ca^{2+} ions. This selectivity can be further enhanced by the incorporation of a Ca^{2+} selective 1,3 alternate calix[4]arene which is functionalized with four amido groups. The highest Ca^{2+} selectivities were obtained with CHEMFETs containing this calix[4]arene ionophore in 3-cyanopropyl-functionalized polysiloxane membranes. © 1997 Elsevier Science B.V.

Keywords: Siloxane; CHEMFETs; Selective detection; Calcium ions; Calix[4]arene; Ionophores; Membrane materials

1. Introduction

Amido functionalities are known to interact preferentially with hard alkaline earth metal ions like Ca^{2+} [1,2]. Aliphatic molecules containing two amido functionalities have been incorporated as receptor molecules in plasticized PVC membranes of ion-selective electrodes, introducing selectivity for Ca^{2+} in the presence of Na^+ , K^+ , and Mg^{2+} ions [3,4]. Calix[4]arenes are very versatile building blocks for the construction of ion receptors, because besides a high lipophilicity which prevents leakage from the membrane, it provides a three dimensional skeleton to arrange donor ligands in optimal spatial position for ion-binding [5,6]. Calix[4]arenes in the cone conformation functionalized with four amido groups exhibit a high extraction capability for Ca^{2+} ions, but these

molecules have not been used as receptor molecule in ion-selective devices [7,8]. Until now only one Ca^{2+} selective ion-selective electrode is known which is based on a calix[4]arene derivative. However, the calix[4]arene was not substituted with amido groups, but with phosphine oxide groups [9]. Therefore, we have investigated the Ca^{2+} selectivity of a novel 1,3 alternate calix[4]arene, functionalized with two pairs of amido groups in diametrical position at the same face of the molecule in CHEMFETs.

For obtaining durable and selective CHEMFETs, not only the properties of the receptor molecule are important but also these of the polymeric membrane. Membranes which do not need a plasticizer, like polysiloxanes, are more promising than plasticized membranes because in the latter case deterioration of the sensing properties is caused by the slow leaching of the plasticizer [10–12]. Polysiloxanes have the advantage of possessing suitable elastomeric proper-

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ties (glass transition temperature far below room temperature) which makes the addition of a plasticizer superfluous. Ca^{2+} selective ISEs based on polysiloxanes containing a Ca^{2+} receptor were reported, but still a plasticizer was needed in order to enhance the compatibility with the receptor [13]. The polarity of (dimethyl)polysiloxanes can be enhanced by the introduction of polar side chains to the polysiloxane backbone. Following this approach, we have previously developed 3-cyanopropyl-functionalized polysiloxanes which were successfully applied for durable membranes on Na^+ and K^+ selective CHEMFETs [14,15]. Van der Wal et al. [16] have reported the use of silanol terminated polysiloxane membranes containing the Ca^{2+} ionophore ETH 5234 on CHEMFETs. However, a disadvantage of this membrane is the restricted solubility of electroactive components. Recently, we have developed a novel synthesis for polysiloxanes that are functionalized with different polar substituents other than cyanopropyl groups (1), like benzoylaminoethyl (2), acetoxypentyl (3) and (*p*-acetylphenoxy)pentyl groups (4) (see Scheme 1 for structures) [17]. Upon use of these polysiloxanes as membrane material, the polar substituents in the membrane can influence the selectivity of the sensor. For the 3-cyanopropyl-functionalized polysiloxane

membranes, it was shown that these are intrinsically selective for Ag^+ ions, because of the affinity of the cyanopropyl groups for Ag^+ [17]. Therefore, it can be expected that polysiloxanes bearing amido functionalities in the side chain, like 3-benzoylaminoethyl-functionalized polysiloxanes, are intrinsically selective for Ca^{2+} ions.

In this paper, we report a study of the properties of polysiloxanes with different substituents as membrane material for Ca^{2+} selective CHEMFETs. Furthermore, the effect of the incorporation of the novel Ca^{2+} selective 1,3 alternate calix[4]arene receptor on the selectivity of the CHEMFETs was studied.

2. Experimental

2.1. Membranes and materials

Siloxane terpolymers in which $x=10$ mol% for (1), (3), (4) and $x=2.5$ –30 mol% for (2) [17] and the Ca^{2+} selective calix[4]arene derivative (5) [18] were synthesized according to procedures described previously. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone ketyl before use. Potassium tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate

Scheme 1. Structures of (1)–(5).

(KTTFPB) was purchased from Fluka. The alkali and alkaline earth chlorides were of analytical grade (Merck Schuchardt). All solutions were made with deionized, doubly distilled water. The pH 4 buffer was purchased from Yokogawa. 2,2'-Dimethoxy-2-phenylacetophenone used as photoinitiator was obtained from Janssen Chimica.

2.2. Fabrication of CHEMFETs

CHEMFETs were prepared from ISFETs with dimensions of 3×4.5 mm fabricated in the MESA clean room facilities (University of Twente, The Netherlands). Details of modification of the ISFETs with poly(hydroxyethylmethacrylate) hydrogel [poly-HEMA] have been described earlier [19]. The modified ISFETs were mounted on a printed circuit board, wire bonded, and encapsulated with silicone rubber (DOW Corning 3140 RTV). The polyHEMA layer of the CHEMFET was conditioned by immersion in an 0.1 M CaCl₂ solution at pH 4 (Yokogawa buffer) for 2 h. The ion-sensitive membrane was cast by adding 2.5 µl THF solution containing 150 mg of a mixture composed of polysiloxane copolymer, 1.5 mg ionophore, 150 mol% KTTFPB (with respect to the ionophore), and 0.75 mg of photoinitiator per 0.9 ml of THF. These CHEMFETs were placed on a developing plateau under nitrogen atmosphere and left for 20 min at room temperature to evaporate the solvent. Subsequently, the polymer was photo-crosslinked by the exposure for 2 min to UV light (100 W high pressure mercury lamp, Osram Sylvania H44GS-100). After photo-crosslinking, the CHEMFETs were stored overnight under a nitrogen atmosphere.

2.3. CHEMFET measurements

The CHEMFET measurements were carried out as described before and the same experimental setup was used [17]. The potentiometric selectivity coefficients, K_{ij}^{pot} , were determined by the fixed interference method (FIM) [20]. Before starting the measurements, the CHEMFETs were conditioned in an 0.1 M CaCl₂ solution for one night.

3. Results and discussion

The siloxane terpolymers (1), (2), (3) and (4) were evaluated for their applicability as membrane materials in CHEMFETs selective for Ca²⁺ ions. The 3-benzoylaminopropyl-functionalized polysiloxane (2) has been previously examined with a Pb²⁺ selective receptor incorporated for Pb²⁺ selective CHEMFETs [17]. Measurements of CHEMFETs with these membranes showed high interference of Ca²⁺ ions, which was attributed to a specific interaction of Ca²⁺ with the amido carbonyl groups of (2). Therefore, we have first investigated this polysiloxane membrane for its intrinsic selectivity for Ca²⁺ ions. CHEMFETs with polysiloxane membranes containing only 2.5 mol% of 3-benzoylaminopropyl groups and 1 wt% of borate anions (KTTFPB) as lipophilic anionic sites are indeed intrinsically selective for Ca²⁺ ions. This selectivity is further enhanced with increasing percentage of 3-benzoylaminopropyl groups, up to 25 mol%. A further increase in amido moieties to 30 mol% did not further enhance the selectivity (Table 1).

These amido functionalized polysiloxanes are the first examples of membranes with intrinsic selectivity

Table 1

Intrinsic Ca²⁺ selectivity (log $K_{Ca,j}$) and sensitivity (slope, mV decade⁻¹) of CHEMFETs with siloxane terpolymers with different percentages of 3-benzoylaminopropyl groups (2) ^a

Interfering ion, j	Log $K_{Ca,j}$ and slope (mV decade ⁻¹ , given in brackets) ^b			
	PS2.5AM ^c	PS10AM	PS25AM	PS30AM
Na ⁺	-0.7 [27]	-1.5 [29]	-1.7 [29]	-1.7 [29]
K ⁺	-0.8 [26]	-1.4 [30]	-2.0 [30]	-2.0 [31]
Mg ²⁺	-2.6 [31]	-2.8 [31]	-2.9 [29]	-2.9 [30]

^a 1 wt% KTTFPB.

^b Log $K_{Ca,j} \pm 0.1$; slope ± 2 mV decade⁻¹ [Ca²⁺].

^c PS X AM: Siloxane terpolymers substituted with X mol% 3-benzoylaminopropyl groups.

Fig. 1. Response curves of Ca^{2+} selective CHEMFETs with siloxane terpolymer (2) containing 10 mol% of 3-benzoylamino-propyl groups and: ($\blacktriangle$) 1 wt% KTTFPB; ($\blacklozenge$) 1 wt% ionophore (5) and 150 mol% (with respect to the ionophore) KTTFPB, in the presence of 0.1 M KCl.

for Ca^{2+} ions. The Ca^{2+} selectivity of the membrane with 10 mol% of 3-benzoylamino-propyl groups is enhanced by addition of calix[4]arene (5) (Scheme 1) with preorganized amido groups ($\log K_{\text{Ca,K}} = -2.0$, Fig. 1) in the presence of 150 mol% of KTTFPB (with respect to the ionophore) as anionic sites [21]. CHEMFETs with ionophore (5) in the polysiloxane membrane with 25 mol% of benzoylamino-propyl groups gave the same selectivities as those of polysiloxanes with 10 mol% benzoylamino-propyl groups.

Siloxane terpolymers (1), (3), and (4) having 10 mol% of 3-cyanopropyl, 3-acetoxypentyl, and 3-(*p*-acetylphenoxy)propyl groups, respectively, show no intrinsic selectivity for Ca^{2+} . This supports the assumption that interaction of Ca^{2+} with the amido functionalities in (2) introduces the Ca^{2+} selectivity. However, incorporation of ionophore (5) in 3-cyanopropyl (1) or 3-(*p*-acetylphenoxy)propyl (4) functionalized polysiloxane membranes, also yields Ca^{2+} selective CHEMFETs (Table 2). This is not the case for the 3-acetoxypentyl-functionalized polysiloxane membrane (3) which gives noisy responses, due to the limited solubility of (5) in the membrane. The highest Ca^{2+} selectivities are obtained with CHEMFETs with ionophore (5) in 3-cyanopropyl-substituted polysiloxane membranes (1) ($\log K_{\text{Ca,Na}} = -1.9$, $\log K_{\text{Ca,K}} = -2.5$, and $\log K_{\text{Ca,Mg}} = -3.2$, respectively). Therefore, these membranes are the best for Ca^{2+} detection in the presence of relatively high concentrations of interfering ions.

Table 2

Selectivity ($\log K_{\text{Ca,j}}$) and sensitivity (slope, mV decade^{-1}) of Ca^{2+} selective CHEMFETs with ionophore (5) in siloxane terpolymers (1), (2), (3), and (4) having 10 mol% of functionalized substituents^a

Interfering ion, j	Log $K_{\text{Ca,j}}$ and slope (mV decade^{-1} , given in brackets) ^b			
	(1)	(2)	(3)	(4)
Na^+	-1.9 [27]	-1.7 [28]	— ^c	-1.7 [30]
K^+	-2.5 [27]	-2.8 [28]	— ^c	-1.9 [30]
Mg^{2+}	-3.2 [29]	-3.1 [30]	— ^c	-3.1 [30]

^a 1 wt% ionophore (5) and 150 mol% (with respect to the ionophore) KTTFPB.

^b Log $K_{\text{Ca,j}} \pm 0.1$; slope $\pm 2 \text{ mV decade}^{-1}$ [Ca^{2+}].

^c 3-Acetoxypentyl (3) functionalized polysiloxane CHEMFETs do not show linear response upon increase in Ca^{2+} activity, due to the limited solubility of ionophore (5) in the membrane.

4. Conclusions

Siloxane terpolymers (1), (2), and (4) have been successfully applied as membrane material in CHEMFETs for the detection of Ca^{2+} ions. These polysiloxane membranes have the advantage that no plasticizer is necessary, which is an advantage for the development of durable CHEMFETs. 3-Benzoylamino-propyl-functionalized polysiloxane membranes (2) are intrinsically selective for Ca^{2+} ions. This selectivity can be further enhanced by the addition of the Ca^{2+} selective calix [4] arene derivative (5). The highest Ca^{2+} selectivity, however, was observed for CHEMFETs with polysiloxane membranes with 3-cyanopropyl groups (1), incorporating Ca^{2+} selective calix [4] arene (5).

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