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Interaction between an organometallic mediator and thiosulfate as an inorganic salt; A new strategy in elecrocatalytic investigation

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Abstract: In this study, we describe interaction between ferrocenemonocarboxylic acid as a organometallic mediator and thiosulfate as a ionrganic salt at as surface of modified multiwall carbon nanotubes paste electrode. This interaction showed a very efficient electrocatalytic activity for the anodic oxidation of thiosulfate, owing to a substantial decrease in the anodic overpotential. Under the optimized conditions, the electrocatalytic oxidation peak current of thiosulfate showed two linear dynamic ranges with a detection limit of 0.1 μmol L^{-1} thiosulfate. This method was also examined as a new electrochemical sensor for the determination of thiosulfate in real samples such as water and waste water.

Keywords: Organometallic mediator, Inorganic salt, Water and waste water analysis, Electrocatalysis, Voltammetry.

Introduction

Organometallic chemistry is the study of chemical compounds containing bonds between carbon and a metal [1, 2]. Since many compounds without such bonds are chemically similar, an alternative may be compounds containing metal-element bonds of a largely covalent character. Organometallic chemistry combines aspects of inorganic chemistry and organic chemistry. Organometallics find practical uses in stoichiometric and catalytic processes, especially processes involving carbon monoxide and alkene-derived polymers. All the world's polyethylene and polypropylene are produced via organometallic catalysts, usually heterogeneously via Ziegler-Natta catalysis [3].

The determination of reduced sulfur species such as

thiosulfate is important in many environmental and industrial situations, particularly when monitoring anoxic waters [4], process liquors and wastewaters from paper mills [5, 6], photographic laboratories [7,8], and off-shore oil-drilling operations [9]. Large amounts of thiosulfate anions are present in spent fixing baths. Silver from such solutions is usually recovered electrolytically [7]. In order to minimize unwanted environmental contamination the conversion of thiosulfate to sulfate is necessary. In the body, thiosulfate converts small amounts of cyanide ion into harmless products and plays a role in the biosynthesis of cysteine, a sulfur-containing amino acid that locks proteins into their correct three-dimensional shapes. Thiosulfate is not found in large quantities in nature. It is routinely used as a titrant to determine concentrations of oxidants such as hypochlorite in bleach and dissolved oxygen in water. It instantly dechlorinates water, and is used to stop bleaching

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action in the paper-making industry. Thiosulfate forms water-soluble complexes with many metals, making it useful in photo processing (where it dissolves excess silver bromide on the surface of exposed film, preventing excessive darkening). Thiosulfate is also useful in the extraction of silver from silver ore, in leather manufacture. Therefore, measurement of this kind of materials seems to be very important from industrial view point.

Electrochemical sensing based on carbon nanotubes (CNTs) is now a developed research field [10-16]. Since the ''rediscovery'' of CNTs by Iijima in 1991 [17], a wealth of properties has been reported. The extraordinary electrochemical features of CNTs make them suitable for use in Faradaic processes (e.g., the fast electron transfer kinetics of CNTs, due to the presence of edge plane graphite sites within the walls and at the ends of CNTs [18]) or in non-Faradaic processes such as the large changes in conductance when CNTs, due to the presence of the cloud of electrons surrounding their walls, can accept or with draw charges from or to molecules in their nearest chemical environment.

In this paper, we describe the use of ferrocenemonocarboxylic acid as a mediator for the electrooxidation of thiosulfate in aqueous media. In addition, the suitability of the ferrocenemonocarboxylic acid modified carbon nanotubes paste electrode (FAMWCNTPE) in the electrocatalysis and determination of thiosulfate are discussed by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and double potential step chronoamperometry.

Results and discussion

Mechanism suggestion:

To our knowledge, there is no any report for investigation of interaction between ferrocenemonocarboxylic acid and thiosulfate under electrochemical process. Therefore, we suggest a mechanism for this process in a voltammetric condition (under control potential in electrochemical cell) and in continuous determine Kinetic and thermodynamic parameter using this mechanism (see scheme 1).

SEM Characterization of FAMWCNTPE:

Structure of FAMWCNTPE was examined using scanning electron microscope (SEM). Fig. **1A** shows the presence of ferrocenemonocarboxylic acid in the carbon nanotubes paste matrixes. Note that no mediator particle is shown at the unmodified carbon nanotubes paste electrode (Fig. **1B**).

Electrochemistry of mediator:

The electrochemical properties of the modified electrode were studied by cyclic voltammetry in a buffer solution (pH 7.0). The experimental results showed a well-defined and reproducible anodic and cathodic peaks related to Fc/Fc^+ redox couple with quasi-reversible behavior, with peak separation potential of ΔE_p $(E_{pa}-E_{pc})=80$ mV. These cyclic voltammograms were used to examine the variation of the peak currents vs. the potential scan rates. The plots of the anodic and cathodic peak currents were linearly dependent on $\nu^{1/2}$ at the all scan rates. This behavior indicates that the nature of redox process is diffusion controlled.
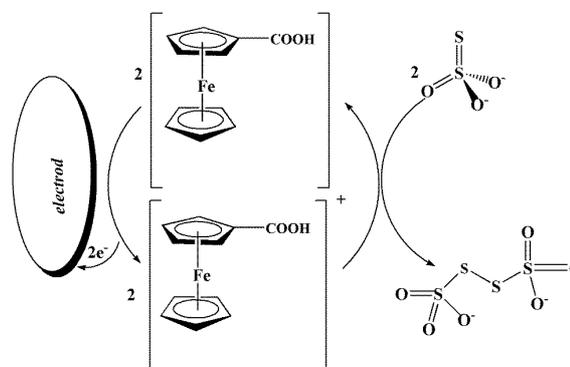
Scheme 1: Propose mechanism for electrochemical interaction between ferrocenecarboxylic acid and thiosulfate.
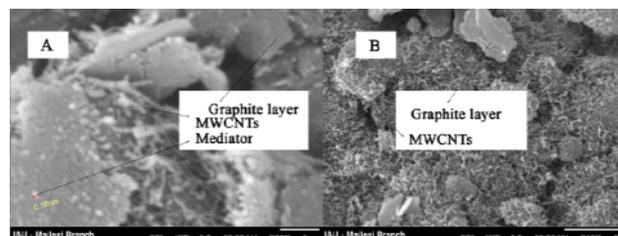
Figure 1: SEM image of A) FAMWCNTPE; B) Unmodified CNTPE.

Catalytic effect:

Figure **2**(b–e) shows the cyclic voltammetric responses from electrochemical oxidation of 100 μmol L^{-1} thiosulfate at different electrodes including FAMWCNTPE (curve c), ferrocenemonocarboxylic acid-modified carbon paste electrode (FAMCPE) (curve b), carbon nanotubes paste electrode (CNTPE) (curve d), and carbon paste electrode (curve e). However, curve a shows cyclic voltammogram FAMWCNTPE in the buffer solution (pH 7.0). The anodic peak potential for thiosulfate oxidation at FAMWCNTPE (curve c) and at FAMCPE (curve b) was about 510 mV, while at CNTPE (curve d) was

about 870 mV. The peak potential of thiosulfate was about 900 mV (curve e) at the unmodified carbon paste electrode (CPE). Based on these results, the best electrocatalytic effect for thiosulfate oxidation was found at FAMWCNTPE (curve c). The peak potential of thiosulfate oxidation at FAMWCNTPE (curve c) was shifted by about 360 and 390 mV toward negative values in compared with that at CNTPE (curve d) and at CPE (curve e), respectively. Similarly, the anodic peak current for the oxidation of thiosulfate at FAMWCNTPE (curve c) was significantly enhanced in comparison to that at FAMCPE (curve b). The data clearly shows that the combination of multiwall carbon nanotubes and the mediator definitely improves the characteristics of thiosulfate oxidation. FAMWCNTPE in 0.1 mol L^{-1} phosphate buffer (pH 7.0) and without thiosulfate in solution exhibited a well-behaved redox reaction (curve a).
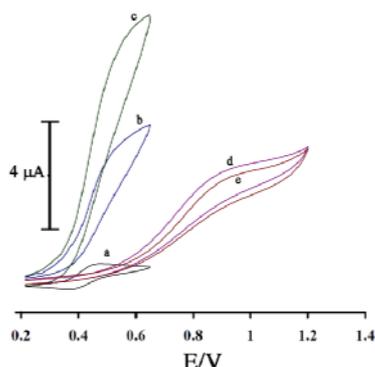
Figure 2: Cyclic voltammograms of 0.1 mol L^{-1} PBS (pH 7.0) with a scan rate of 20 mV s^{-1} for: (a) in the absence and (b) in the presence of 100.0 μmol L^{-1} thiosulfate at FAMWCNTPE; (b) is as (c) at FAMCPE; (d) and (e) are as (b) at CNTPE and CPE, respectively.

In order to obtain information on the rate determining step, a Tafel plot was developed for FAMWCNTPE, using the data derived from the raising part of the current–voltage curve (Fig. **3**, inset A). The slope of the Tafel plot is equal to n(1−α)F/2.3RT which comes up to 6.0287 V decade^{-1}. Assuming n = 1, then α = 0.64.

In addition, the value of αnα (n$_α$ is the number of electrons involved in the rate determining step) was calculated for the oxidation of thiosulfate at pH 7.0 for both the modified and unmodified carbon nanotube paste electrodes using the following equation [19,20]:

$$\alpha n_\alpha = 0.048/(E_P - E_{P/2}) \qquad (1)$$

where $E_{P/2}$ is the potential corresponding to $I_{P/2}$. The values for αn$_α$ were found to be 0.64 and 0.20 at the

surface of both FAMWCNTPE and the unmodified carbon nanotube paste electrode, respectively. These values showed that the over-potential of thiosulfate oxidation is reduced at the surface of FAMWCNTPE, and also that the rate of electron transfer process is greatly enhanced. This phenomenon is, thus, confirmed by the larger I_{pa} values recorded during cyclic voltammetry at FAMWCNTPE.
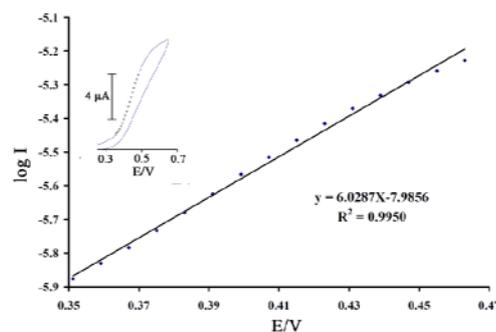
Figure 3: Tafel plot for FAMWCNTPE in 0.1 mol L^{-1} PBS (pH 7.0) with a scan rate of 20 mVs^{-1} in the presence of 100 μmolL^{-1} thiosulfate.

Also, a plot of peak height (I_p) versus the square root of the scan rate ($v^{1/2}$), over the range of 2 – 20 mV s^{-1}, was constructed. This plot was found to be linear, suggesting that the process (at sufficient overpotential) was diffusion rather than surface controlled (Not shown).

The catalytic oxidation of thiosulfate by FAMWCNTPE was also studied by chronoamperometry. Chronoamperometric measurements using different concentrations of thiosulfate at FAMWCNTPE were performed by setting the working electrode potential to 300 mV (step 1) and 600 mV (step 2) (Fig. **4A**).
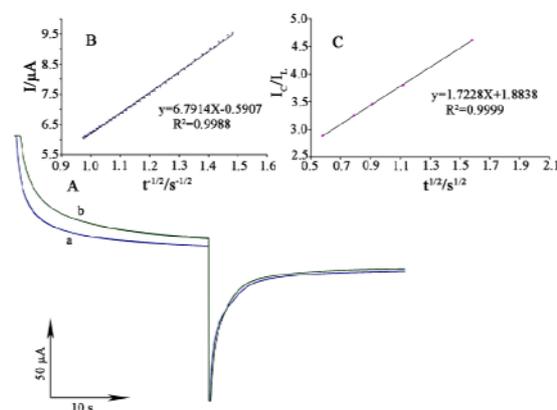
Figure 4: A) Chronoamperograms obtained at FAMWCNTPE in the absence (a) and in the presence of (b) 100.0 μmol L^{-1} thiosulfate in a buffer solution (pH 7.0). B)

Cottrell's plot for the data from the chronoamperogram. (C) Dependence of I_C/I_L on the $t^{1/2}$ derived from the chronoamperogram data.

In chronoamperometric studies, we have determined the diffusion coefficient (D) of thiosulfate. Experimental plots of I versus $t^{-1/2}$, with the best fits for different thiosulfate concentrations, were employed. The slopes of the resulting straight lines were then plotted versus thiosulfate concentrations (Fig. **4B**). Using the Cottrell equation and these slope values, we calculated a diffusion coefficient of 4.7×10^{-5} cm^2 s^{-1} for thiosulfate.

The rate constant for the chemical reaction between thiosulfate and redox sites in FAMWCNTPE, k_h can be evaluated by chronoamperometry according to the method described in [19]:

$$I_C/I_L = \pi^{1/2} \gamma^{1/2} = \pi^{1/2} (K_h C_b t)^{1/2} \qquad (2)$$

Where I_C is the catalytic current of FAMWCNTPE in the presence of thiosulfate and I_L is the limited current in the absence of thiosulfate, C_b is the bulk concentration of thiosulfate (mol L^{-1}), k_h and t are the catalytic rate constant (M^{-1} s^{-1}) and time elapsed (s) respectively. The above equation can be used to calculate the rate constant of catalytic process (k_h). The value of k_h can be simply calculated for a given concentration of substrate from the slope of I_C/I_L versus $t^{1/2}$ plot. The calculated value of k_h is 9.452×10^3 M^{-1} s^{-1} using the slope of I_C/I_L-$t^{1/2}$ plot (Fig. **4C**). This value of k_h explains as well as the sharp feature of the catalytic peak observed for catalytic oxidation of thiosulfate at the surface of FAMWCNTPE.

Electrochemical impedance spectroscopy studies:

Figure **5** presents Nyquist diagrams of the imaginary impedance (Z_{im}) vs. the real impedance (Z_{re}) of the EIS obtained at the modified electrode recorded at 0.4 V dc-offset in the absence (curve a) and in the presence of 300 µmol L^{-1} thiosulfate (curve b) in 0.1 mol L^{-1} PBS (pH 7.0), respectively. In the absence of thiosulfate, the Nyquist diagram comprises a depressed semicircle at high frequencies which may be related to the combination of charge transfer resistance of ferrocenemonocarboxylic acid electrooxidation and the double-layer capacitance, followed by a straight line with a slope of nearly 45°. The latter is due to the occurrence of mass transport process via diffusion. In the presence of thiosulfate, the diameter of the semicircle decreases, confirming the electrocatalytic capability of the mentioned electrocatalyst for oxidation of thiosulfate. This is due to the instant

chemical reaction of thiosulfate with the high-valence ferrocenemonocarboxylic acid species. The catalytic reaction of oxidation of thiosulfate that occurred via the participation of ferrocenemonocarboxylic acid species virtually caused an increase in the surface concentration of low valence species of electrocatalyst, and the charge transfer resistance declined, depending on the concentration of thiosulfate in the solution.
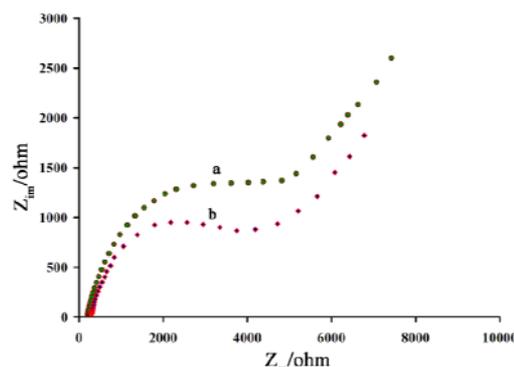
Figure 5: Nyquist diagrams of FAMWCNTPE in the absence (a) and presence of (b) 5300.0 µmol L^{-1} thiosulfate at pH 7.0. Bias is 0.40 V with E_{ac}=5 mV with frequency range of 10 kHz to 1.0 Hz.

Dynamic range and limit of detection:

Cyclic voltammetry method was used to determine the concentration of thiosulfate. The plot of peak current vs. thiosulfate concentration consisted of two linear segments with slopes of 0.0211 and 0.0149 µA/µmol L^{-1} in the concentration ranges of 0.5–70.0 µmol L^{-1} and 70.0–450.0 µmol L^{-1}, respectively. The decrease in sensitivity (slope) of the second linear segment is likely due to kinetic limitation. The detection limit (3σ) of thiosulfate was found to be 0.1 µmol L^{-1}.

Interference study and real sample analysis:

The influence of various substances as compounds potentially interfering with the determination of thiosulfate were studied with 3.0 µmol L^{-1} thiosulfate. The potentially interfering substances were chosen from the group of substances commonly found with thiosulfate in water samples. The tolerance limit was defined as the maximum concentration of the interfering substance that caused an error of less than ±5% for the determination of thiosulfate. The result of interfering studied showed that many substances such as Ni^{2+}, CN^-, Ca^{2+}, Br^-, Ag^+, Zn^{+2}, SO_4^{2-}, Pb^{+2}, Mn^{+2}, and SCN^- did not any interferences (about 800–fold) for electroctalytic determination of thiosulfate using the modified electrode. However, 500–fold sulfide

(after removal with 1.0 mmol L^{-1} Zn(II)) did not any affect for the electroctalytic determination of thiosulfate.

Real sample analysis:

In order to demonstrate the ability of the sensor for analysis of thiosulfate in a real sample, we examined this ability of the sensor in determining thiosulfate in color fixing waste water, film fixing waste water photographic effluents, water and urine samples. The determination of thiosulfate in samples was carried out by the standard addition method. The results obtained are given in Tables **1** and **2**. The results suggest that the present method is comparable with the standard method (oxidation-reduction titration in acid solution of KIO$_3$/KI in the presence of starch as indicator).

Table 1: Results of the analysis of photographic waste samples.

Sample	Thiosulfate (mg/l)	Iodimetry
	Present method mean (n=4)	
Color fixing waste [1]	48.5±1.1	49.3±1.9
Color fixing waste [2]	45.2±1.5	44.2±2.1
Film fixing waste[1]	50.5±1.8	50.0±2.0
Film fixing waste[2]	52.6±1.7	51.9±1.5

Table 2: Results of the analysis of water and urine samples.

Sample	Added (μmol L^{-1})	Expected (μmol L^{-1})	Founded (μmol L^{-1})	Standard method (μmol L^{-1})
Drinking water	—	—	<Limit of detection	<Limit of detection
	5.00	5.00	5.23±0.31	5.33±0.45
	15.00	20.00	20.55±0.61	21.01 ±1.23
River water[1]	—	—	<Limit of detection	<Limit of detection
	10.00	10.00	10.14±0.25	10.71±0.98
River water[2]	—	—	<Limit of detection	<Limit of detection
	50.0	50.0	50.44±0.51	50.78±0.78
Industrial water	—	—	<Limit of detection	<Limit of detection
	60.0	60.0	60.66±0.71	60.72±0.85
Urine	—	—	<Limit of detection	<Limit of detection
	150.00	150.00	150.81±1.02	149.85±1.25

±Shows the standard deviation; [1]River water from Zayandehrood, Isfahan, Iran; [2]River water from Tejan, Iran, Iran

Conclusion

This work demonstrates the application of ferrocenemonocarboxylic acid for determination of thiosulfate at a surface of multiwall carbon nanotubes paste electrode as a mediator. The results show that the thiosulfate is catalyzed by the mediator at pH=7.0. The catalytic peak current obtained by cyclic voltammetry was linearly dependent on the thiosulfate concentrations and the lower quantitation of 0.1 μmol L^{-1}. Current sensitivity, low detection limit, and high selectivity of the FAMWCNTPE for the detection of thiosulfate prove its potential sensing applications for the determination of thiosulfate in real samples.

Experimental

Chemicals:

All chemicals used were of analytical reagent grade purchased from Merck (Darmstadt, Germany) unless

otherwise stated. Doubly distilled water was used throughout.

A 1.0×10^{-2} mol L^{-1} thiosulfate stock solution was prepared daily by dissolving 0.248 g thiosulfate in water and the solution was diluted to 100 mL with water in a 100–mL volumetric flask. Further dilution was made with buffer solution.

Phosphate buffer (sodium dihydrogen phosphate and disodium monohydrogen phosphate plus sodium hydroxide, 0.1 mol L^{-1}) solutions (PBS) with different pH values were used.

High viscosity paraffin (d = 0.88 kg L^{-1}) from Merck was used as the pasting liquid for the preparation of the carbon paste electrodes. Spectrally pure graphite powder (particle size<50 μm) from Merck and multiwall carbon nanotubes (>90% MWNT basis, d × 1 = (100 – 80 nm) × (5 – 9 μm) from Fluka were used as the substrate for the preparation of the electrodes.

Apparatus

Cyclic voltammetry (CV), electrochemical impedance spectroscopy and chronoamperometry were performed in an analytical system, Autolab with PGSTAT 302N (Eco Chemie, the Netherlands). The system was run on a PC using GPES and FRA 4.9 software. For impedance measurements, a frequency range of 100 kHz to 1.0 Hz was employed. The AC voltage amplitude used was 5 mV, and the equilibrium time was 15 minutes. A conventional three-electrode cell assembly consisting of a platinum wire as an auxiliary electrode and an Ag/AgCl/KCl$_{sat}$ electrode as a reference electrode was used. The working electrode was either an unmodified carbon nanotubes paste electrode, or a FAMWCNTPE. The prepared electrodes with carbon nanotubes and without carbon nanotubes were characterized by scanning electron microscopy (SEM).

Preparation of the electrode:

One mg of ferrocenemonocarboxylic acid was hand-mixed with 89 mg of graphite powder and 10 mg of multiwall carbon nanotubes in a mortar and pestle. Using a syringe, 0.50 g of paraffin was added to the mixture and mixed well for 40 min until a uniformly-wetted paste was obtained. The paste was then packed into a glass tube. Electrical contact was made by pushing a copper wire down the glass tube into the back of the mixture. When necessary, a new surface was obtained by pushing an excess of the paste out of the tube and polishing it on a weighing paper. The unmodified carbon paste electrode (CPE) was prepared in the same way without adding ferrocenemonocarboxylic acid and carbon nanotubes to the mixture to be used for comparison purposes.

Preparation of real samples:

Ten milliliters color fixing waste water, film fixing waste water, urine and water samples were centrifuged for 10 min at 2000 rpm. The supernatant was filtered using a 0.45 μm filter and then diluted 5–times with the universal buffer pH 7.0. The solution was transferred into the voltammetric cell to be analyzed without any further pretreatment. Standard addition method used for the determination of thiosulfate in real samples.

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