Bisulfite Addition Reaction as the Basis for a Hydrogensulfite Bulk Optode

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The reversible addition of hydrogensulfite to benzaldehydes was employed as the basic reaction type for the construction of a new kind of hydrogensulfite sensor. The membrane of the sensor consists of plasticized PVC, electrically neutral, lipophilized benzaldehyde compounds, and a basic chromoionophore. The coextraction of a proton together with the monovalent analyte ion into the membrane is accompanied by a change in the absorption spectrum due to protonation of the chromoionophore. Hence, an optical transduction in the visible range is achievable. A mathematical formalism is discussed that accounts for the dependence of the sensor response on the properties of the membrane. The experimental calibration curve for various hydrogensulfite concentrations in buffered solution is understood, within experimental precision, in terms of the theoretical model. These so-called bulk optode membranes allowed the detection of hydrogensulfite within a dynamic range of about three decades, down to 6 mg of HSO_3^{-}/L (7.6 × 10⁻⁵ M) depending on the pH of the solution. Sufficient selectivity and reproducibility in addition to a response time in the range of minutes make this optode a promising system for application in environmental and food analysis. This simple and economical sensor will be built in a sulfur dioxide sensing arrangement.

INTRODUCTION

The application of sulfur dioxide and sulfites is of importance in the food chemistry and paper industry. The combustion of fossil fuels produces sulfur oxides, among other gases, which are dissolved in rain drops as hydrogensulfite and sulfite. Both species are rapidly oxidized to sulfate by the catalytic effect of metal ions,¹ leading to the phenomenon of acid rain. Swiss legislation admits a 24-h average concentration of 100 μg of SO₂/m³ in air,² while in the United States the limit is $365 \,\mu g$ of $SO_2/m^{3.3}$ Although many sulfur dioxide sensor systems have been developed in the past few years, indirect monitoring of SO2 is still widely used. A certain amount of air is brought in contact with an oxidizing aqueous

solution. Sulfur dioxide is subsequently detected photometrically as sulfate.4-7

In the paper industry, sulfite lye is used in the production of sulfite cellulose. Sulfite waste water is harmful to the environment due to its reducing properties, which strongly influence the oxygen concentration of polluted water.⁸ In Switzerland the maximum concentration of sulfites allowed is 1 mg/L for surface water and 10 mg/L for sewage.⁹

The sulfite concentration can be measured photometrically¹⁰ or gravimetrically as barium sulfate.^{8,11} There is also a more sophisticated polarographic method.¹¹

Sulfur dioxide and sulfur(IV) anions are used in a variety of food products because of their dehydrating and antimicrobial activity and other desirable preservative effects.¹² Sulfites are commonly added to wine, fruits and vegetables, fruit juices and purees, syrups, and condiments. Swiss legislation allows up to 2000 mg of SO₂/kg of dried apricots and 80 mg of SO_2/L of grape and apple juices, while beer must not contain more than 20 mg of SO₂/L.¹³ Under regulations of the U.S. Treasury Department, Alcohol and Tobacco Tax Division, finished wines should not have an excess of 350 mg of SO₂/L. Several sulfite salts and sulfur dioxide are generally recognized as safe for use in foods by the U.S. Food and Drug Administration (FDA) except for foods which are substantial sources of thiamin. Sulfur dioxide and sulfites are oxidized in the body to harmless sulfates and eliminated with the urine.¹² The FDA has established 10 mgof SO₂/L as the threshold for declaration of sulfites in foodstuff.14

A method widely used for determining sulfite additives in food is based on their conversion into gaseous sulfur dioxide and acidimetric titration as sulfuric acid after dissolving in diluted hydrogen peroxide solution,15,16 although less cum-

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(16) Rauscher, K., Engst, R., Freimuth, U., Eds. Untersuchung von Lebensmitteln; Einführung und Anleitung zur Untersuchung der Lebensmittel pflanzlicher und tierischer Herkunft einschliesslich Fremdstoffe und Trinkwasser, 2. Aufl.; VEB Fachverlag: Leipzig, 1986; p 219.

bersome instrumental methods are available (see also ref 17).¹⁷ Many recent reports on the development of more accurate and faster techniques¹⁸⁻²² show the vital interest in detecting sulfites. However, these methods suffer from time-consuming operation and, partially, the consumption of very expensive reagents. Hence, sensors become increasingly important in this field. Some sensors have been described recently.

Pranitis and Meyerhoff have developed a sulfite-sensitive membrane electrode based on the mercury(II) complex of diethyl dithiocarbamate, Hg(DDC)2.23 Their system responds to sulfite as well as to hydrogensulfite down to 8 mg/L with sufficient selectivities, even over lipophilic anions such as perchlorate and salicylate. Several systems are based on enzymatic recognition processes. Rapid decrease of the enzyme activity and interferences induced by ascorbic acid and other redox agents are the major drawbacks of these systems. However, an electrode described by Smith detects sulfite at concentrations as low as 10 mg/L in complex sample matrices.¹⁷ Even electrodes containing immobilized microorganisms in the sensing layer have been developed.²⁴

Although the sulfite oxidase dip coated TTF-TCNQ/ silicone oil electrode improves transduction (transformation of the recognition process into an electrical signal), its mechanical stability and lifetime are not fully satisfactory yet.²⁵

The latter sensor systems make use of an electrical transduction. The drawbacks of this type of transduction are electronic and electromagnetic interferences. The present paper describes a simple and economical hydrogensulfite sensor utilizing the hydrogensulfite addition reaction as molecular recognition process, thereby allowing direct optical transduction without any of the interferences mentioned above.

Hydrogensulfite addition products are formed with aldehydes, methyl ketones, cyclic ketones (in general, sevenmembered and smaller rings), α -ketoesters and isocyanates, while most other ketones do not undergo the reaction, probably for steric reasons.²⁶ The reaction can be reversed by treating the addition product with either acid or base.²⁷ In the sensor described, lipophilic benzaldehydes contained in a bulk optode membrane selectively add hydrogensulfite. Bulk-response membranes based on plasticized PVC matrices for sensing anions such as nitrate and chloride have already been presented.²⁸⁻³⁰

Previous investigations on the applicability of classic organic reactions in polymeric membranes led to the development of a humidity³¹ and an ethanol sensor,³² in which

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lipophilic trifluoroacetophenones act as acceptor compounds for water and ethanol.

EXPERIMENTAL SECTION

Reagents. For membrane preparation: poly(vinyl chloride) (PVC; high molecular weight), bis(2-ethylhexyl) sebacate (DOS), 2-nitrophenyl octyl ether (o-NPOE), 1,2-benzo-7-(diethylamino)-3-(2'-octyldecylimino)phenoxazine (ETH 5350), and methyltridodecylammonium chloride from Fluka (Buchs, Switzerland).

For the sample solutions: glycerol, sodium hydrogensulfite (aqueous solution), sodium salts of chloride, nitrate, thiocyanate, and perchlorate from Fluka of the highest purity available.

For the iodometric titration procedure for the determination of the standard hydrogensulfite solution: sodium iodate from Fluka.

For the buffer solutions: trisodium citrate and citric acid, obtained from Fluka. Hydrochloric acid, sulfuric acid, and sodium thiosulfate (all in Titrisol quality) were purchased from Merck (Darmstadt, Germany), p-octylbenzaldehyde was from Eastman Kodak Co. (Rochester, NY), and tris(hydroxymethyl)aminomethane (Tris) was from Sigma Chemical Co. (St. Louis, MO). Aqueous solutions were prepared with doubly quartz distilled water.

Syntheses. The syntheses of vinyl chloride/vinyl alcohol copolymer (OH-PVC) has been described in ref 33.

4-Formylbenzoic Acid Chloride. A solution of 1.5 g (10 mmol) of 4-carboxybenzaldehyde (Fluka, puriss.) in 2 mL of thionyl chloride (Fluka, puriss.) and 20 mL of toluene (Fluka, puriss. p.a.) was stirred at reflux temperature for 90 min. The solvent and the excess of thionyl chloride were evaporated, and the residue was dried at high vacuum to yield 1.65 g (9.8 mmol, 97.9%) of the product, which was used without further purification.

Octadecyl 4-Formylbenzoate (ETH 5444). A 0.96-g (9.5 mmol) aliquot of triethylamine (Fluka, puriss. p.a.) was added to a solution of 1.6 g (9.5 mmol) of 4-formylbenzoic acid chloride and 2.6 g (9.5 mmol) of 1-octadecanol (Fluka, purum) in 30 mL of CH₂Cl₂ (Fluka, puriss. p.a.). The reaction mixture was stirred at room temperature for 30 min, then diluted with 100 mL of CH_2Cl_2 , and washed with 200 mL of H_2O . The organic phase was dried over MgSO₄. The solvent was evaporated and the residue purified by flash chromatography (silicagel, hexane/ethyl acetate 9:1) and recrystallized from hexane to yield 1.5 g (3.7 mmol, 39.2%; mp 55-56 °C) of pure ETH 5444. Anal. calcd for C₂₈H₄₂O₈ (402.62): C, 77.56; H, 10.51. Found: C, 77.54; H, 10.59. The constitution of ETH 5444 was confirmed by 1H NMR (300 MHz, CDCl₃), IR (CHCl₃), and MS

Membrane Preparation. For compositions of the optode membranes see Table I. The membrane components ($\sim 200 \text{ mg}$ altogether) were weighted out and dissolved in 1.8 mL of freshly distilled THF. By means of a spin-on device, two identical membranes of $\sim 3 \,\mu m$ thickness were cast on two glass plates (Herasil quartz glass, Möller, Zürich, Switzerland), which were then mounted in a specially designed measuring cell.³⁴ Before use, the membranes were conditioned for a few minutes in the proper buffer solution.

Apparatus. UV/visible absorbance measurements of the PVC membranes were made with an Uvikon Model 810 double-beam spectrophotometer (Kontron AG, Zürich, Switzerland). For all flow-through measurements, a Perpex minipump Model A/80 (Guldener, Zürich, Switzerland) and silicon tubes (Sikolit, Angst & Pfister AG, Zürich, Switzerland) were used. The pH values were determined with a pH glass electrode (Orion Ross Model 8103, Orion Research AG, Uetikon am See, Switzerland).

Experimental Procedures. Solutions. The solutions were prepared from 10-2 M citrate buffer solution³⁵ of pH 4.6 or 10-2 M Tris buffer solution³⁵ of pH 7.9 by adding various volumes of the respective buffered stock solutions. The sodium hydrogensulfite stock solution was iodometrically titrated using the

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| | | | | membrane | | | |
|--------------------------------------|-------|-------|-------|----------|-------|-------|-------|
| | Id | II | III | IV | v | VI | VII |
| ETH 5350 ^a (M) | | 0.038 | 0.039 | 0.041 | 0.035 | 0.042 | 0.073 |
| ETH 5444° (M) | | 0.079 | | 0.027 | 0.279 | 0.073 | |
| p-octylbenzaldehyde ^a (M) | 0.202 | | | | | | |
| PVC ^b (%) | 30.6 | | | | | 29.6 | 31.8 |
| OH-PVC ^{b,c} (%) | | 31.4 | 29.6 | 31.4 | 28.1 | | |
| DOS ^b (%) | 63.6 | | | | | 65.9 | 64.0 |
| o-NPOE ^b (%) | | 64.4 | 68.2 | 65.5 | 62.6 | | |

^a Calculated using a specific weight for the membrane of 1 g/cm³. ^b In weight percent. ^c ETH 3538. ^d In addition 0.025 M methyltridodecylammonium chloride.

procedure described in ref 36. All hydrogensulfite solutions were stabilized by addition of 0.1% (v/v) glycerol.

Absorption Experiments. A flow-through system with a constant flow of $\sim 2 \text{ mL/min}$ was used. All measurements were performed in transmittance mode.

Calculations. Nonlinear least-squares fitting was performed utilizing the Mathematica system. The properties $K_{\text{extr.}}, K_{\text{d}}, \beta_{\text{d}}$, and β_{a} were treated as adjustable parameters. (For definitions and equations see Principle of Operation and Theory below). The limiting absorbance value A_1 was determined with pure buffer solutions (10-2 M citrate buffer for measurements at pH 4.6 or 10^{-2} M Tris buffer for measurements at pH 7.9). A_0 was measured with 10⁻¹ M sodium perchlorate solutions buffered to the respective pH.

Activity coefficients for all ions except hydrogensulfite were calculated according to a Debye-Hückel formalism.^{37,38} No data of sufficient quality could be found for hydrogensulfite. Hydrogensulfite activities were calculated using the equations in ref 39. The parameters for hydrogencarbonate were used. This seems justified as the activity coefficients of sulfite and carbonate are essentially equal within an ionic strength range from 10^{-3} to 10-1 M.38

Selectivitiy Measurements. The selectivities were measured by determining the calibration curve with solutions of a single interferent (SSM).

RESULTS AND DISCUSSION

Measurement Based on an Anion-Exchange Optode. The principal applicability of the bisulfite reaction for a sensor was first investigated by measuring the response of a plasticized PVC membrane, containing commercial p-octylbenzaldehyde, on hydrogensulfite. The anion-exchange system used is well-known.⁴⁰ The exchange equilibrium is described as follows:

$$HSO_3^-_{aq} + X^-_{mem} + L_{mem} \rightleftharpoons X^-_{aq} + L HSO_3^-_{mem}$$

where aq denotes the species in the aqueous solution, and mem the species in the organic membrane phase. L represents the ionophore (aldehyde), and L-HSO3-mem the corresponding hydrogensulfite adduct. X⁻ is the anion exchanged against hydrogensulfite, e.g., Cl-. The interaction of hydrogensulfite with the electrophilic carbonyl atom leads to a loss in electron delocalization of the carbonyl group with the aromatic ring and, therefore, to a hypsochromic shift of the absorption band at λ_{max} . Although *p*-octylbenzaldehyde is of moderate reactivity toward nucleophilic attack, the response of membrane I is satisfactory (see Figure 1). The system resembles classical anion exchangers in terms of selectivity. The lipophilicity of the anions governs selectivity in classical ion exchangers.



Figure 1. Response of membrane I to various concentrations of hydrogensulfite as an indication for the addition of hydrogensulfite to p-octylbenzaldehyde in a plasticized PVC matrix. The membrane contains 12 mol % methyltridodecylammonium chloride relative to the chromoionophore as anion exchanger.

Selectivity is thus a function of the hydration enthalpies, constituting the well-known Hofmeister sequence:12

$$ClO_4^- > SCN^- > I^- > NO_3^- > Br^- > Cl^-$$

The low absorbance maximum of the ionophore ($\lambda_{max} = 256$ nm) in the UV region makes sensing troublesome due to high background absorbance. In addition, the decrease of the absorbance at 256 nm is larger than expected for a mere exchange. Therefore, an exchange of X⁻ against HSO₃⁻ as well as a coextraction of H⁺ together with HSO₃⁻ must be expected.

The extraction system subsequently discussed additionally incorporates a chromoionophore and does not show any of the drawbacks mentioned. In particular, selectivities drastically deviate from the Hofmeister sequence, a prerequisite for the selective detection of an anion as hydrophilic as hydrogensulfite.

Principle of Operation and Theory. Earlier descriptions of bulk optode membranes for sensing anions by coextraction neglect any association between ionic species in the organic membrane phase.^{29,30,40-42} This restriction is well-founded in some cases, but has been lifted in the present work. Partial dissociation has also been allowed for.

Ion-Pair Formation in the Organic Membrane Phase. Only few studies on ion association in PVC membranes have been published so far. Armstrong et al. calculated some K_d values of tetraphenylborates in PVC/DOS membranes from bulk resistance measurement.^{43,44} Salts are likely to be dissociated completely if o-NPOE is used as a plasticizer,

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| Table II. Extrac | ction Equilibrium and Diss PVC | ociation Constants /DOS | OH-PVC/0-NPOE | | |
|-------------------|---|------------------------------------|---|------------------------------------|--|
| HX | $K_{\text{extr}}^{\text{HX}a}$ (M ⁻²) | K _d ^{CHXa} (M) | $K_{\rm d}^{{ m CHX}_{a}}\left({ m M}^{-2} ight)$ | K _d ^{CHXa} (M) | |
| H_2SO_3 | $(2.71 \pm 0.34) \times 10^4$ | $(6.78 \pm 2.23) \times 10^{-3}$ | $7.2 \times 10^{4 b}$ | $2.0 \times 10^{1 b}$ | |
| HCl | $(2.25 \pm 0.20) \times 10^4$ | $(2.28 \pm 0.49) \times 10^{-3}$ | $4.7 \times 10^{6 b}$ | 3.5×10^{1} b | |
| HNO ₃ | $(1.71 \pm 0.07) \times 10^{6}$ | $(4.60 \pm 2.64) \times 10^{-4}$ | $(7.73 \pm 3.01) \times 10^{7}$ | $(2.09 \pm 0.93) \times 10^{-1}$ | |
| HSCN | $(4.88 \pm 0.37) \times 10^7$ | $(2.75 \pm 0.88) \times 10^{-3}$ | $(7.47 \pm 2.24) \times 10^9$ | $(1.35 \pm 0.88) \times 10^{-2}$ | |
| HClO ₄ | $(1.57 \pm 0.21) \times 10^{8}$ | $(4.06 \pm 1.98) \times 10^{-3}$ | $(6.47 \pm 1.11) \times 10^9$ | $(3.65 \pm 1.02) \times 10^{-2}$ | |

^a Calculated from three series with 10 data points each. ^b No error calculation.

because of its high dielectric constant of $\epsilon_{mem} = 14$. In contrast, 94–99% of tetraphenylborate salts are associated when dissolved on a millimolar level in a PVC/DOS (1:2 w/w) membrane with a dielectric constant of $\epsilon_{mem} = 4.8$. The dissociation of tetraalkylammonium salts in organic solvents has been investigated several times. These salts are extensively used in organic chemistry, e.g., for numerous reactions involving carbanions and related species.⁴⁵ Sigvartsen and co-workers found that tetrabutylammonium perchlorate is dissociated up to 2% in chloroform ($\epsilon = 4.7$) and up to 34% in pyridine ($\epsilon = 12.3$), which agrees with the empirical ln K_a – ϵ^{-1} relationship (K_a is the association constant).⁴⁶

The optode system containing a lipophilized basic chromoionophore, electrically neutral in its unprotonated form, can be used to estimate the amount of associated species in the membrane phase. The response of such a system is described by the following equations:

$$X_{aq}^{-} + H_{aq}^{+} + C_{mem} \stackrel{K \ }{\approx} CH^{+} \cdot X_{mem}^{-}$$
(1)

$$CH^{+} \cdot X^{-}_{mem} \rightleftharpoons CH^{+}_{mem} + X^{-}_{mem}$$
(2)

 $K_{\rm extr}^{\rm HX}$ is the overall extraction equilibrium constant and $K_{\rm d}^{\rm CHX}$ the dissociation equilibrium constant. Consideration of the mass balance of the chromoionophore

$$[C_{T}] = [C_{mem}] + [CH^{+}_{mem}] + [CH^{+} \cdot X^{-}_{mem}]$$
(3)

where $[C_T]$ is the total amount of the chromoionophore (pH indicator) in the membrane leads to the response function

$$a_{\rm H+}a_{\rm X-} = \frac{K_{\rm d}^{\rm CHX}}{4K_{\rm extr}^{\rm HX}} \frac{1}{\alpha[\rm C_T]} \left[-1 + \left(1 + \frac{4}{K_{\rm d}^{\rm CHX}} [\rm C_T](1-\alpha) \right)^{1/2} \right]^2$$
(4)

The absorbance A of this system is related to the relative absorbance α :

$$\alpha = \frac{[C_{mem}]}{[C_{T}]} = \frac{A - A_{0}}{A_{1} - A_{0}}$$
(5)

where A_1 and A_0 are the limiting absorbance values for $\alpha = 1$ (neutral chromoionophore) and $\alpha = 0$ (fully protonated chromoionophore), respectively.

For the derivation of eq 4, the activity coefficients in the organic membrane phase were assumed to be constant over the entire measuring range. This assumption is not quite satisfying from a thermodynamic point of view.^{41,42} However, the maximum ionic strength is given by the total concentration of chromoionophore, typically being as small as 0.04 M; thus changes in the activities of the species in the membrane phase have a small influence on the equilibrium. In addition, only monovalent ions are involved.

Experimental values for K_{extr} and K_{d} were obtained by least-squares fitting (see Table II). The comparison of the



Figure 2. Response for perchlorate obtained from measurements with a PVC/DOS membrane (O) and OH-PVC/o-NPOE membranes (\bullet). Theoretical response curves are shown: (1) lons fully associated in the membrane phase, (2) ions fully dissociated, (3) calculated from eq 4 with $\mathcal{K}_{extr}^{HCO_4} = 1.57 \times 10^8 \, \text{M}^{-2}$ and $\mathcal{K}_{d}^{CHCO_4} = 4.06 \times 10^{-3} \, \text{M}$, and (4) calculated from eq 4 with $\mathcal{K}_{extr}^{HCO_4} = 6.47 \times 10^9 \, \text{M}^{-2}$ and $\mathcal{K}_{d}^{HCO_4} = 3.65 \times 10^{-2} \, \text{M}$.

 K_{extr} values clearly shows that an anion together with a proton are better coextracted into OH-PVC/o-NPOE membranes than into PVC/DOS membranes. For this reason the pH was held at 7.9 for measurements with OH-PVC/o-NPOE membranes, while a lower pH of 4.6 was chosen for measurements with PVC/DOS membranes.

The K_d values for OH-PVC/o-NPOE membranes are 1 or 2 orders of magnitude larger than for PVC/DOS. Hydrogensulfite as an example is dissociated to 7.9% in PVC/DOS and to 95.4% in OH-PVC/o-NPOE. Nitrate is dissociated to 2.1% in PVC/DOS and to 36.4% in OH-PVC/o-NPOE. This is in accordance with the finding described in the literature, that the association constant increases with decreasing dielectric constant of the membrane matrix.^{43,44} The variability among the K_d values for OH-PVC/o-NPOE membranes is much larger than for PVC/DOS membranes.

The influence of K_d on the shape of the response curve is shown in Figure 2. Higher K_d values are favorable, as the response curve is flat, leading to a larger dynamic measuring range.

Response of Hydrogensulfite-Selective Membranes to the Primary Anion. The hydrogensulfite-selective optode membrane contains an ionophore and an electrically neutral chromoionophore. For a description of the hydrogensulfiteselective system, two more main equilibria have to be considered in addition to the eqs 1-3:

$$HSO_{3_mem} + L_{mem} \stackrel{\beta_d}{\approx} L \cdot HSO_{3_mem}$$
(6)

$$CH^{+} \cdot HSO_{3\text{ mem}} + L_{mem} \stackrel{\rho_{a}}{\approx} L \cdot HSO_{3} \cdot CH^{+}_{mem}$$
(7)

 β_a and β_d denote the corresponding adduct formation constants.

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The expression of the response function for an optode membrane becomes rather complex if equilibria 6 and 7 are taken into account. Therefore, it is reasonable and sufficient to simplify the expression for two special cases:

Association is almost negligible in OH-PVC/o-NPOE membranes due to the high dielectric constant. The response function for the primary ion with regard to the mass balance for the ionophore L is then given by

$$a_{\rm H*}a_{\rm HSO_{3^{-}}} = \frac{1}{2K_{\rm extr}^{\rm H_2SO_3}K_{\rm d}^{\rm CH_2SO_3}} \times \left\{ -\left[[L_{\rm T}] - (1-\alpha)[C_{\rm T}] + \frac{1}{\beta_{\rm d}} \right] + D_1^{1/2} \right\}$$
(8a)

with

$$D_{1} = \left[[L_{T}] - (1 - \alpha) [C_{T}] + \frac{1}{\beta_{d}} \right]^{2} + \frac{4(1 - \alpha) [C_{T}]}{\beta_{d}}$$
(8b)

In PVC/DOS membranes, with low dielectric constant, the ions are almost completely paired. Neglecting dissociation leads to the following expression for the response curve:

$$a_{\rm H+}a_{\rm HSO_{3^{-}}} = \frac{1}{2K_{\rm extr}^{\rm H_{3}SO_{3}}} \left\{ -\left[[L_{\rm T}] - (1-\alpha)[C_{\rm T}] + \frac{1}{\beta_{\rm a}} \right] + D_{2}^{1/2} \right\}$$
(9a)

with

$$D_{2} = \left[[L_{T}] - (1 - \alpha) [C_{T}] + \frac{1}{\beta_{a}} \right]^{2} + \frac{4(1 - \alpha) [C_{T}]}{\beta_{a}}$$
(9b)

 $[L_T]$ denotes the total concentration of ionophore in the membrane.

Response of Hydrogensulfite-Selective Membranes to Interferents. It is assumed that the interferents discussed in this paper do not build an adduct with the ionophore and thus have the response of an optode system without ionophore. The theoretical description is the same as above (eq 4). The selectivity behavior of such an optode membrane is expressed by the Hofmeister sequence.

Definition of the Selectivity Coefficient. According to the definition of the selectivity coefficients in ref 42, for a fixed pH and for a certain membrane composition, the SSM selectivity coefficients for monovalent interferents are given by

$$K_{\text{HSO}_{3^{-},Y^{-}}}^{\text{Opt}} = \frac{\text{right-hand side of eq 8a}}{\text{right-hand side of eq 4}}$$
(10)

for OH-PVC/o-NPOE membranes and by

$$K_{\text{HSO}_{8}^{-},Y^{-}}^{\text{Opt}} = \frac{\text{right-hand side of eq 9a}}{\text{right-hand side of eq 4}}$$
(11)

for PVC/DOS membranes. In the expression out of eq 4, $K_{\text{extr}}^{\text{HX}}$ and $K_{\text{d}}^{\text{CHX}}$ have to be replaced for $K_{\text{extr}}^{\text{HY}}$ and $K_{\text{d}}^{\text{CHY}}$. If only monovalent ions are considered, the selectivity

If only monovalent ions are considered, the selectivity coefficient can be found by a graphical method. The two single-ion response functions α are plotted vs $\log(a_{\rm H}+a_{\rm X}-)$ according to eqs 4, 8a, and 9a for a certain degree of deprotonation a of the chromoionophore, usually $\alpha = 0.5$. The selectivity coefficient is simply the horizontal distance between the two curves.

$$\log K_{\rm HSO_{5}^{-},Y^{-}}^{\rm Opt}(\alpha=0.5) = \log(a_{\rm H^{+}}a_{\rm HSO_{5}^{-}})_{\alpha=0.5} - \log(a_{\rm H^{+}}a_{\rm Y^{-}})_{\alpha=0.5}$$
(12)

Interferences induced by multiply charged anions were neglected, because the extraction properties of multivalent anions are at least 1 order of magnitude smaller than those of monovalent anions. However, bivalent anions would have to be considered if present in very high concentrations relative to the primary ion.



Figure 3. Absorption spectrum of membrane II containing ETH 5350 as the chromolonophore and ETH 5444 as the ionophore in a OH-PVC/o-NPOE matrix. The protonated form of ETH 5350 shows its absorption maximum at 652 nm, the deprotonated form at 508 nm.



Figure 4. Degree of deprotonation (expressed by α) of optode membranes II (top) and III (bottom) as a function of $\log(a_{H}+a_{X})$. The addition of carrier leads to a drastic shift of the response curve for hydrogensulfite, while the responses of the interferents are not significantly influenced.

Response and Measuring Range. Figure 3 shows the spectral changes of membrane II (see Table I), containing ETH 5350, due to the variation in hydrogensulfite concentration at pH 7.9. The neutral form of the chromoionophore in a OH-PVC/o-NPOE matrix has an absorption maximum at a wavelength of $\lambda_{max}^{prot} = 508$ nm, while the maximum for the protonated form is at $\lambda_{max}^{prot} = 652$ nm. The calibration curve is shown in Figure 4 (top) together with the calibration curves of some interferents. Figure 4 (bottom) shows the calibration curves for a membrane without ionophore (membrane III). The curves were obtained by least-squares fitting. Equation 8a was used in conjunction with membrane II. The



Figure 5. Response for membranes containing chromoionophore ETH 5350 and ionophore ETH 5444 in various ratios of $[C_T]/[L_T]$. The shape and the relative position of the response curve on the $\log(a_{H}+a_{X'})$ scale strongly depend on this molar ratio. The response curves were obtained by least-squares fitting.

remaining curves were calculated using eq 4. The differences between the experimental data and the fitted function values, i.e., the residuals, show an erratic behavior as expected for experimental error. This confirms that the model is able to reproduce the principal effects of the experiment.

The addition of 2 mole equiv of ETH 5444 relative to the concentration of the chromoionophore to membrane II (leading to membrane III), results in a drastic shift of the dynamic range for hydrogensulfite, leaving the response curves of the interferents unaffected. The lower detection limit for hydrogensulfite is 5.6 mg of HSO_3^{-}/L (6.9 × 10⁻⁴ M) at pH 7.9 (membrane II, relative absorbance $\alpha = 0.95$). Due to the acid/base equilibrium of hydrogensulfite, 44 mg of SO_3^{2-}/L $(5.5 \times 10^{-4} \text{ M})$ is also present at the detection limit (pH 7.9). The best lower detection limit of 0.3 mg HSO₃-/L (4.2×10^{-6} M) at pH 7.9 was measured with membrane V. As it can be seen from Figure 2, $\log(a_{H}+a_{X}-)$ is shifted to higher values if the dielectric constant of the membrane decreases. Therefore, PVC/DOS membranes with a small dielectric constant allow measurements at a low pH. A detection limit of 6.1 mg/L $(7.6 \times 10^{-5} \text{ M})$ at pH 4.6 was achieved with a PVC/DOS membrane of composition similar to membrane II. At this pH, the concentrations of sulfite and sulfurous acid are negligible. Since the response curves for systems with the highest dielectric constant are the flattest, the dynamic range is extended by $\Delta \log(a_{\rm H}+a_{\rm X}-) = 0.8$. Unfortunately the selectivity behavior of PVC/DOS membranes is not as favorable as for OH-PVC/DOS membranes (see later). Thus the specific application has to be kept in mind when the membrane matrix is being chosen.

Selectivity. The shape and the position of the response curve α vs log($a_{H^+}a_{HSO_8^-}$) strongly depend on the ratio [C_T]/[L_T], as eqs 8a and 9a show (Figure 5). The response curves of the interferents are not significantly influenced by an addition of carrier. As a consequence, the selectivity coefficient similarly depends on this ratio (Figure 6). In membrane V the selectivity coefficient for hydrogensulfite over the highly lipophilic perchlorate anion is log $K_{HSO_8^-,CIO_8^-}^{Opt} = 0$, allowing the detection of hydrogensulfite down to 10⁻⁴ M HSO₈⁻ (8 mg of HSO₈⁻/L) with an accuracy of 1% in the presence of 10⁻⁶ M ClO₄⁻ (0.1 mg ClO₄⁻/L).

The membrane matrix not only influences the dynamic range, but also selectivity. For numerical values, see Table III. The range of selectivity coefficients is smaller for PVC/ DOS membranes (VI, VII) than for OH-PVC/o-NPOE membranes (III, V), at least for the ions considered. Hence, membranes III and V are particularly suited for lipophilic anions.



Figure 6. Selectivity plot for membranes containing ETH 5350 as chromoionophore and ETH 5444 as ionophore in variable molar ratios.

| Pable III. SSM Selectivity Coefficients of OH-PVC/o-NPOE and PVC/DOS Optode Membranes $\log K_{\text{HSO},-Y}^{\text{Opt}}(\alpha = 0.5)$ | | | | | | | |
|---|----------------------|------------|-----------------------|------------------------|--|--|--|
| Y- | membr V ^a | membr IIIª | membr VI ^b | membr VII ^b | | | |
| HSO3- | 0 | 0 | 0 | 0 | | | |

-0.7

+1.0

+1.5

+1.4

+3.1

+3.6

+0.9

+2.3

+2.6

| • • | ~4 | ÷ | | | | | |
|-----|-----------|-------|-------|-----------|-------|-----|--|
| | | | | | | | |
| a | According | to eq | 11. 0 | According | to eq | 10. | |

-1.7

-0.3

0

NO₃-

SCN

C107-



Figure 7. Short-term reproducibilities of the absorbance for two optode membranes V. Thickness of the membranes, 3 μ m. Hydrogensulfite concentration changes between 10⁻³ and 5 × 10⁻³ M.

Sulfite causes interference at a pH above 8. The theoretical expressions become cumbersome if extraction of bivalent sulfite into the membrane phase is taken into consideration. Thus measurements at a lower pH were preferred.

Short-Term Reproducibility and Stability. Optode membrane V was repeatedly exposed to a change in hydrogensulfite concentration between 10^{-3} and 5×10^{-3} M. The reproducibility of the optical signal was remarkable, as shown in Figure 7. The mean absorbance value measured after 12 min is 0.3085 with a standard derivation of 0.0031 for the 10⁻³ M solution. The corresponding figures for the 5×10^{-3} M solution are 0.1614 ± 0.0012 . Washing out of the chromoionophore caused a loss in absorbance of 2.6% (0.3136 – 0.3056) and 2.0% (0.1632 - 0.1600). A high flow rate of 2 mL/min is necessary for sufficient solution exchange in the measuring cell. Otherwise hydrogensulfite may decompose in the light beam or in contact with the membrane. The absorbance signal of OH-PVC/o-NPOE membranes at 508 nm dropped by 8-14% within 30 solution changes. This is equivalent to a permanent flow of 8 h. The loss of chromoionophore can be detected by measuring the absorbance at the isobestic point. A correction of the sensor signal is therefore possible. Optimizing the flow rate will certainly reduce the washing out of components.

Freshly prepared membranes as well as solutions of membrane components in THF are stable for several weeks when stored in a nitrogen atmosphere. Membranes in use are necessarily exposed to light and oxygen. Decomposition of the chromoionophore and oxidation of the ionophore have to be expected. Used membranes have been kept in doubly distilled water for more than 2 weeks without significant loss of their properties.

CONCLUSIONS

Optode membranes based on lipophilized benzaldehydes can selectively detect hydrogensulfite in the presence of chloride, nitrate, and thiocyanate. The response behavior is theoretically well-understood. Improvement of the selectivity and optimization of the measurement conditions are vigorously addressed.

The presented optode system successfully extends the field of reversible organic reactions in bulk optodes to selectively

sense organic and inorganic neutral and charged compounds and, thus, encourages further investigations on this topic.

Preliminary experiments showed that ETH 5444 and p-octylbenzaldehyde may also be used as carriers in ion-selective electrodes.

Future work will concentrate on the practical application of this sensor system and its implementation in a sulfur dioxide sensing device.

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