A Selective Optical Chemosensor Based on a Thia-containing Schiff-Base Iron(III) Complex for Thiocyanate Ion

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A new optode membrane for the sensitive and selective determination of thiocyanate ion, based on a change in the absorption spectrum of a polymer film, is proposed. A membrane composed of plasticized poly vinyl chloride (PVC), an Fe(III) Schiff-base complex as a chromoionophore and hexadecyl trimethyl ammonium bromide (HDTMABr) as a cationic additive was prepared. The influence of different plasticizers was studied concerning the sensitivity, linear range and selectivity of the membrane film. Satisfactory analytical sensing characteristics for determining thiocyanate ion were obtained in terms of the selectivity, reversibility and reproducibility with a good detecting range. In addition, the optical film responds to thiocyanate ion reversibly over a wide dynamic range 1.0×10^{-8} to 1.0×10^{-3} M with fast response and recovery times. The optode membrane has been applied to determine the thiocyanate ion in urine samples.

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Introduction

Many areas of applied analytical chemistry, such as process control, clinical, food, beverage and environmental samples require a fast and simple method for determining the concentration of ionic species in an aqueous system. There are considerably fewer examples of analogous sensors for anionic species, with those that employ solely hydrogen bonding in order to bind the anionic guest species functioning only in organic solvent media. There is, however, a high demand for anion sensors that function in water, and for use in medicine, food analysis, environmental monitoring and biotechnology. In the literature, there are few examples of PVC-supported liquid membrane electrodes designed to sensing in aqueous solution anions such as: nucleotides, maleate, fumarate, phthalate and fluoride. Numerous efforts have been devoted to the development of optical molecular chemosensors for anionic species, especially during the last decade.^{1,2}

Metal-based sensing systems use metal-ligand interactions for the recognition of target anions, and thus result in high selectivity, a large binding constant and good solubility in aqueous solution when used for sensing.^{3,4}

The importance of determining thiocyanate levels in effluent downstream from a plant outlet can not be underestimated. Though not as toxic as cyanide, thiocyanate is harmful to aquatic life. Thiocyanate is a common constituent of hydrometallurgical solutions. It is formed when pyretic substances are leached with solutions containing cyanide. For efficient plant control it is important to continuously monitor and determine the level of thiocyanate and subsequent consumption of the free cyanide in these process solutions.⁵

Thiocyanate ion is usually present in low concentration in

human serum, saliva and urine as a result of the digestion of some vegetables of the genus containing glucosinolates (cabbage, turnip, kale) or by the intake of thiocyanate-containing foods, such as milk and cheese. Higher concentrations of this ion, which is a metabolic product of cyanide, arise from tobacco smoke. Thus, the level of thiocyanate is considered to be a good probe for distinguishing between smokers and non-smokers.^{6,7} The aim of the present work was to develop a new procedure for the selective determination of thiocyanate in different sample solutions. To the best of our knowledge, there has been no report on how to synthesis and apply this pyridine unit and a thia group containing a Schiff base (FepytBrsal) constructed an optical sensor. In recent years, we have reported on selective sensors for important cations, anions and drugs in different samples.⁸⁻¹⁰

Experimental

Reagents

Reagents-grade dioctyl phthalate (DOP), dioctyl sebacate (DOS), hexadecyl trimethyl ammonium bromide (HDTMABr), nitrophenyl octyl ether (NPOE) and high relative molecular weight PVC and tetrahydrofuran (THF) were purchased from Merck and used as received. The sodium salts of the anions used (all from Merck) were of the highest purity available, and used without any further purification, except for vacuum drying. The iron(III) Schiff-base complex (FepytBrsal) was synthesized and used after recrystallization. Doubly distilled deionized water was used throughout.

Instrumentation

All absorbance measurements were carried out with a Perkin-Elmer double-beam spectrophotometer with quartz cells. A Metrohm combined pH glass electrode was used for pH measurement at $25.0 \pm 0.1^\circ\text{C}$.

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Scheme 1 General procedure for synthesis of the complex.

Synthesis of Fe(III)-complex

The target Schiff-base metal-complex, FepytBrSal, was synthesized from in one-step according to the procedure in Scheme 1.¹¹ The structure of the product was confirmed by CHN analysis and the IR spectrum. Mp, 210°C (decomposed); Fw, 527.066 g mol⁻¹, elemental analysis: Calcd. for C₁₆H₂₀BrCl₂FeN₂SO₃: C, 36.46%; H, 3.82%; N, 5.31%. Found: C, 36.68%; H, 3.77%; N, 5.52%. IR (KBr): 3450 cm⁻¹ ν(O-H), 3030 and 3080 cm⁻¹ ν(C-H)_{aromatic}, 2840 and 2950 cm⁻¹ ν(C-H)_{aliphatic}, 1618 cm⁻¹ ν(C=N)_{imin}.

Preparation of optode films

The general procedure to prepare a PVC membrane was to thoroughly mix 30 mg of powdered PVC and 2.0 mg of hexadecyltrimethyl ammonium bromide with 66 mg of NPOE as a solvent mediator in the minimum amount of THF. To this mixture was added 1 mg of chromoionophore (FepytBrSal), and the solution was mixed well. The resulting mixture by using a laboratory-made spin-on-device was used to cast two identical membranes of 5 μm thick cast on two glass plates which were subsequently mounted in a UV-visible quartz cell. Blank reference membranes were prepared in a similar way, except without using FepytBrSal. Then a glass plate covered with the membrane was placed vertically inside a sample quartz cell containing 2 mL of an aqueous solution; a blank membrane (without chromoionophore) covered on a glass plate was put in the reference cell. The sample cell was finally titrated with standardized anion ion solutions.

Results and Discussion

Solution studies

In order to find a clue about the stability and selectivity of the new complex, in preliminary studies, the UV-visible spectra of FepytBrSal with different important anions in acetonitrile solution were investigated. When a 1.0 × 10⁻⁶ M solution of FepytBrSal in acetonitrile was titrated with standard solutions of different anions, a rapid color change occurred after the addition of thiocyanate ion (Fig. 1). As can be seen in Fig. 1, a decrease occurred in the absorption UV-band Fe(III)-complex at 322 and 385 nm and an increase appeared in the absorption band of the complex at 466 nm. While adding other anions, including I⁻, Br⁻, SO₄²⁻, NO₃⁻, NO₂⁻, SCN⁻, CN⁻, ClO₄⁻ and Sal⁻, no spectral changes was observed in the sensing solution. This high selectivity was attributed to the formation of a new adduct between the Fe(III) in the center of the complex and the thiocyanate ion.¹² Thus, based on this selectivity the FepytBrSal compound is expected to act as a selective chromoionophore in the preparation of a PVC-based ion-selective optode for SCN⁻.

Fig. 1 Absorption spectra of FepytBrSal after equilibration with a 1.0 × 10⁻⁶ M thiocyanate ion.

Operation principle

The response mechanism of the optical sensor membrane based on the change in absorption spectrum can be explained as follows. When the sensing membrane film contacts with various concentrations of SCN⁻ ions in an aqueous solution phase (aq) and FepytBrSal in the membrane phase (mem), equilibrium is established along with the formation of a *m*:*n* complex:^{13,14}

Here, *K* is the equilibrium constant. The difference between the activities and concentrations is neglected. According to the law of mass action, *K* can be expressed as

$$K = \frac{[\text{SCN}^-_{(\text{m})}(\text{FepytBrSal})_n] (\text{mem})}{[\text{SCN}^- (\text{aq})]^m [\text{FepytBrSal}]^n} \quad (2)$$

The relative absorbance intensity is defined as the ratio of uncomplexed FepytBrSal in the membrane phase, [FepytBrSal]_{org}, to its total amount, [C]_{T,org}, so that

$$\alpha = [\text{FepytBrSal}]_{\text{org}} / [C]_{\text{T,org}} \quad (3)$$

In practice, the *α*-value during the titration of membrane with SCN⁻ ions can be determined by measuring the absorption intensity of the optical sensor, *A*, at λ = 466 nm,

$$\alpha = (A - A_0) / (A_1 - A_0) \quad (4)$$

Here, *A*₀ and *A*₁ are the limiting absorption intensities of the optical sensor at *α* = 0 (uncomplexed FepytBrSal) and *α* = 1 (totally complexed FepytBrSal), respectively. The relationship between the *α*-value and the concentration of SCN⁻ ion in aqueous sample solution, [SCN⁻]_{aq}, can be obtained from Eqs. (2) and (3), as follows:

$$\alpha^n / 1 - \alpha = 1 / (K [C]_{\text{T}})^{n-1} [\text{SCN}^-]^m \quad (5)$$

Equation (5) could be used as a basis for a quantitative determination of the thiocyanate ion concentrations using the proposed optical sensor.

Response behavior of different membrane formulations

It is well known that the membrane film composition may

Table 1 Optimization of optode membrane film ingredients

Membrane No.	PVC/mg	Plasticizer/mg	FepytBrsal/mg	HDTMABr/mg	Linear range/M
1	30	NPOE, 69	1	—	$1 \times 10^{-4} - 1 \times 10^{-7}$
2	30	NPOE, 67	1	2	$1 \times 10^{-3} - 1 \times 10^{-8}$
3	30	DOP, 67	1	2	$1 \times 10^{-4} - 1 \times 10^{-7}$
4	30	DOS, 67	1	2	$1 \times 10^{-5} - 1 \times 10^{-8}$
5	30	NPOE, 66	2	2	$1 \times 10^{-3} - 1 \times 10^{-6}$

Fig. 2 Effect of the pH on the optical response of the proposed SCN⁻-selective optosensor.

greatly influence the response characteristics and working concentration range of optical sensors.¹⁵⁻¹⁷ Thus, in this work, five PVC-membranes with about the same plasticizer/PVC ratios, but a varying nature and amount of other ingredients, were prepared (Table 1). It should be noted that the plasticized PVC-membranes used in sensors will usually result in the response membrane characteristics at a plasticizer/PVC ratio of about 2.¹ Since in bulk membrane optodes, the membrane must be in thermodynamic equilibrium with the sample, a mass transfer of analyte into the membrane is required.¹⁸

Thus, for the proposed thiocyanate selective optosensor containing FepytBrsal as a neutral chromoionophore, the presence of a lipophilic additive, like HDTMABr, is necessary to facilitate the ion-exchange equilibrium. The absence of HDTMABr was found not only to effect the working concentration range of the sensor (Table 1), but also to cause its prolonged response time and reduced selectivity.¹⁹

The presence of 66 – 69% plasticizer in PVC-membranes resulted in the optimum physical properties, as well relatively high mobilities of their constituents.²⁰⁻²² The nature of the plasticizer is well known to considerably influence the measuring range of the solvent polymeric membrane sensors and their selectivity coefficients.²³⁻²⁵ As is obvious from Table 1, the use of NPOE as a plasticizer resulted in a large widening of the measuring range of the proposed optical sensor over the membrane based on DOP and DOS due to the increased polarity of NPOE.

Effect of pH, calibration curve and response time

The influence of the pH of the test solution on the response of the optode membrane film was tested for a 1.0×10^{-5} M SCN⁻ solution in the pH range 3.0 – 11.0 (adjusted with HNO₃ or NaOH) and the results are shown in Fig. 2. As can be seen, the response of the sensor remains constant from pH 3.0 – 8.0, beyond which the α-value changes considerably. The observed drift at lower and higher pH values could be due to protonation

Table 2 SSM optical selectivity coefficient of various interfering anions^a

Anion	$\log K_{\text{SCN},A}^{\text{opt}}$
I ⁻	-2.1
F ⁻	-4.5
SO ₃ ²⁻	-5.3
SO ₄ ²⁻	-5.1
NO ₃ ⁻	-3.6
NO ₂ ⁻	-3.9
ClO ₄ ⁻	-2.5
Cl ⁻	-4.0
CN ⁻	-4.5

a. The pH of solutions was fixed with 0.05 M acetate buffer in pH 5.5.

of the ion carrier and the formation of some hydroxy complexes of SCN⁻ ion in solution, respectively.

The optical response of the proposed thiocyanate selective optosensor at different thiocyanate concentrations was tested under the optimal experimental conditions. The resulting calibration graphs for SCN⁻ ions were obtained at the wavelength 466 nm. The dynamic concentration range of the proposed sensor for SCN⁻ ion was 1.0×10^{-8} to 1.0×10^{-3} M. The limit of detection, as determined based on the 3σ of the blank membrane film was 4.0×10^{-9} M. The static response time obtained for the sensor was only about 60 s, over the entire concentration range. For reuse, an investigation of the reversibility of each membrane sensor used for the determination of SCN⁻ ions was immersed in 0.05 M solution of acetate buffer at pH 5 for about 1 h. After this time, the membrane was ready for the next measurement for titration with thiocyanate ion. The optode membrane films could be used at for least 4 weeks when stored in a dark environment and being dry when not in use.

Interference tests

In order to investigate the selectivity of the proposed optosensor toward SCN⁻ with respect to various interfering ions, the selectivity coefficients ($K_{\text{SCN}}^{\text{opt}}$), describing the performance of the new sensor for an interfering ion, B, relative to SCN⁻ ion, A, was determined by the separate solution method (SSM).¹⁷⁻²⁶ The resulting $K_{\text{SCN}}^{\text{opt}}$ values are summarized in Table 2. As can be seen, the selectivity pattern is SCN⁻ > I⁻ > ClO₄⁻ > NO₃⁻ > NO₂⁻ > Cl⁻ > F⁻ = CN⁻ > SO₄²⁻ > SO₃²⁻. From the data given in Table 2, it is obvious that the proposed thiocyanate sensor is highly selective with respect to other anions.

Application for real samples

The proposed optical sensor was also successfully applied to a direct determination of thiocyanate in samples from the urine of smokers and non-smokers. Urine samples were collected from a non-smoker and a heavy smoker in order to demonstrate the effectiveness of this method as a means of evaluating smoking behavior. The results are compared with the standard

Table 3 Determination of thiocyanate in urine samples

Sample	SCN ^{-a} /mmol l ⁻¹	
	Proposed method	Colorimetric method
Non-smoker urine	0.24 ± 0.05	0.25 ± 0.05
Smoker urine	0.75 ± 0.05	0.76 ± 0.08

a. Mean value ± standard deviation (three determinations).

colorimetric method.^{8,27} The results were for three replicate are presented in Table 3.

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References

1. P. Buhlmann, E. Pretsch, and E. Bakker, *Chem. Rev.*, **1998**, 97, 3083.
2. S. H. Li, C. W. Yu, W. T. Yuan, and J. G. Xu, *Anal. Sci.*, **2004**, 20, 1375.
3. R. M. Manezand and F. Sancenon, *Chem. Rev.*, **2003**, 103, 3083.
4. W. Qin, P. Parzuchowski, W. Zhang, and M. E. Meyerhoff, *Anal. Chem.*, **2003**, 75, 332.
5. Z. Glatz, S. Novokova, and H. Sterbova, *J. Chromatogr. A*, **2001**, 916, 4419.
6. J. Potter, R. M. Smith, and A. M. Api, *Food. Chem. Toxicol.*, **2001**, 39, 141.
7. M. Shamsipur, G. Khayatian, and S. Tangestaninjad, *Electroanalysis*, **1999**, 11, 1340.
8. M. Shamsipur, S. Ershad, N. Samadi, A. Rezvani, and H. Haddadzadeh, *Talanta*, **2005**, 65, 991.
9. M. Shamsipur, S. Ershad, N. Samadi, A. Moghimi, and H. Aghabozorg, *J. Solid State Electrochem.*, **2005**, 9, 788.
10. M. Shamsipur, S. Ershad, and F. Jalali, *J. Pharm. Biomed. Anal.*, **2005**, 37, 973.
11. N. Daneshvar, A. A. Entezami, A. A. Khandar, and L. A. Saghatforoush, *Polyhedron*, **2003**, 22, 1437.
12. M. Shamsipur, T. Poursaberi, A. R. Karami, M. Hosseini, A. Momeni, N. Alizadeh, M. Yousefi, and M. R. Ganjali, *Anal. Chim. Acta*, **2004**, 501, 55.
13. W. E. Morf, K. Seiler, B. Lehmann, C. Behringer, K. Hartman, and W. Simon, *Pure Appl. Chem.*, **1989**, 61, 1613.
14. I. Badr, R. Johnson, M. Diaz, M. Diaz, M. Hawthorne, and L. Bachas, *Anal. Chem.*, **2000**, 72, 4249.
15. J. P. Desvergne and A. W. Czamic (ed.), "Chemosensors for Ion and Molecule Recognition", **1997**, Kluwer Academic Publishers, Boston.
16. A. Prasanna de Silva, H. Q. Nimal Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, and T. E. Rice, *Chem. Rev.*, **1997**, 97, 1515.
17. M. F. Choi, K. Chang, and X. Wu, *Talanta*, **2002**, 56, 1027.
18. A. A. Ensafi and A. Kazemzadeh, *Microchem. J.*, **2002**, 72, 193.
19. T. Rostazin, E. Bakker, K. Suzuki, and W. Simon, *Anal. Chim. Acta*, **1993**, 280, 197.
20. G. J. Moody, R. B. Oke, and J. D. R. Thomas, *Analyst*, **1970**, 95, 910.
21. M. A. Simon and R. P. Kusy, *Polymer*, **1993**, 34, 5106.
22. A. D. C. Chan and D. J. Harrison, *Talanta*, **1994**, 41, 849.
23. P. Anker, E. Wieland, D. Amman, R. E. Dohner, R. Asper, and W. Simon, *Anal. Chem.*, **1981**, 53, 1970.
24. D. Ammann, R. Bissig, M. Guggi, E. Pretsch, W. Simon, I. J. Borwitz, and I. Weiss, *Helv. Chim. Acta*, **1981**, 58, 1970.
25. E. Bakker, A. Xu, and E. Pretsch, *Anal. Chim. Acta*, **1994**, 295, 233.
26. N. Alizadeh, A. Momeni, and M. Shamsipur, *Anal. Chim. Acta*, **2002**, 464, 187.
27. T. G. Whinston and G. W. Cherry, *Analyst*, **1962**, 87, 816.