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Synthesis of Fe(III) and Co(II) Thia-Containing Schiff Base Complex and Applications for Optical Chemosensor

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A new optode membrane for the sensitive and selective determination of thiocyanate ion based on a change in absorption spectrum of a polymer film, is proposed. A membrane composed of plasticized poly vinyl chloride (PVC), Fe(III) and Co(II) Schiff-base complex as chromo-ionophore and hexadecyl trimethyl ammoniuom bromide (HDTMABr) as cationic additive was prepared. The influence of different plasticizers was studied for the sensitivity, linear range, 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. The optical film based on Fe(III)-complex responds to thiocyanate ion reversibly over a wide dynamic range 1.0×10^{-7} 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.

Key Words: Chemosensor, Thiocyanate ion, Schiff base, Polymeric film, Chromoionophore.

INTRODUCTION

There is a high demand for anion sensors which function in water, 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. Some lipophilic organometallic compounds and metalloporphyrin derivatives were reported as unusual anion ionophores that have specific anion selective behaviour, which is different from those of the classical anion exchange, when they were used as the anion sensing component of polymeric membrane electrodes[3]. Their anion selectivity were mainly governed by the specific metal-ligand interactions between the center metal and

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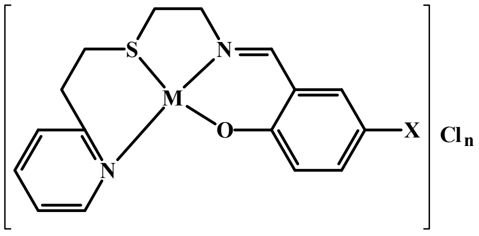
anions rather than the lipophilicity of the anions or simple opposite charge interactions with anions. Therefore, there are possibilities for the additioned investigations of the interaction between organometals and anions will lead to the development of novel anion sensing ligands for an anion selective electrodes[4].

Schiff bases have often been used as chelating ligands in the field of coordination chemistry and their metal complexes are of great interest for many years. It is well known that N and S atoms play a key role in the coordination of metals at the active sites of numerous metallobiomolecules[5]. Schiff base metal complexes have been widely studied because they have industrial, antifungal, antibacterial, anticancer and herbicidal applications[6,7]. They serve as models for biologically important species and find applications in biomimetic catalytic reactions. Chelating ligands containing N, O and S donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions. It is known that the existence of metal ions bonded to biologically active compounds may enhance their activities[8-10]. The variety of possible Schiff base metal complexes with wide choice of ligands and coordination environments, has prompted us to undertake research in this area[11]. As a part of our continuing work on dissymmetric tetradentate Schiff base complexes containing N, S and O donor atoms and in light of the importance of Fe(III) and Co(II) ion metals, the synthesis and characterization of iron(III) and cobalt(II) azo derivative complexes of the tetradentate unsymmetric Schiff base ligand 2-((E)-(2-(2-(pyridine-2-yl)ethylthio)ethylimino)methyl)-4-azophenol and a brief study of its coordination behaviour with different anion in non-aqueous solvent and analytical applications are reported.

The importance of determing 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 are leached with solutions containg cyanide. For efficient plant control it is important continuously to monitor and determine the level of thiocyanate and the subsequent consumption of the free cyanide in these process solutions[12]. 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 intake of thiocyanate-containing foods such as milk and cheese. Higher concentration of this ion, which is a metabolic product of cyanide, arises from tobacco smoke. Thus, the level of thiocyanate is considered a good probe for distinguishing between smokers and non-smokers[13]. The aim of the present work is to develop a new procedure for the selective determination of thiocyanate in different sample solutions. To best of our knowledge, there is no report to synthesis and application of this pyridine unit and thia group containing Schiff base metal complex L_1 and L_2 for construction optical sensors. In the recent years, we have reported the selective sensors for important cations, anions and drugs in different samples[14-17].

EXPERIMENTAL

Reagents grade dioctyl phthalate (DOP), dioctyl sebacate (DOS), hexadeyl trimethyl ammonium bromide (HDTMABr), nitrophenyl octyl ether (NPOE), 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 Schiff base complexes (Fig. 1) synthesized and used after recrystallization. Doubly distilled deionized water was used throughout.



L_1 (M=Fe), L_2 = (M=Co), X = N_2Ph

Fig. 1. Chemical structure of tested chromoionophore

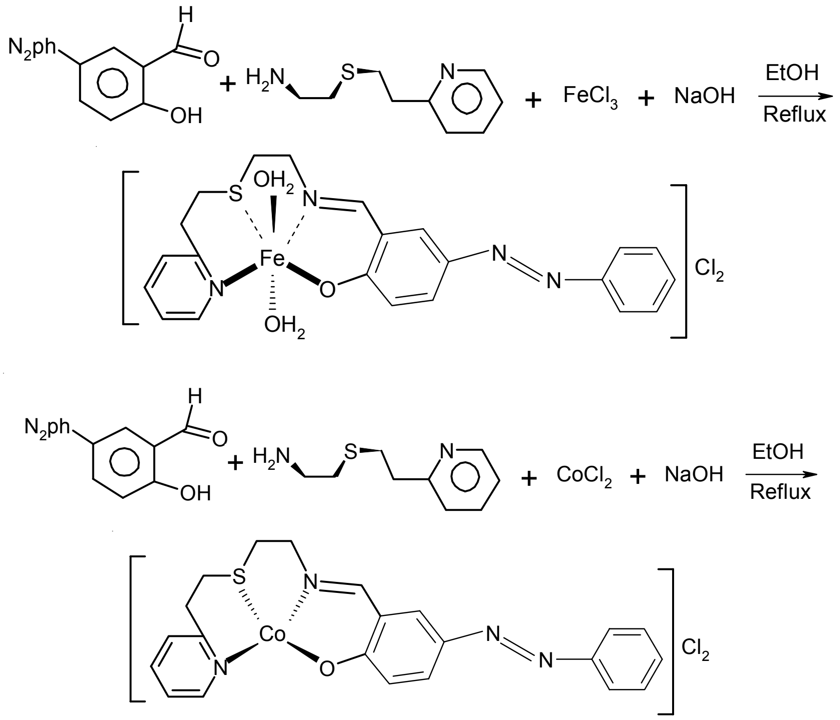
All Absorbance measurements were carried out with a Perkin-Elmer double beam spectrophotometer with quartz cells. A Metrohm combined pH glass electrode was used for pH measurement at 25.0 ± 0.1 ºC.

Synthesis of Fe(III) and Co(II) complexes: The target Schiff base metal-complexes L_1 and L_2 was synthesized from in one-step according to the following procedure **Scheme-I**. The structure of the product was confirmed by ^{1}H NMR, CHN analysis and IR spectrum.

Preparation of optode films: The general procedure to prepare the PVC membrane was to mix thoroughly 30 mg of powdered PVC and 2 mg of hexadecyltrimethyl ammonium bromide with 66 mg of nitrophenyl octyl ether as solvent mediator in the minimum amount of THF. To this mixture was added 1 mg of chromoionophores L_1 or L_2 and the solution was mixed well. The resulting mixture by using a laboratory-made spin-on-device, were cast two identical membranes of 5 µm thick cast on two glass plates that were subsequently mounted in the UV-visible quartz cell. Blank reference membranes were prepared in a similar way, except without using chromo-ionophores.

RESULTS AND DISCUSSION

In order to find a clue about the stability and selectivity of new complexes, in the preliminary studies, the UV-visible spectra of L_1 and L_2 with different important anions in acetonitrile solution were investigated. When a 8.0×10^{-5} M solution of each ligand in acetonitrile was titrated with standard solutions of different anions, a rapid colour change occurred after the addition of thiocyanate ion (Fig. 2). As seen



Scheme-I: General procedure for synthesis of complexes

in Fig. 2, a decrease in the absorption UV-band of Fe(III)-complex at 376 nm and increase in the absorption band of complex at 245 nm. While adding other anions, including I^-, Br^-, SO_4^{2-}, NO_3^-, NO_2^-, ClO_4^- and Sal^- spectral changes was not observed in the sensing solution. This high selectivity was attributed to the formation of new adduct between the Fe(III) in the center of complex and the thiocyanate ion[18]. Thus, on the basis of this selectivity L_1 compound has stronger interaction and was expected to act as a selective chromoionophore in the preparation of a PVC-based ion selective optode for SCN^-. Thus, L_1 is used in the preparation of membrane films for experiments.

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 aqueous solution phase (aq) and L_1 in membrane phase (mem) and equilibrium is established with the formation of a m:n complex[19,20]:

$$m\,SCN^-\,(aq) + n\,L(mem) \rightleftharpoons SCN^-_{(m)}\,(L)_n\,(mem) \qquad (1)$$

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:

$$K = [\,SCN^-_{(m)}\,(L)_n]\,(mem)\,/\,[SCN^-(aq)]^m[L]^n \qquad (2)$$

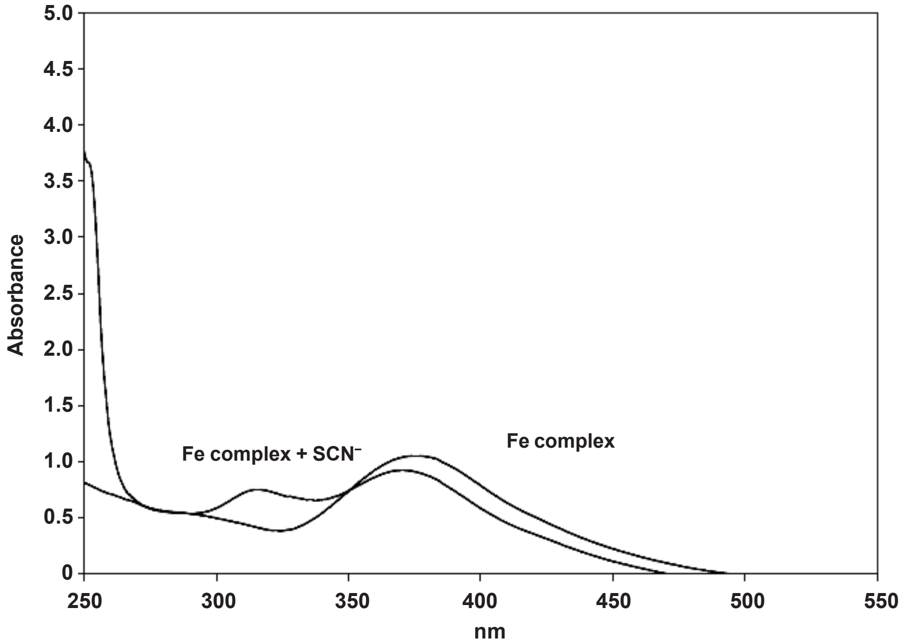


Fig. 2. Absorption spectra of L_1 after equilibration with 8×10^{-5} M concentration of thiocyanate ion

The relative absorbance intensity is defined as the ratio of uncomplexed L in the membrane phase, $[L]_{org}$, to its total amount, $[C_T]_{org}$, so that:

$$\alpha = [L]_{org} / [C_T]_{org} \tag{3}$$

In pratice, the α-value during titration of membrane with SCN^- ions can be determined by measuring the absorption intensity of the optical sensor, A in λ = 466 nm,

$$\alpha = (A-A_0) /(A_I - A_0)$$

where A_0 and A_I are the limiting absorption intensities of the optical sensor at $\alpha = 0$ (uncomplexed L) and $\alpha = 1$ (totally complexed L), respectively. The relationship between the α-value and the concentration of SCN^- ion in aqueous sample solution, $[SCN^-]aq$, can be obtained from eqns. 2 and 3 as follows:

$$\alpha^n/(1-\alpha) = 1/nK[C_T]^{n-1}[SCN^-]^m \tag{4}$$

Eqn. 4 could be used as a basis for the quantitative determination of thiocyanate ion concentrations using the proposed optical sensor.

It is well known that the membrane film composition may largely influence the response characteristics and working concentration range of the optical sensors[21,22]. Thus, in this work, five PVC-membranes with about the same plasticizer/PVC ratios, but 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

TABLE-1
OPTIMIZATION OF OPTODE MEMBRANE FILM INGREDIENTS

Membrane No.	PVC	Plasticizer	L_1	Additive (HDTMABr)	Linear range (M)
1	30	NPOE, 69	1	-	1×10^{-4}–1×10^{-7}
2	30	NPOE, 67	1	2	1×10^{-3}–1×10^{-8}
3	30	DOP, 67	1	2	1×10^{-4}–1×10^{-7}
4	30	DOS, 67	1	2	1×10^{-5}–1×10^{-8}
5	30	NPOE, 66	2	2	1×10^{-3}–1×10^{-6}

the response membrane characteristics at a plasticizer/PVC ratio[1] of about 2. 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[23].

Thus, the proposed thiocyanate selective optosensor containing L_1 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 the working concentration range of the sensor (Table-1), but also caused its prolonged response time and reduced selectivity[24].

The presence of 66-69 % plasticizer in the PVC-membranes resulted in optimum physical properties, as well relatively high mobilities of their constituents[25-27]. The nature of plasticizer is well known to influence considerably the measuring range of the solvent polymeric membrane sensors and their selectivity coefficients[28,29]. As is obvious from Table-1, the use of NPOE as plasticizer resulted in a large widening of measuring range of the proposed optical sensor over the membrane based on DOP and DOS due to the increased polarity of NPOE.

The influence of 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 HNO_3 or NaOH) and the results are shown in Fig. 3. As it is seen response of the sensor is remain 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 the protonation of the ion carrier and 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 optimal experimental conditions. The resulting calibration graph for SCN^- ions were obtained at 466 nm. The dynamic concentration range of the proposed sensor based on L_1 for SCN^- ion was 1.0×10^{-7} to 1.0×10^{-3} M. The limit of detection, as determined based on the 3σ of the blank membrane film was 5.0×10^{-8} M The static response time obtained for the sensor is only about 70 s, over entire concentration range. The optode membrane films could be used at least 4 weeks when stored in the dark environment and dry when not in use.

In order to investigate the selectivity of the proposed optosensor toward SCN^- with respect to various interfering ions, the selectivity coefficients (K_{SCN}^{opt}), describing the performance of the new sensor for an interfering ion, B, relative to SCN^- ion, A,

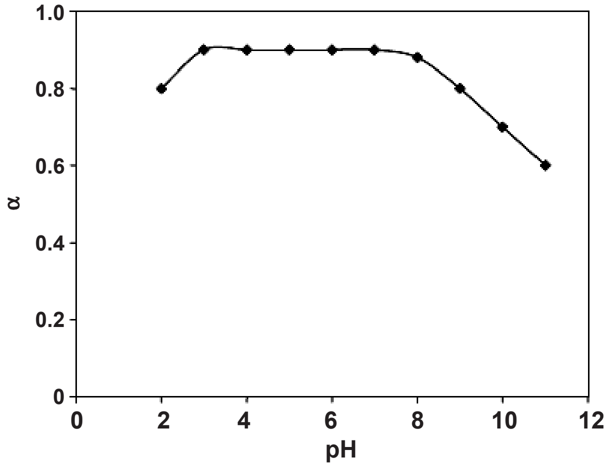


Fig. 3. Effect of the pH on the optical response of the proposed SCN^--selective optosensor

were determined by the separate solution method (SSM)[18-28]. The resulting K_{SCN}^{opt} values are summarized in Table-2. As seen, the selectivity pattern is $SCN^- > I^- > ClO_4^- > NO_3^- > NO_2^- > Cl^- > F^- > SO_4^{2-} > SO_3^{2-}$. From the data given in Table-2, it is obvious that the proposed thiocyanate sensor is highly selective with respect to other anions.

TABLE-2
SSM OPTICAL SELECTIVITY COEFFICIENT OF VARIOUS INTERFERING ANIONS

Anion	log $K_{SCN,A}^{opt}$	Anion	log $K_{SCN,A}^{opt}$
I^-	-2.5	NO_3^-	-4.0
F^-	-5.0	NO_2^-	-3.9
SO_3^{2-}	-5.3	ClO_4^-	-2.5
SO_4^{2-}	-5.1	Cl^-	-4.0

The proposed optical sensor was also successfully applied to the direct determination of thiocyanate in samples from the smoker and non-smoker urine and saliva. Urine and saliva 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 colorimetric method[30]. The results for three replicate are presented in Table-3.

TABLE-3
DETERMINATION OF THIOCYANATE IN URINE SAMPLES

Sample	SCN^- (mmol L^{-1})	
	Proposed method	Colorimetric method
Nonsmoker urine	0.24 ± 0.05	0.25 ± 0.05
Smoker urine	0.75 ± 0.05	0.76 ± 0.08

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