

Development of Durable K^+ -Selective Chemically Modified Field Effect Transistors with Functionalized Polysiloxane Membranes

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Durable K^+ -selective chemically modified field effect transistors (CHEMFETs) with functionalized polysiloxane membranes have been developed. Polysiloxane membranes of different polarity, i.e., with different amounts of (cyanopropyl)siloxane groups, incorporating a free or covalently bound hemispherand as the ionophore and free or covalently bound tetraphenylborate anions as ionic sites, were investigated for their performance as sensing membranes. The CHEMFETs based on polysiloxane with both ionophore and anionic site covalently attached to the membrane matrix showed K^+ responses with an almost Nernstian slope in the range of concentration 10^{-4} – 10^{-1} M in the presence of 0.1 M Na^+ ($\log k_{K,Na}^{pot} = -3.2$). Durability tests showed that these sensors respond satisfactorily in the desired range of potassium concentrations even after 10 months of continuous exposure to washing in a stream of tap water.

In our work on the design and synthesis of selective molecular receptors, we have developed sensors based on field effect transistors for K^+ ,¹ Na^+ ,² Ag^+ ,³ some transition metal cations⁴ and anions.⁵ In these sensors, the gate oxide of ion-sensitive field effect transistors (ISFETs) is covered with an ion-selective membrane and an intermediate poly(hydroxyethyl methacrylate) layer (vide infra). In general, good ion selectivity and sensitivity is obtained with plasticized poly-

(vinyl chloride) (PVC) membranes incorporating 1–2 wt % of lipophilic ionophore.

Although the use of plasticized PVC membranes has the major advantage of their easy preparation, ISFETs and ion-selective electrodes using these membranes suffer from serious limitations with respect to lifetime in various applications.⁶ Depending on the conditions, the lifetime can be seriously shortened due to leaching of the plasticizer and the electroactive components, i.e., ionophore and anionic sites, from the membrane to the sample solution. The former feature results in a membrane in which the mobility of the electroactive component is significantly lowered, giving rise to noisy responses, whereas leaching of the electroactive components results in a gradual loss of selectivity and sensitivity. For example, nitrate-selective chemically modified field effect transistors (CHEMFETs)⁵ based on PVC membranes, with 65% (w/w) 2-nitrophenyl octyl ether (NPOE) as plasticizer and 0.1% (w/w) tetra-*n*-octylammonium ions as cationic sites, showed a strong increase of noise after 3 months of exposure to a flow of tap water. Analysis of the membrane composition revealed that the NPOE content had decreased to 58% (w/w). Freshly prepared CHEMFETs with 58% (w/w) NPOE and 0.1% tetra-*n*-octylammonium ions gave similar noisy responses, indicating the importance of the plasticizing properties of the membrane.

Moreover, field effect transistors on which the polymeric sensing membrane is directly cast by physical adsorption onto the hydrophilic gate oxide surface (MEMFETs) suffer from additional problems. As the physical adhesion of the apolar membrane to the polar surface is not very strong, the membrane tends to become detached from the surface as a result of water intrusion between membrane and ISFET surface.^{7,8}

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Various membrane materials with improved adhesion to the gate surface of the ISFET have been investigated like polymerized imide⁹ and butyl methacrylate.¹⁰ However, these membrane materials still need the addition of an external solvent mediator.

Chemical modification of the gate surface and covalent anchoring of the sensing membrane improves the binding of the membrane to the surface. Harrison et al.¹¹ reported the chemical attachment of a carboxylated PVC membrane to the gate surface. In the same way Meyerhoff et al.¹² applied mixtures of hydroxylated PVC and polyurethane to obtain ISFETs with an increased lifetime. An ISFET modified with a styrene membrane matrix containing chemically attached K⁺-selective ionophores, i.e., vinylbenzo-18-crown-6, and di(vinylbenzo)-18-crown-6 was reported by Tietje-Girault.¹³ The device gave a response of 37 mV/decade, but no information was given about the lifetime.

The membranes in the examples described above are directly cast on the ISFET surface and do not possess an internal reference solution, as is the case in ISEs. Carbon dioxide that permeates through the membrane may cause pH changes at the gate oxide-membrane interface, resulting in changes of the surface potential and consequently in an interfering response of the ISFET.¹⁴ Moreover, due to the absence of an internal reference solution between the gate oxide and inner membrane interface, no buffered equilibrium exists between common potential-determining species at this interface. Consequently, it can be expected that in practice MEMFETs will be more sensitive to instability and drift than conventional ISEs.

ARCHITECTURE OF DURABLE CHEMFETS

An important improvement of the stability of membrane-covered ion-sensitive field effect transistors was obtained by the introduction of a poly(hydroxyethyl methacrylate) hydrogel layer (polyHEMA layer) between the field effect transistor surface and the sensing membrane.^{15,16} By conditioning this hydrogel layer in a pH-buffered solution containing the primary cation (K⁺) prior to use of the sensor, the protonation equilibrium at the gate oxide and the ion partition equilibrium at the inner side of the sensing membrane are effectively buffered by the hydrogel, and interference by carbon dioxide is eliminated. Moreover, the hydroxyethyl functionalities of the polyHEMA layer can be utilized for covalent binding of the sensing membrane.¹⁷ This can be realized by methacrylation of the surface layer of the

polyHEMA hydrogel and introduction of methacrylate groups in the sensing membrane. These groups are then linked by photopolymerization. For the sensing membrane of this CHEMFET, materials were chosen with intrinsic elastomeric properties, so that addition of an external solvent mediator is not needed. Polysiloxanes, i.e., Wacker RTV-ME 625, Dow Corning 3140 RTV, and Bayer Silopren, have been shown to possess suitable elastomeric properties in the preparation of potassium-selective CHEMFETs.¹ Therefore, new polysiloxanes with methacrylate side groups were designed and synthesized in order to enable the covalent attachment of the membrane to the polyHEMA layer and to bind appropriately modified electroactive components in the membrane matrix.^{1,18} The new polysiloxanes are terpolymers composed of dimethylsilyl, (cyanopropyl)methylsilyl, and (methacryloxypropyl)methylsilyl units. The dimethylsiloxane backbone gives the polymer a sufficiently low glass transition temperature (T_g), and the incorporation of 2.1–8.7 mol % of (cyanopropyl)methylsiloxane units in the chain makes it possible to modify the polarity of the membrane material. The (methacryloxypropyl)methylsiloxane units (1–1.5 mol %) in the polysiloxane are for cross-linking and covalent binding of methacrylate electroactive components in the membrane matrix and for the covalent attachment of the membrane to the polyHEMA layer. After casting of the polysiloxane membrane on the transistor surface, the methacryloxy function can be easily polymerized by UV irradiation using 2,2'-dimethoxy-2-phenylacetophenone as photoinitiator. This procedure was used for the construction of K⁺-selective CHEMFETs in which the ionophore is covalently anchored in the membrane matrix via the methacryloxy group.¹ The highly elastic properties of the photocrosslinked polysiloxanes give the membranes sufficient resistance to osmotic pressure in the cases where the inner hydrogel solution and sample solution are different in ionic strength. Even after prolonged exposure of the sensors to sample solutions of one decade lower ionic strength, no cracking of the membranes was observed.

In this paper, a study to the development of durable K⁺-selective CHEMFETs with functionalized polysiloxane membranes is presented. Polysiloxane membranes of different polarity, i.e., with different amounts of (cyanopropyl)siloxane groups, incorporating free or covalently bound ionophore and free or covalently bound tetraphenylborate anions as ionic sites were investigated for their performance as sensing membranes. Various ionophore/tetraphenylborate combinations, free and chemically attached to the membrane matrix, were studied in order to reveal the influence of covalent binding of the electroactive components in the membrane on the sensing behavior of the CHEMFET. Except for the fact that the ultimate goal is a durable K⁺-selective CHEMFET¹⁹ in which all electroactive compounds are covalently bound to prevent leaching out of these compounds, the first point of investigation was whether a well-functioning sensor with this modification could be obtained. From a theoretical model describing the membrane potential²⁰ it was concluded that complete immobilization of both ionophore and anionic sites would lead

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Table 1. Composition of the Polysiloxane Monomers in the Reaction Mixture and in the Product^a

siloxane copolymer code	cyanosiloxane		methacrylsiloxane	
	in reaction mixture	in product	in reaction mixture	in product
PS(2.8)CN	2.8	2.1	1.3	1.0
PS(10)CN	10.0	8.7	2.0	1.5

^a Values are in mole percent of the corresponding siloxane unit.

to a decrease of the membrane potential, due to a counteracting diffusion potential. However, the covalent attachment of ionophore and anionic sites to the polymer backbone does not necessarily mean that the mobility in the membrane is completely reduced.

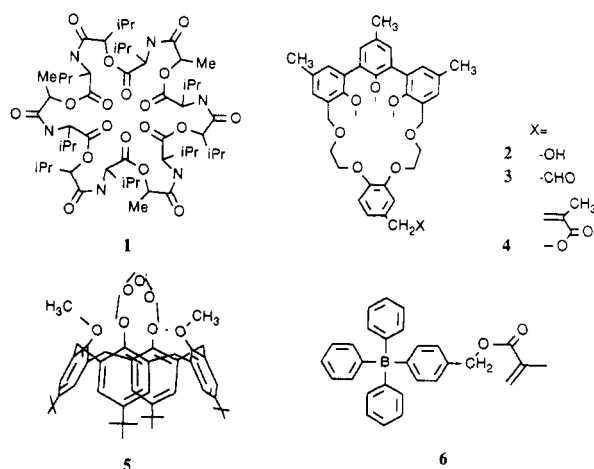
EXPERIMENTAL SECTION

Reagents. The chloride salts of the alkali and alkaline earth metals used were of analytical grade (Merck-Schuchardt), except for sodium and potassium, which were even of higher purity (Suprapur, Merck-Schuchardt). All solutions were made with deionized, doubly distilled water. Buffer pH 4 was purchased from Yokogawa. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone ketyl before use. The nutrition water in which the K⁺ response of the CHEMFETs was measured had the following composition: 30 mM Na⁺, 10 mM Mg²⁺, 10 mM Ca²⁺, 20 mM NO₃⁻, 10 mM SO₄²⁻, 10 mM H₂PO₄⁻/HPO₄²⁻, and 20 mM Cl⁻, pH 4.5.

Valinomycin (**1**) was purchased from Fluka. Ionophores **2–4** (hsphOH (**2**), hsphCHO (**3**), hsphMeth (**4**)) were synthesized according to procedures reported earlier,^{1a} as was dimethoxycalix[4]arene crown ether (**5**).²¹ Potassium tetrakis-[3,5-bis(trifluoromethyl)phenyl]borate (KTFPB) was purchased from Fluka, and potassium triphenyl-4-[[methacryloyloxy)methyl]phenyl]borate (**6**) was synthesized according to known procedures.²² All silane and siloxane reagents were purchased from Petrarch Systems. 2,2'-Dimethoxy-2-phenylacetophenone used as a photoinitiator was obtained from Janssen Chimica. The polysiloxane copolymers were synthesized according to an earlier described procedure.¹⁵ The variation in the ratio of reactants in the preparation of the copolymers is given in Table 1. The amount of (cyanopropyl)-methyl- and (methacryloxypropyl)methylsiloxane in the copolymer was determined by ¹H NMR and elemental analysis.

CHEMFET Fabrication. The ISFETs used in this study have dimensions of 1.2 × 3.0 mm. The SiO₂ gate oxide was thermally grown in an oxygen atmosphere for 10 min at 1150 °C (thickness ~700 Å). Further details of the fabrication are as described previously.^{1a} ISFETs with a silicon dioxide gate were chosen because the modification of SiO₂ surfaces is nowadays well established. For our purposes, the gate of the ISFETs was covered with an intermediate hydrogel layer

Chart 1. Structures of Potassium-Selective Ionophores and the Methacrylated TetraphenylBorate Derivative



of polyHEMA, which was anchored chemically to the gate oxide by the photolithographic procedure described earlier.¹⁵ The polyHEMA layer was covered with the sensing membrane, and the ISFETs thus obtained will be referred to with the acronym CHEMFETs. Subsequently, the CHEMFETs were mounted on a support, a printed circuit board, wire bonded, and encapsulated with silicone rubber (Dow Corning 3140 RTV). The composition of the polysiloxane membranes was as follows: polysiloxane copolymer (98.4 ± 0.2 wt %), ionophore (0.5 ± 0.05 wt %), tetraphenylborate (25 ± 2.5 mol%, with respect to the ionophore), and photoinitiator (1 wt %). This mixture with a total weight of ~100 mg was dissolved in 600 μL of THF. On top of the polyHEMA layer, which was conditioned by immersion in a buffered (pH 4) 0.1 M KCl solution for 3–6 h, 2–3 μL of the polysiloxane membrane solution was cast by means of a micropipet. These CHEMFETs were placed on a developing plate under a nitrogen atmosphere and left for 15–20 min at room temperature in order to evaporate the solvent. Subsequently, the membranes were photocured by exposure for 2.5 min to UV light (100 W high-pressure mercury lamp, Black-Ray B-100A). The CHEMFETs were stored overnight under an atmosphere of nitrogen. Before starting the measurements, the membranes were conditioned in a 0.1 M KCl solution for 2 days.

CHEMFET Measurements. The output signal of the CHEMFETs was measured in a constant drain-current mode ($I_d = 100 \mu A$), with a constant drain-source potential ($V_{ds} = 0.5 V$).²³ This was achieved using a CHEMFET amplifier of the source-drain follower type (Electro Medical Instrumentation, Enschede, The Netherlands). The developed membrane potential was compensated by an equal and opposite potential (ΔV_{gs}) via the reference electrode. A saturated calomel electrode (SCE) was used as a reference, connected to the sample solution via a salt bridge, filled with 1.0 M LiOAc. Ten ISFETs were monitored simultaneously, and the data were collected and analyzed by use of an Apple IIGS microcomputer. Computer-controlled switches followed disconnection of CHEMFETs that showed a too high leakage

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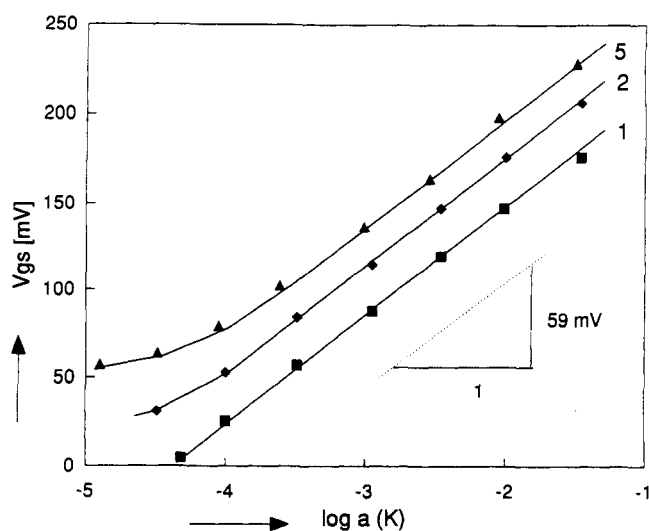


Figure 1. Potassium responses of CHEMFETs in the presence of 0.1 M NaCl. Membranes: 0.5 wt % ionophore 1, 2, or 5 and 25 mol% (with respect to the ionophore) borate (KTTFPB) in polysiloxane with 2.8 wt % of cyanopropoxy units.

current ($I_d \geq 50$ nA). All equipment was placed in a dark and grounded metal box in order to eliminate any effects from static electricity and photosensitivity of the CHEMFETs.

The potentiometric selectivity coefficients, k_{ij}^{pot} , were determined by the fixed interference method (FIM).²⁴ The constant background concentration of the interfering ions was 0.1 M, unless stated otherwise. All concentrations were converted to single-ion activities, and the mean activity coefficient was obtained by the extended Debye-Hückel equation.²⁵ The obtained response curves were analyzed according to the Nicolsky-Eisenman equation.²⁵

RESULTS AND DISCUSSION

The potassium-selective ionophores that have been studied for their sensing properties in polysiloxane membranes are given in Chart 1. The hydrophobic ionophores (2–5) have been synthesized as these compounds have a sufficient K^+/Na^+ selectivity and can be chemically linked to the membrane matrix, which cannot be simply done with valinomycin.

In order to test the suitability of the synthesized polysiloxane copolymers as sensing membranes, we first studied the response behavior of CHEMFETs with these polymeric membranes. The polysiloxane membranes (PS(2.8)CN) contained 0.5 wt % of the ionophore 1, 2, or 5 and 25 mol% (with respect to the ionophore) potassium tetra(*m*-trifluoromethyl)phenylborate (KTTFPB) as anionic sites. As can be seen from the response behavior depicted in Figure 1, all tested ionophores show potassium responses in the presence of a fixed concentration of NaCl (0.1 M) with a Nernstian slope and with selectivity coefficients $\log k_{\text{K,Na}}^{\text{pot}} < -3$.

In Figure 2, the K^+ responses of CHEMFETs based on polysiloxane membranes containing 0.5 wt % ionophore and 0.25 mol% KTTFPB are given. The ionophore is either free (2, 3) or covalently attached to the membrane matrix (4). Membranes with chemically attached ionophore show a

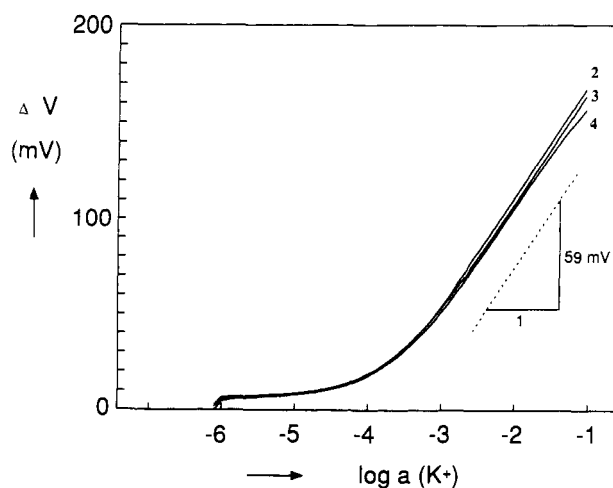


Figure 2. Potassium responses of CHEMFETs based on polysiloxane membranes containing different free 2, free 3, or covalently attached 4 ionophore. Background electrolyte, 0.1 M NaCl. Membranes, see Figure 1.

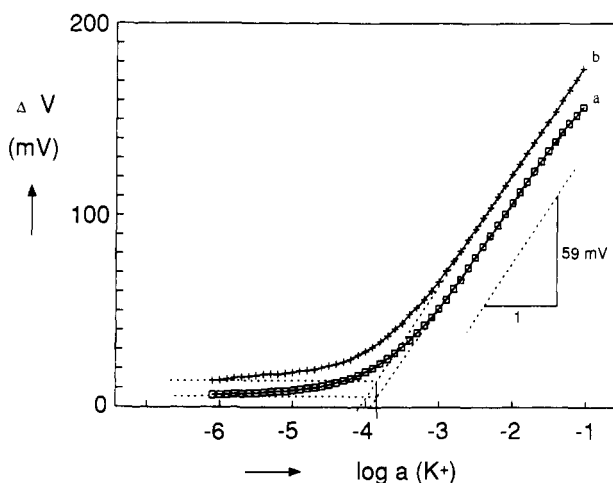


Figure 3. Potassium responses of CHEMFETs based on polysiloxane membranes containing covalently attached ionophore 4 and free (KTTFPB) (line a) or covalently attached 6 (line b) as anionic sites. Background electrolyte, 0.1 M NaCl. Membranes, see Figure 1.

slightly smaller slope of response (56 mV/ $\log a(\text{K}^+)$) but an unchanged K/Na selectivity in comparison to membranes with free ionophore.

In experiments to test the long-term performance of potassium CHEMFETs with covalently attached ionophore 4 and KTTFPB, these sensors show a constant response of ~ 52 mV/decade over a period of 20 weeks when stored in 0.1 M KCl solution. However, during the continuous monitoring of nutrition water in greenhouses, the response deteriorated to ~ 40 mV/decade after 5 weeks of exposure to a continuous flow (3 mL/min).

In order to enhance the lifetime of the sensor, the methacrylate tetraphenylborate 6 was synthesized and applied as covalently bound anionic site by linking it to the polysiloxane membrane matrix during photopolymerization. Figure 3 gives the potassium responses of CHEMFETs with covalently bound ionophore 4 and free KTTFPB and covalently attached borate 6 in the presence of a fixed concentration of NaCl (0.1 M) in the sample solution. It is shown that the chemical attachment of the anionic sites to the polysiloxane membrane has no significant influence on the K/Na selectivity or on the

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Table 2. Long-Term Performance of CHEMFETs with PS10CN Polysiloxane Membranes

ionophore	1	3	4	4
borate	6	6	KTTFPB	6
no. of sensors tested	22	4	16	22
days of exposure	no. of working sensors			
40 ^a	2	3	8	20
60 ^a	1		6	16
75 ^a	1		6	16
115 ^a	1		5	15 ^d
160 ^b			5 ^c	13
230 ^b			4	13

^a Sensors were continuously washed in tap water (flow 25 mL/min).

^b Sensors were continuously washed in tap water (flow 500 mL/min).

^c One sensor showed leakage current. ^d Two sensors showed leakage current.

slope of the response. However, the reproducibility in the fabrication of these CHEMFETs with good sensor properties was unsatisfactory. Generally the yield of good functioning sensors with all components immobilized was only 20%. After deposition of the solution of the membrane components in THF on the CHEMFET surface, the mixture became cloudy upon evaporation of the THF. Optically inspection of the membranes after photopolymerization with a microscope revealed the presence of small particles in the membrane. Apparently the low solubility of the methacrylate borate anion **6** limited the total amount of electroactive components that can be added to the polysiloxane membrane.

Optimization of Membrane Composition. First the polysiloxane membranes with 2.8 wt % of cyanopropylsiloxane groups were tested for their ability to solubilize the potassium receptor molecules and tetraphenylborate salts. Transparent polysiloxane membranes were obtained by reducing the amount of ionophore **2** to 0.2 wt % and that of methacrylate borate **6** to 10 mol%. CHEMFETs based on this composition showed noisy signals due insufficient conductivity of the membrane. It was concluded that increase of the membrane polarity might lead to more stable signals and an improved solubility of charged species such as tetraphenyl borate anions in the polysiloxane prepolymer.

In order to find the optimal polarity of such membranes, CHEMFETs modified with polysiloxane membranes incorporating various mole percents of (cyanopropyl)siloxane groups were investigated. Sensors based on polysiloxane membranes with 10 mol% cyanopropyl groups containing 0.5 wt % methacrylate ionophore **4** and 25 mol% methacrylated borate **6** gave K⁺ responses with a slope of 56–57 mV/decade and a very good selectivity, $\log k_{K,Na}^{pot} = -3.2$. We also tested more polar siloxane terpolymers containing 25 and 50 mol% cyanopropyl groups. In these cases, transparent membranes were obtained with concentrations of electroactive components up to 1 wt % ionophore and 50 mol% methacrylate borate. However, these siloxane terpolymers were not stable during the preparation procedure of the CHEMFETs and polymerized spontaneously before photocuring.

Long-Term Performance Measurements. In order to evaluate the long-term performance of the potassium CHEMFETs with polysiloxanes containing 10 mol % cyanopropyl groups, a number of sensors were prepared with different

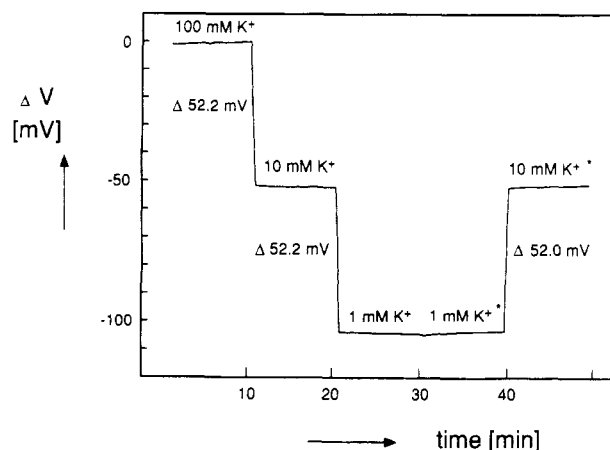


Figure 4. Step potassium response of durable CHEMFETs based on polysiloxane (PS(10)CN) membrane with covalently attached ionophore **4** and covalently attached anionic sites **6**. Measurements were done in flow system in the presence of 0.1 M NaCl at pH 5 and pH 3 (*).

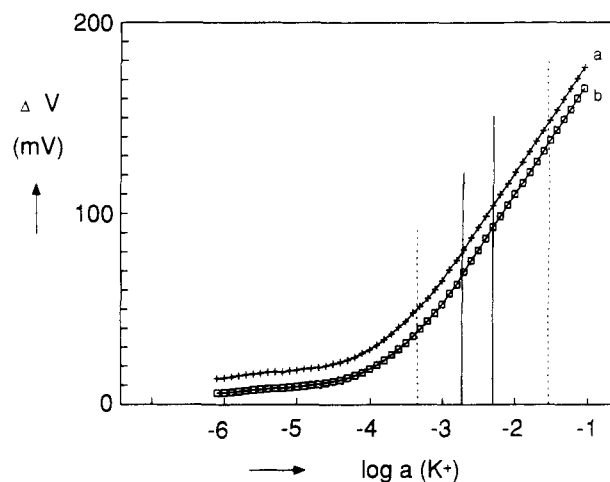


Figure 5. Potassium responses of durable CHEMFETs in an electrolyte mixture containing the maximum concentration of feeding ions. (a) after 40 days of continuous exposure to a flow of nutrition water (25 mL/min); (b) after 115 days. The vertical lines give the maximum (dashed line) and normal (solid line) range of potassium concentration in the nutrition water. Membranes: 0.5 wt % ionophore **4** and 25 mol% (with respect to the ionophore) borate **6** in the polysiloxane with 10 wt % of cyanopropoxy units.

compositions of ionophores and borates. The response of the sensors was verified after the preparation, and only those sensors (67%) which showed responses of at least 50 mV/decade were selected for durability tests. In these tests, sensors were washed continuously in a stream of tap water and their potassium response was measured every 2 weeks by the FIM method (titration curves in 0.1 M CaCl₂ and in 0.1 M NaCl). In Table 2, the state of the sensors during 230 days of continuous washing in tap water is presented. Sensors with free valinomycin (**1**) or ionophore **3** and covalently bound **6** in the membrane lose their response behavior after 40 days of exposure to the water flow. Sensors with covalently bound ionophore **4** and free borate (KTTFPB) also lose their response behavior gradually. However, a considerable amount of the sensors with polysiloxane membranes having both ionophore and anionic sites covalently attached still give a response of at least 52 mV/log *a*(K⁺) even after 230 days of washing in tap water. The responses of these sensors after 230 days is illustrated in Figure 4. Sensors based on plasticized PVC

membranes lose their responses within 25 days under similar circumstances.¹⁹

Sensors with covalently bound ionophore **4** and borate **6** were also tested under conditions applied in horticulture irrigation. The responses of sensors that have been washed for 115 days in a stream of tap water (25 mL/min) were measured in an electrolyte mixture containing the maximum concentration of feeding ions, i.e., 30 mM Na⁺, 10 mM Mg²⁺, 10 mM Ca²⁺, 20 mM NO₃⁻, 10 mM SO₄²⁻, 10 mM H₂PO₄⁻/HPO₄²⁻, and 20 mM Cl⁻. The variable range of K⁺ concentration in the feeding electrolyte that has to be monitored and the responses of sensors in this range are displayed in Figure 5. CHEMFETs respond with an almost Nernstian

slope in the desired range of potassium concentration in the feeding solution.

In order to accelerate the ageing process of the sensors under investigation, we increased the flow of tap water from 25 to 500 mL/min. This procedure was used as a simple simulation of real sensor treatment in environmental and process monitoring. Even after 10 months of continuous washing, the CHEMFETs based on the polysiloxane with both ionophore and anionic site covalently attached to the membrane matrix showed K⁺ responses with good selectivity.

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