

Influence of plasticizer on the selectivity of nitrate-sensitive CHEMFETs

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Abstract

By chemical modification of an ion-sensitive field-effect transistor, a sensor (CHEMFET) has been developed whose sensitivity for nitrate has been tested. A plasticized poly(vinyl chloride) (PVC) membrane, which contains lipophilic tetra-*n*-octyl-ammonium ions, is responsible for the nitrate sensitivity of the device. This membrane has been attached physically on top of a pH-buffered hydrogel, which itself has been attached covalently to the gate oxide of the field-effect transistor. The influence of the plasticizer in the PVC membrane on the selectivity pattern of the CHEMFET for the detection of nitrate has been investigated.

Introduction

Selective sensors for (an)ions are of great interest in view of their potential applications in, e.g., clinical analysis [1], analytical chemistry [2], process control [3] and agriculture [4]. Different ion sensors, based on optical [5], amperometric [6] and potentiometric principles, are currently being investigated. Potentiometric sensors can be ion-selective electrodes (ISEs) [7], ion-sensitive field-effect transistors (ISFETs) [8] or coated wire electrodes [9].

Chemical modification of ISFETs [10] enables ion activities of species other than H^+/OH^- to be measured. This can be achieved by placing an ion-sensitive membrane on top of the gate oxide (silicon oxide) whose membrane potential is modulated by the activity of a specific ionic species in solution. This membrane potential determines the source-drain current in the channel of the semiconductor (p-doped silicon). A pH-buffered (slightly acidic) hydrogel inserted between the gate oxide and the sensing membrane eliminates CO_2 interference and serves as a reference electrolyte by keeping the inner boundary potential constant [11, 12] (see Fig. 1).

Immobilized or lipophilic ionic sites present in these membranes introduce sensitivity for mobile counter ions. Differences in partition coefficients of the hydrophilic counter ions between the membrane and aqueous phase determine the membrane's intrinsic selectivity. For anion-sensitive membranes containing positively charged

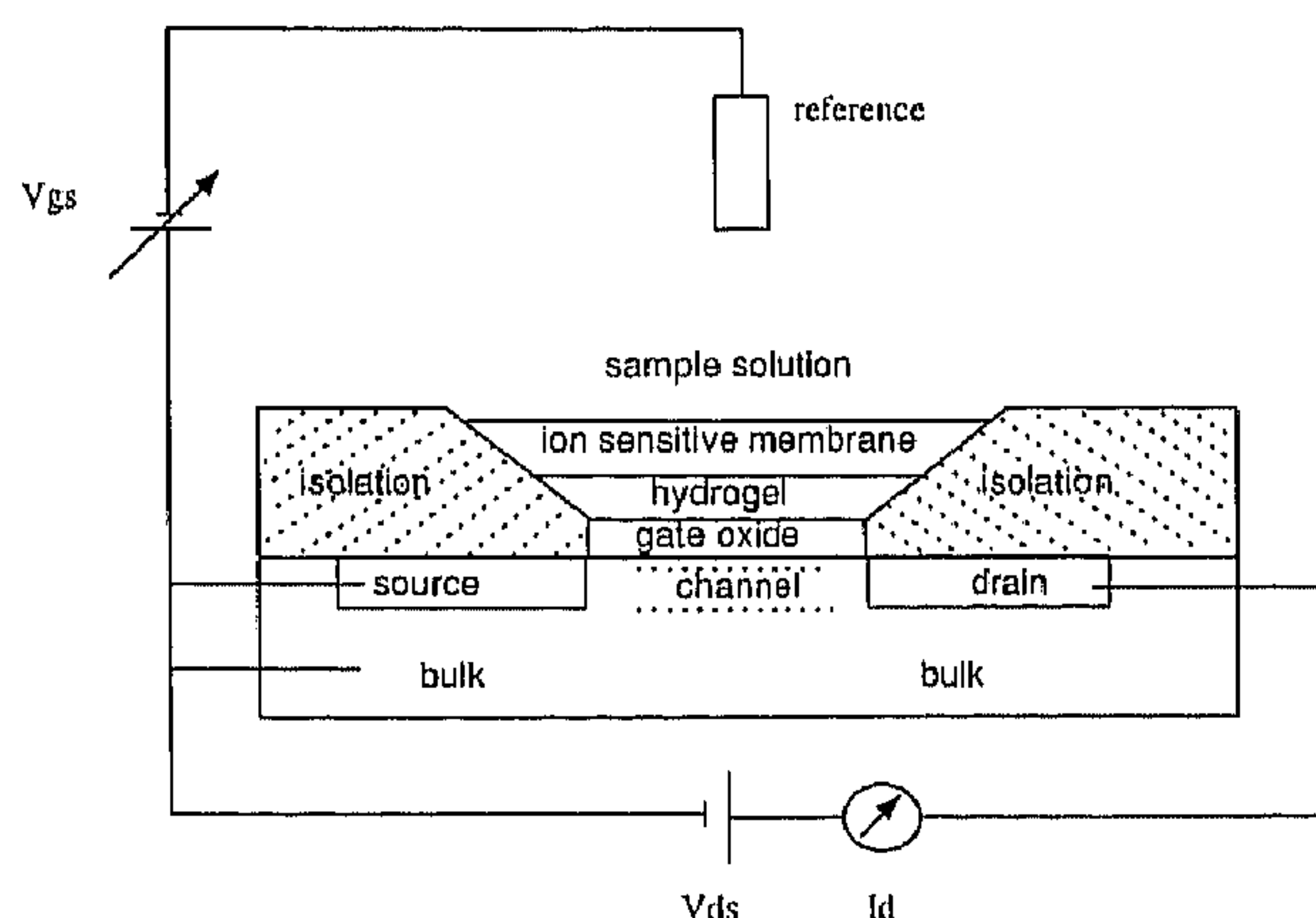
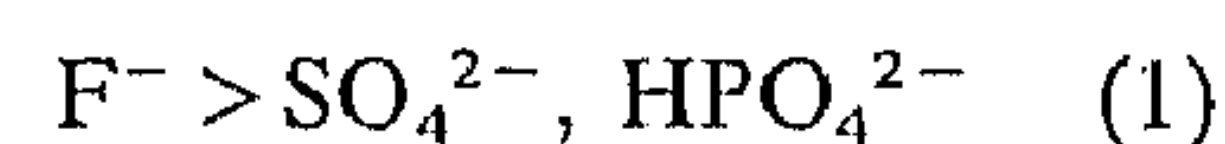


Fig. 1. Cross section of a CHEMFET.

ionic sites, an overview of the selectivity pattern is given by the Hofmeister series



which is reversely related to the hydration energies of the anions [13, 14].

Essential for the functioning of an ion-selective membrane in a potentiometric sensor is the fact that the activity of the primary ion in the membrane phase is not dependent on the activity of this ion in the sample solution. Effective buffering of the primary ion in the membrane phase can be achieved, either by addition of a suitable ionophore [15, 16] or by avoiding (more lipophilic) interfering ions. If this demand is fulfilled, an electric boundary potential is established by which

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the thermodynamic equilibrium between aqueous and membrane phases is maintained and which is logarithmically dependent on the activity of the primary ion in the solution.

Although the Hofmeister series gives a fairly qualitative indication of the intrinsic selectivity of anion-sensitive membranes, the solvation behaviour of the plasticizer in the membrane ($\approx 65\%$ w/w) is thereby neglected. Differences in the free energy of solvation of anions in the aqueous phase and the membrane phase are given by the free energy of transfer of anions from the aqueous to the membrane phase and determine the partition of anions for the two phases. Since the selectivity of the membrane is determined by the partition of the interfering ions in the membrane phase, it can be expected that the dielectric constant ϵ_r of the plasticizer in the membrane may play an important role.

Ion selectivity is commonly obtained by using sensing membranes based on poly(vinyl) chloride (PVC) with a plasticizer [17, 18], polypyrrole [19], liquid membranes [20] or solid-state membranes based on insoluble salts, e.g., AgI/Ag₂S [21]. For the potentiometric nitrate sensors described so far, membrane selectivity is based upon the relatively large lipophilicity of the nitrate ion [22–24]. However, only little is known about the dependence of the intrinsic selectivity on the nature of the plasticizer in membranes, although differences in selectivity have been reported for some liquid membrane systems [25a, 26]. Usually these additives are primarily used for their plasticizing properties. Ryba and Petr nek showed for a series of Ca²⁺-selective electrodes that the influence of the plasticizer can be considerable [27]. It appeared that the selectivity of Ca²⁺ over Li⁺ varies by a factor of 30 depending on the dielectric constant of the plasticizer.

From studies dealing with the influence of the nature of lipophilic cationic groups added to anion-sensitive membranes, it was concluded that symmetrical long-chain tetra-alkyl ammonium salts give best nitrate selectivity [7, 15, 28]. However, the effect of the plasticizer in PVC membranes has not been studied systematically. Therefore we have investigated the influence of plasticizers (and their dielectric constant) on the selectivity of nitrate-sensitive CHEMFETs. The results were compared with literature data for the free energies of transfer of anions from water to different organic solvents.

Experimental

All sodium salts used were of p.a. grade and were purchased from Janssen Chimica. Other chemicals, of p.a. grade, were purchased from Fluka and were used

as such unless otherwise stated. Tetrahydrofuran (THF) was distilled under a nitrogen atmosphere over sodium/benzophenone. ISFETs [29] with a poly(2-hydroxyethyl methacrylate) (polyHEMA) hydrogel were obtained from the MESA Laboratories of the University of Twente.

Membrane solutions were prepared by dissolving ≈ 7 mg of tetra-n-octylammonium bromide, 100 mg of PVC (high molecular weight) and 200 mg of plasticizer in 2 ml of THF. The hydrogel (polyHEMA) of the ISFETs was conditioned for at least 16 h with a pH-buffered solution (pH 4.01, Yokogawa) containing 0.1 M NaNO₃. Onto the conditioned polyHEMA was brought $\approx 25 \mu\text{l}$ of the membrane solution, which spread out over the whole ISFET. The THF was allowed to evaporate for 8–10 h, after which the CHEMFETs were conditioned in a 0.1 M NaNO₃ solution for at least 16 h in order to allow the exchange of the bromide ions in the membrane for nitrate ions. The response of the CHEMFETs was measured with a source and drain follower-type ISFET amplifier in a constant drain-current mode ($I_d = 100 \mu\text{A}$), with a constant drain-source potential ($V_{ds} = 0.5 \text{ V}$). The reference electrode was a calomel electrode in a salt bridge containing 0.3 M NaCl and 0.7 M NaOAc.

For the determination of the anion (nitrate) selectivity, the CHEMFETs were placed in a sample solution containing the interfering anion, which was titrated with a solution of NaNO₃. Titrations were controlled and carried out automatically by an Apple 2GS computer, as was the collection of data. Selectivity coefficients were determined by using the fixed interference method with a fixed concentration (0.1 M) of interfering anion as the sodium salt and a variable concentration of the nitrate anion in the range 10^{-6} – 10^{-1} M.

Results and discussion

Table 1 gives the free energies of transfer of selected anions from water to some organic solvents. The anions have an increasing ranking in the Hofmeister series and the solvents differ in hydrogen-bond-donating properties and in dielectric constant. The free energies of transfer to the alcohols are considerably lower than those of the non-hydroxylic solvents, especially for the more hydrophilic anions such as F[−] and Cl[−]. Comparison of the free energies of transfer to the non-hydroxylic solvents shows as a general trend that the free energy of transfer increases as the dielectric constant ϵ_r decreases. Qualitatively, the order of free energies of transfer for the anions is in agreement with the Hofmeister series. However, quantitatively the absolute magnitude and difference in free energies of transfer are much smaller than the hydration energies.

TABLE 1. Free energy of transfer (water to solvent), in kJ mol⁻¹^a

Anion	Solvent						$\Delta H_{\text{hydr.}}$ 78
	MeOH $\epsilon_r=32.7$	EtOH 24.6	DMSO 46.7	MeCN 37.5	PhNO ₂ 34.8	1,2DCIE 10.4	
ClO ₄ ⁻	6	10	-1	2	8	17 ^b	-214
I ⁻	7	13	10	17	19	26 ^b	-283
NO ₃ ⁻	13	14		21	24	34 ^b	-306
Br ⁻	11	18	27	37	29	39	-321
Cl ⁻	13	20	40	42	35	52	-347
F ⁻	17 ^c	26 ^c	73 ^c	70 ^c	70 ^c	65 ^c	-472

MeOH=methanol, EtOH=ethanol, DMSO=dimethylsulfoxide, MeCN=acetonitrile, PhNO₂=nitrobenzene, 1,2 DCIE=1,2 dichloroethane, $\Delta H_{\text{hydr.}}$ =hydration energy. Data from: ^aref. 30; ^bref. 31; ^cref. 32, ^dref. 33.

This clearly indicates that the Hofmeister series does not give a good estimation of the partition coefficients of anions between aqueous and organic phases.

Since the free energy of transfer of an anion is dependent on the solvent, which for a CHEMFET means on the solvation properties of the membrane, it should be expected that the sensitivity of the device will be influenced by the composition of the membrane material. Therefore, we have studied the anion selectivity of PVC-modified CHEMFETs with four different plasticizers. The selectivity coefficients for the nitrate ion in the presence of 0.1 M of different interfering anions are presented in Table 2. Qualitatively the selectivity patterns for the anions obtained from the CHEMFETs with the four different plasticizers in the membrane are in agreement with the Hofmeister series. The selectivity coefficients, determined with the fixed interference method using the Nicolsky equation [25b], show that the selectivity for nitrate over other anions, especially divalent anions, is very good ($\log K_{\text{NO}_3, X} \leq -3.5$). For all plasticizers used the selectivity for nitrate over chloride ($\log K_{\text{NO}_3, \text{Cl}} = -2.5$) is the lowest, because chloride is the least hydrophilic anion in this series. A more detailed examination of the data in Table 2 reveals that qualitative deviations from the

Hofmeister series occur. Trioctylphosphate (TOP) induces a very high selectivity of nitrate over sulfate and carbonate ($\log K_{\text{NO}_3, X} \leq -4.1$). For practical applications this means that in solutions containing only these interfering anions, the detection limit for NO₃⁻, which is approximately 3.2×10^{-5} M for pure solutions, is not affected. CHEMFETs based on 2-nitrophenyl-octyl ether (NPOE)-plasticized membranes show a lower selectivity for nitrate over other anions, except chloride. The selectivity is reduced by a factor of five in comparison with the TOP-based membranes.

From the data given in Table 1 and the results reported by Ryba and Petr nek [27], it was expected that the selectivity pattern for PVC membranes with the low polar plasticizers dioctylsebacate (DOS) and TOP would differ from that of membranes containing the polar plasticizers NPOE and 2-fluorophenyl-2-nitrophenyl ether (FPNPE). However, our results show that no direct correlation exists between the bulk dielectric constant and the selectivity pattern. Remarkably, the selectivity of CHEMFETs based on FPNPE-plasticized membranes (highest ϵ_r) is almost identical with that of CHEMFETs based on DOS-plasticized membranes (lowest ϵ_r). Nevertheless, it is obvious from our data that the type of plasticizer has significant effects

TABLE 2. Potentiometric selectivity coefficients^a and slope^b of nitrate-selective CHEMFETs

Interfering anion	Plasticizer			
	DOS $\epsilon_r=3.88^c$	TOP 4.90 ^c	NPOE 24 ^d	FPNPE 50 ^d
Cl ⁻	-2.4 ^a (-56) ^b	-2.5 (-52)	-2.5 (-60)	-2.5 (-59)
SO ₄ ²⁻	-3.5 (-57)	-4.1 (-57)	-3.5 (-58)	-3.8 (-58)
H ₂ PO ₄ ⁻	-3.2 (-57)	-2.8 (-56)	-2.3 (-56)	-3.2 (-57)
HPO ₄ ²⁻	-3.6 (-55)	-3.5 (-56)	-3.1 (-57)	-3.6 (-56)
HCO ₃ ⁻	-3.2 (-57)	-3.2 (-57)	-2.6 (-60)	-3.2 (-58)
CO ₃ ²⁻	-3.6 (-57)	-4.1 (-57)	-3.3 (-59)	-3.7 (-60)

DOS: dioctylsebacate, TOP: trioctylphosphate, NPOE: 2-nitrophenyl octyl ether, FPNPE: 2-fluorophenyl 2-nitrophenyl ether. ^a $\log K_{\text{NO}_3, X}$. ^bSlope in mV (± 2 mV) decade⁻¹ [NO₃⁻]. ^cData from ref. 34. ^dData from ref. 26.

on the selectivity of the sensor. Therefore the choice of a suitable plasticizer should depend on the anion to be detected and the interfering anions present.

Although the nature of the PVC plasticizer influences the selectivity of the nitrate sensor, other parameters like slope, drift and noise level are hardly or not at all influenced. All slopes are Nernstian or near-Nernstian within the accuracy of measurement (± 2 mV decade⁻¹ [NO₃⁻]). There are no indications that noise and/or drift contribute to the observed signal. No deterioration could be observed in any sensor examined during the period of the measurements, approximately one month.

Conclusions

In this paper we have demonstrated that for nitrate-sensitive CHEMFETs, based on plasticized PVC membranes, the plasticizer has a distinct effect on the selectivity. For a nitrate-selective CHEMFET the most suitable plasticizer is TOP, whereas NPOE appeared to be the least suitable. However, for CHEMFETs which have to be selective for anions other than nitrate this is not necessarily the case. In that case selectivity over the nitrate ion has to be introduced by a suitable anion-selective ionophore in the membrane and the plasticizer of choice in such a system seems to be NPOE, being the one with the lowest intrinsic selectivity for interfering nitrate ions.

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