

Carriers for chemical sensors: Design features of optical sensors (optodes) based on selective chromoionophores

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Abstract - Macrocyclic and non-macrocyclic ion-selective carriers containing structural elements that heavily change their optical properties in the UV / VIS region upon ion complexation have been introduced earlier as chromoionophores and fluoroionophores, respectively. Here we present different membrane morphologies resulting in a successful design of corresponding sensor membranes with an optical transduction of chemical signals, i.e. for optical measurements of concentrations resp. activities. Workable examples of novel optodes based on chromoionophores are presented, and their response behavior is discussed in more detail.

INTRODUCTION

Membrane-active ion-complexing and -transporting agents, such as mobile ion carriers, that drastically change their optical properties in the ultraviolet and visible region upon complexation were earlier introduced as chromoionophores [1] and fluoroionophores [2], respectively. Since such lipophilic ligands can be tailored to exhibit extremely high ion selectivities [3,4], they must be considered as very promising candidates for the development of a novel class of optical sensors (optodes [5]; for a review, see [6-16]). So far, however, they have been applied only as membrane components in potentiometric sensors (ion-selective electrodes).

Here we report on some principles and design features of optodes based on lipophilic chromoionophores, and we present prototypes of such sensor systems.

DESIGN FEATURES OF A NOVEL CLASS OF OPTODES

Ionophores, especially electrically neutral carriers, have been widely used in ion-selective membrane electrodes for potentiometric determinations of cation or anion activities. The first representatives have been macrocyclic molecules but nonmacrocyclic ionophores may exhibit even superior membrane properties [3] (for a review, see [3,4,17,18]). They induce a membrane potential response which is related to the equilibrium distribution of the selected ions between the bulk of the membrane and the contacting aqueous solutions. Ideally, such membrane electrode half-cells therefore respond reversibly to single-ion activities according to the Nernst equation [3,18-20]. It was shown for valinomycin-containing plasticized PVC membranes that only a small percentage of the carriers is usually complexed [19-21]. Furthermore, the concentration of cation/carrier complexes in such membranes appears to be roughly constant and predetermined by the content of anionic sites (probably mainly immobilized impurities) existing in the polymeric material [21-29].

From the above-mentioned findings it becomes clear that entirely analogous membranes with electrically neutral chromoionophores (or fluoroionophores) are not directly applicable as active constituents of reversibly responding optical sensors. First, such attempts would obviously fail since the extent of complexation in the membrane phase - and hence the resulting optical signal - is either too small and/or even nearly independent of the sample solution contacting the membrane.

For any sensor system using an ionophore-based bulk membrane it must a priori be taken into account that sample dependent variations of complex formation in the electroneutral membrane phase can be realized only by the following two processes:

- 1) Simultaneous coextraction of cations and anions or extraction of electrically neutral ionogenic species from the sample into the membrane, and/or
- 2) Simultaneous ion-exchange of cations or of anions (or of corresponding ionogenic species) between the sample and the membrane.

For case 1) an ideally working membrane optode can thus at best respond to products of cation and anion activities in the sample (i.e., to salt activities or activities of neutral ionogenic species), whereas for case 2) the response can at best be related to ratios of cation or anion activities. This is in clear contrast to the response behavior of an analogous ion-selective membrane electrode responding to single ion activities [3,18-20].

Furthermore, electrically neutral ionophores are, as a rule, relatively weak complex formers. This is a prerequisite for their fast and reversible ion-binding [30], and it also explains the low ion-extraction capability found for unmodified carrier membranes. Accordingly, an extension of the dynamic response range, as expected for optodes based on chromoionophores, can be achieved only by adequate modifications of the membrane composition. In the present contribution, the following modified membrane systems are described:

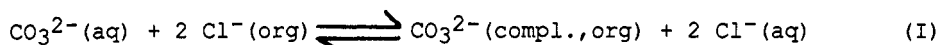
- 1) Combination of a cation-selective and an anion-selective neutral carrier in a membrane (coextraction; cotransport) of which at least one is a chromoionophore, and/or
- 2a) Combination of a cation-selective neutral carrier with a negatively charged ligand or cation exchanger in a membrane (and vice versa for anion-exchanger systems) of which at least one is a chromoionophore (ion exchange; countertransport), or
- 2b) Combination of two different cation-selective neutral carriers in a membrane with negatively charged sites (and vice versa for anion-exchanger systems) of which carriers at least one is a chromoionophore (ion exchange; countertransport).

In both cases, it may be preferable or even essential for an optimized response behavior that interfering effects by the endogenic ionic sites confined to the polymeric material be carefully outbalanced.

Coextraction membranes of the type 1) would also be capable of mediating a cotransport of ions, whereas the modified ion-exchange membranes given by system 2) would exhibit a facilitated countertransport of ions [31,32]. In membranes for optical sensors, however, the ion-extraction properties rather than the ion-transport properties of the chromoionophores are of primary relevance. A version of a sensing device of type 2a) utilizing electrically neutral ionophores for cations and cation exchangers as indicators has been suggested recently [33] for an assay of these cations in a hydrogen ion buffered sample.

NOVEL OPTODES BASED ON CHROMOIONOPHORES

Recently, we reported the synthesis of electrically neutral chromoionophores with anion selectivity [34]. These ligands as well as structurally related ionophores exhibit a remarkably high preference of carbonate ion over other anions in potentiometric membrane electrodes [35-38]. A corresponding optical membrane sensor, conforming to a modified ion-exchanger system of type 2a), was realized by combining in a solvent polymeric membrane a carbonate-selective neutral chromoionophore [39] with methyltridodecylammonium chloride as anion exchanger. Such a membrane is expected to favour the following ion-exchange reaction:



Accordingly, this optode should in principle yield an optical response as a

function of the activity ratio $a_{\text{CO}_3}/(a_{\text{Cl}})^2$ in the aqueous sample solution. Assuming a thermodynamic distribution equilibrium for the ionic species (distribution coefficients k_{Cl} and k_{CO_3}) between the bulks of aqueous and organic phase, the formation of 1:2 complexes (stability constant β_2) between CO_3^{2-} and the chromoionophore C, and constant total concentrations of chromoionophores ($c_{\text{C,tot}}$) and of quaternary ammonium ions ($c_{\text{Q,tot}}$) in the electroneutral membrane, we obtain the relationship [40]:

$$\frac{1 - \alpha}{2 c_{\text{C,tot}} (c_{\text{Q,tot}} - (1 - \alpha) c_{\text{C,tot}})^2 \alpha^2} = \frac{K a_{\text{CO}_3}}{(a_{\text{Cl}})^2} \quad (1)$$

where α is the relative concentration of uncomplexed chromoionophores, and K is the overall equilibrium constant of the basic ion-exchange reaction (I):

$$\alpha = \frac{c_{\text{C}}}{c_{\text{C,tot}}} \quad (2)$$

$$K = \frac{\beta_2 k_{\text{CO}_3}}{(k_{\text{Cl}})^2} \quad (3)$$

Equation (1) allows determination of the quantity α as a function of the sample activity ratio α which is relevant for the optical response, i.e. for the absorbance A at a given wavelength:

$$A = A_1 \cdot \alpha + A_0 \cdot (1 - \alpha) \quad (4)$$

where A_1 and A_0 are the limiting absorbance values for $\alpha = 1$ and $\alpha = 0$, respectively. Figure 1 demonstrates very convincingly that such an optical transduction of the chemical recognition process was indeed realized in practice. The absorbance at 298 nm of the uncomplexed chromoionophore is found to decrease with increasing value of $a_{\text{CO}_3}/(a_{\text{Cl}})^2$. The solid curve interconnecting the experimental points in Figure 1 was fitted according to Equations (1) and (4). The perfect fit is clear evidence for a reversible, theoretical response of the present optode (more details will be given elsewhere [40, 41]).

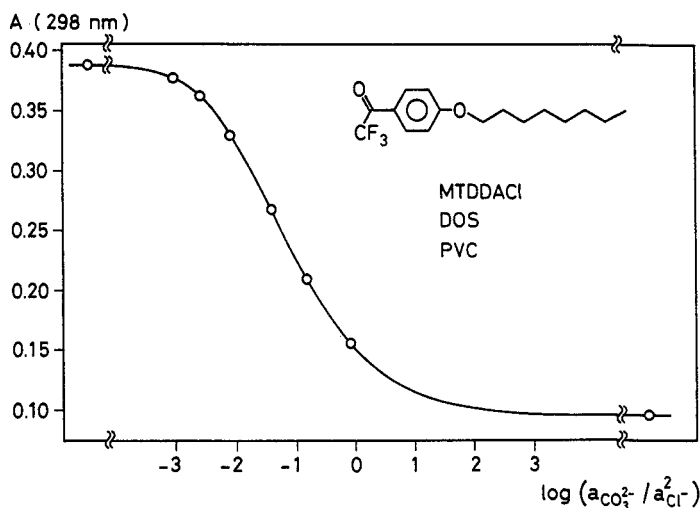


Figure 1 Absorbance-response at 298 nm of an optode membrane based on a carbonate-selective chromoionophore in combination with a liquid anion-exchanger in the chloride form (ion-exchange system I). The activity ratio $a_{\text{CO}_3}/(a_{\text{Cl}})^2$ in the aqueous sample solution was varied. The curve interconnecting the experimental points was calculated from Equations (1) and (4) using $c_{\text{C,tot}} = 0.040\text{M}$, $c_{\text{Q,tot}} = 0.112\text{M}$, and $K = 10^{4.65}$ [40,41].

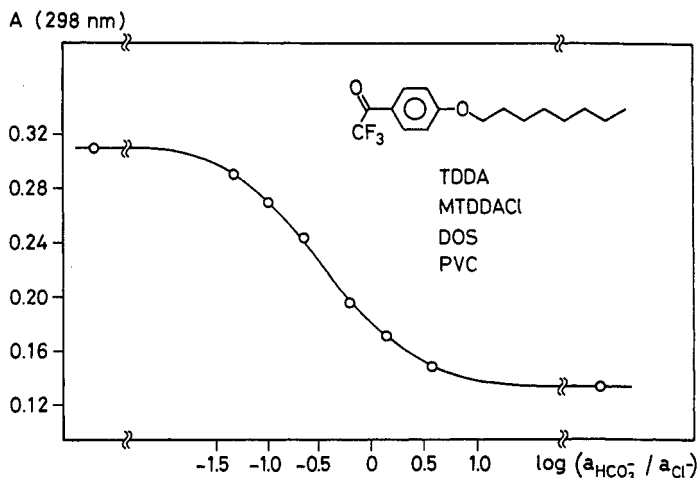
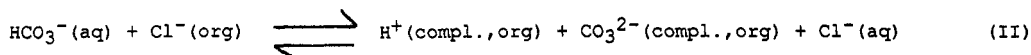


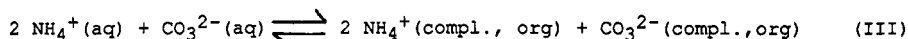
Figure 2 Absorbance-response at 298 nm of an optode membrane based on a carbonate-selective chromoionophore in combination with a hydrogen-ion-selective ionophore and with a liquid anion-exchanger in the chloride form (ion exchange/coextraction system II). The experimental points are given as a function of the activity ratio $a_{\text{HCO}_3^-}/a_{\text{Cl}^-}$ [41].

A slightly modified membrane optode contains the same chromoionophore and the same anion exchanger but, in addition, an electrically neutral ionophore for hydrogen ion (tridodecylamine). The underlying principle is the anion-exchange reaction:



This would correspond to a case intermediate between a coextraction system 1) and a pure ion-exchange system 2a), and the optical response should depend on the activity ratio $a_{\text{HCO}_3^-}/a_{\text{Cl}^-}$ in the sample solution. Figure 2 shows the response curve obtained for this optical sensing device. Such optodes are of considerable interest for biomedical applications.

The attempts to realize a workable optode membrane of the type 1) that directly responds to CO_2 (resp. H_2CO_3) as ionogenic substrate were not successful so far. However, another example of a coextraction system was accomplished by combining carbonate-selective chromoionophores and ammonium-selective macrotetrolides in the same membrane. The optical response of this sensor type is evidently governed by the extraction/complexation equilibrium:



and the pivotal chemical property sensed is the activity product $(a_{\text{NH}_4^+})^2 \cdot a_{\text{CO}_3^{2-}}$. Figure 3 shows the absorbance at 261 nm of such a membrane in contact with ammonium carbonate solutions of different concentrations. Membranes of this type are highly attractive as transducing components in a wide range of novel optical biosensors.

A variety of cation-sensitive optodes is likely to be realized by combination of conventional neutral carriers for selected cations with appropriate chromoionophores selective for hydrogen ions or other cations. Obviously, analogous anion-selective optodes will be at hand. Work aiming at such new developments is in full progress.

EXPERIMENTAL

Reagents

All electrolyte solutions were prepared with doubly quartz distilled water. NaCl and NaHCO_3 (p.a. grade) were obtained from E. Merck, Darmstadt, FRG, ammonium carbamate and tris(hydroxymethyl)aminomethane (puriss.) from Fluka AG, Buchs, Switzerland.

For systems I and II the sample solutions were mixed solutions containing different $\text{NaHCO}_3 / \text{NaCl}$ ratios at a constant ionic strength ($I = 0.106 \text{ M}$).

The samples were buffered with a 5 mM tris(hydroxymethyl)aminomethane (Tris) buffering solution adjusted to pH 7.3 with H_2SO_4 .

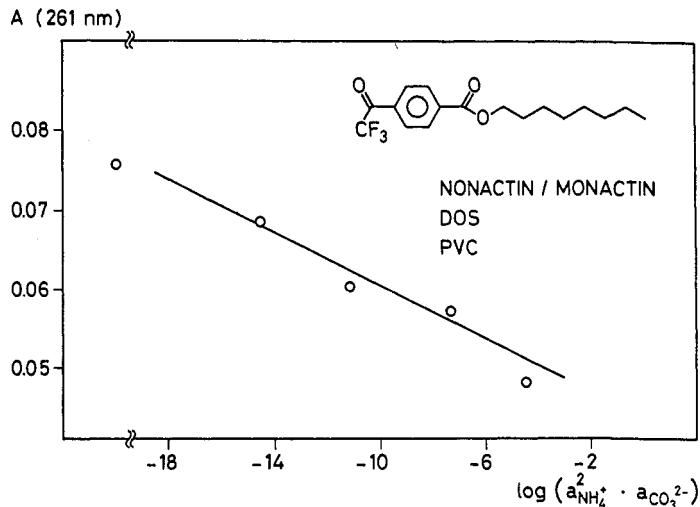


Figure 3 Absorbance-response at 261 nm of an optode membrane based on a carbonate-selective chromoionophore in combination with the ammonium-selective ionophore mixture nonactin/monactin (coextraction system III). The experimental points are given as a function of the activity product $(a_{\text{NH}_4^+})^2 \cdot a_{\text{CO}_3^{2-}}$ [41].

For the salt extraction system III the sample solutions containing ammonium and carbonate ions were prepared by dissolving varying ammonium carbamate concentrations (10^{-4} , 10^{-3} , 10^{-2} and 10^{-1} M) in the same pH - buffer. Hydration of carbamate and formation of bicarbonate ions causes a pH - increase.

For membrane preparation, poly(vinyl chloride) (PVC high molecular), the plasticizer bis(2-ethylhexyl)sebacate (DOS), tetrahydrofuran (THF, puriss., distilled before use), tridodecylamine (TDDA), and nonactin/monactin were obtained from Fluka AG, Buchs, Switzerland.

Tridodecylmethylammonium chloride (TDMACl) was obtained from Polysciences, Inc. (Warrington, PA).

The ionophores 1-heptyloxycarbonyl-4-trifluoroacetylbenzene (ETH 6010) and 1-octyloxy-4-trifluoroacetylbenzene (ETH 6011) were synthesized as described elsewhere [34,39], and the additive tetradodecylammonium tetrakis(p-chloro-phenyl)borate (ETH 500) was prepared according to [42].

Membrane preparation

The optode membranes of the anion-exchange system I contained 3 mg of ETH 6011, 8 mg of TDMACl, 39.6 mg of PVC and 74 mg of the plasticizer DOS. For reducing the response time a small amount of TDDA (0.4 mg) was also added. The optode membranes of the system II contained 3 mg of ETH 6011, 3.8 mg of TDDA, 4 mg of TDMACl, 40.2 mg of PVC and 74 mg of DOS. The optode membranes of the extraction system III contained 5 mg of ETH 6010, 11.5 mg of nonactin/monactin, 37 mg of PVC, 1.5 mg of ETH 500, and 70 mg of DOS.

The membrane components were dissolved in 25ml freshly distilled tetrahydrofuran (THF). 0.5 ml of this solution were then poured on a dust-free glass plate of 35 mm diameter (Herasil quartz glass, W. Möller AG, Zürich, Switzerland), which was placed in a saturated THF - atmosphere. After about 5 h the glass plate with the PVC membrane was removed and stored at air during half an hour for further drying.

Apparatus

UV absorbance measurements and spectra of the PVC membranes were taken using a flow-through cell in a UVIKON Model 810 (Kontron AG, Zürich) double-beam spectrophotometer.

UV absorption experiments

Two glass plates with identical membranes of about $2\mu\text{m}$ thickness were mounted into the measuring cell. The reference cell contained two glass plates without membranes. The solutions of the measuring and the reference cell were changed from outside of the spectrophotometer.

The absorbance measurements were made at a fixed wavelength of 261nm (ETH1010) and 298 nm (ETH1011), respectively.

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