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# New thiocyanate potentiometric sensors based on sulfadimidine metal complexes: Experimental and theoretical studies



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## ABSTRACT

Three sulfadimidine metal complexes ( $M = \text{Fe(III)}$ ,  $\text{Cu(II)}$ , and  $\text{Ag(I)}$ ) were prepared, characterized, and examined as neutral carriers for the determination of  $\text{SCN}^-$  using modified carbon paste electrode. These sensors were successfully applied in the pure samples, and biological fluids. The electrode mechanism was investigated by UV–vis and FT IR. The experimental studies were complemented by quantum chemical calculations at DFT/B3LYP level of theory. The best performance was observed for  $\text{Cu(II)}$  electrode (**C**) containing 7.0% complex, 53.0% *o*-nitrophenyloctyl ether, 37.0% graphite and 3.0% cetylpyridinium chloride, and also for  $\text{Fe(III)}$ -electrode (**A**) having 6.0% complex, 52.0% *o*-nitro phenyloctyl ether, 40.5% graphite and 2.5% cetylpyridinium chloride.

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## 1. Introduction

Chemically modified carbon paste electrodes (CMCPs) were successfully applied as potentiometric sensors for determination of various species (Abu-Shawish and Saadeh, 2007; Kalcher et al., 1995; Pei et al., 1991). Compared to the other types of ion selective electrodes, CMCPs are extremely simple to prepare, easy to regenerate, have stable response and very low ohmic resistance (Svancara and Schachi, 1999; Vytras et al., 1997), probably due to the formation of a very thin film of pasting liquid coated onto small particles of carbon powder (Svancara et al., 1996).

Thiocyanate is widely used in medicine, dyeing, photography, and prevention of erosion. When chlorinated, thiocyanate is converted to the highly toxic and volatile cyanogen chloride. Therefore, the determination of thiocyanate in food, waste water, and biological samples is of important practical significance. Several thiocyanate ion-selective electrodes based on a variety of ion carriers (Ardakani et al., 2002; Singh et al., 2007; Xu et al., 2009; Yuan et al., 2003; J.Y. Dai et al., 2005) were reported. Most of these electrodes have high detection limit, and/or narrow working concentration range or have serious interfering affect of other anions such as  $\text{I}^-$ ,  $\text{ClO}_4^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{IO}_4^-$  (Xu et al., 2009; J.Y. Dai et al., 2005; Erden et al., 2006; Huang et al., 2004). These electrodes showed apparently deviation from the Hofmeister sequences, due to the unique interaction of the central

metals with anion rather than from the hydration free energy change. So, the search for new carriers with non-Hofmeister sequence is still a challenging area of research for chemists in the field of electrochemical sensors.

Sulfadimidine (SD) is clinically the most used sulfa-drug in veterinary medicine as antibacterial agent to treat livestock diseases such as gastrointestinal and respiratory tract infections. Structural studies of sulfadimidine metal complexes ( $M = \text{Cu(II)}$  (Tommasino et al., 2011),  $\text{Fe(III)}$  (Tella and Obaleye, 2010),  $\text{Pt(II)}$ , and  $\text{Ru(III)}$  (Mansour, 2013)) were reported. Both  $\text{Fe(III)}$ - and  $\text{Cu(II)}$ -SD complexes have been synthesized from HSD in presence of ammonia as a deprotonating agent. In the present work, three sulfadimidine metal complexes (Fig. 1) were prepared, characterized, and explored as neutral ionophores for the determination of  $\text{SCN}^-$  using CMCP electrode. The ionic sites of the reported ionophores in the membrane bulk are necessary to improve the electrode selectivity by reducing the membrane resistance and the interference from lipophilic counterions (Morf, 1981; Bakker et al., 1997). In addition, quantum chemical calculations were performed to elucidate and explore the working mechanism of the prepared electrodes.

## 2. Experimental

### 2.1. Chemicals

Graphite powder, KSCN,  $\text{AgNO}_3$ , sodium tetraphenylborate (NaTPB), cetylpyridinium chloride (CPC), cetyltrimethylammonium bromide (CTAB) and the plasticizers, *o*-nitrophenyloctyl ether

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(*o*-NPOE), dioctyl phthalate (DOP), dibutyl-butyl phosphonate (DBBP) were purchased from Aldrich chemical company, USA.  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , were supplied from Oxford laboratory products, Mumbai, India. To investigate the selectivity of the proposed electrodes, the following sodium salts were used,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{I}^-$ ,  $\text{F}^-$ ,  $\text{SO}_3^{2-}$ ,  $\text{ClO}_4^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{CH}_3\text{COO}^-$ , oxalate, and salicylate.

## 2.2. Apparatus

Digital Jenway 4330 conductivity-pH meter with 1.02 cell constant was used for potential, pH and conductance measurements. A SENTEK R1/2MM Ag/AgCl electrode was used as the outer reference electrode. UV/vis spectra were recorded on a Shimadzu Lambda 4B spectrophotometer. Elemental microanalysis was performed using Elementer Vario EL III. Mass spectra were recorded with the aid of a SHIMADZU QP-2010 PLUS mass spectrometer (at 70 eV). The thermal analysis (TGA/DTA) was carried out in dynamic nitrogen atmosphere ( $20 \text{ mL min}^{-1}$ ) with a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  in platinum crucible using DTG-60H SIMULTANEOUS DTA-TG APPARATUS-SHIMADZU. FT IR-460 plus JASCO  $4000\text{--}400 \text{ cm}^{-1}$  KBr pellets was used for IR spectra. INSPECT-S FEI Company electron scanning microscope was used for surface scanning.

## 2.3. Preparation of sulfadimidine complexes

The Fe(III), Cu(II), and Ag(I) sulfadimidine complexes (FeSD<sub>3</sub>, CuSD<sub>2</sub>, and AgSD) were prepared by adding 20 mL aqueous solution containing 3, 2, and 1 mmol of sodium sulfadimidine (NaSD) to 10 mL aqueous solution (1 mmol) of  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{AgNO}_3$ , respectively, where solid complexes were precipitated (Herole and Velingkar, 2011). Besides, another Fe(III)–SD (1:3 M:L) complex was synthesized from  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ .

## 2.4. Preparation of modified carbon paste electrodes

The modified paste was prepared by mixing the appropriate weight of the complex and high purity graphite with acetone. The mixture is homogenized, left at room temperature to evaporate acetone, then a weighed amount of plasticizer is added and a very intimate homogenization is then achieved by careful mixing with agate pestle in agate mortar. The paste is then packed into the hole of the electrode body. The carbon paste was used directly for potentiometric measurements without preconditioning (Issa et al., 2012). All EMF measurements were carried out with the following cell assembly:

Ag//AgCl, KCl (3M)//test solution//filling graphite modified paste//carbon paste electrode

## 2.5. Selectivity of the sensor

Potentiometric selectivity factor ( $K_{A,B}^{\text{pot}}$ ) was evaluated using two methods, the matched potential method (MPM) (Umezawa et al., 2002) and separate solution method (SSM) (Umezawa et al., 2000). In MPM, the selectivity coefficient was calculated using the following equation:

$$K_{A,B}^{\text{pot}} = \frac{a_A' - a_A}{a_B}$$

where  $a_A'$  is the initial concentration of the analyte,  $a_A$  is the concentration of the added analyte, and  $a_B$  is the concentration of the added interferent producing the same potential change.

In SSM, the selectivity coefficient was calculated using the following equation:

$$K_{A,B}^{\text{pot}} = \frac{E_B - E_A}{S} + \left(1 - \frac{Z_A}{Z_B}\right) \log a_A$$

where  $E_A$ , and  $E_B$  are the electrode potentials of  $1 \times 10^{-3} \text{ mol L}^{-1}$  solution of each of thiocyanate and interfering anion,  $Z_A$ , and  $Z_B$

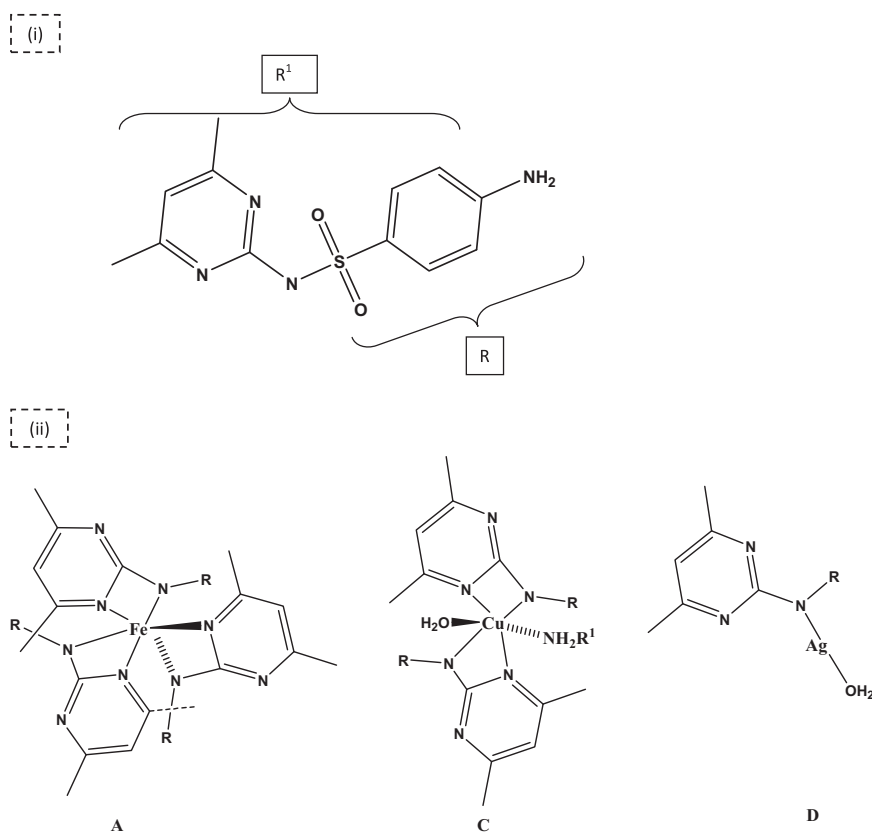


Fig. 1. (i) Structure of sulfadimidine anion (SD<sup>-</sup>), and (ii) structures of ionophores (A, C, and D).

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