

The effect of concentration in electrochemical oxidation of thiocyanate on platinum electrode

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Abstract Electrochemical oxidation of thiocyanate (SCN^-) on platinum electrode in the sulfuric acid medium was studied using cyclic voltammetry, in situ UV-visible absorption measurement, rotating ring-disc electrode voltammetry, and electrical impedance spectroscopy. Two oxidation processes are involved in the electrochemical oxidation of SCN^- in sulfuric acid medium. The adsorbed SCN^- undergoes oxidation at potential values higher than 0.900 V versus saturated calomel electrode (SCE). Trithiocyanate, $(\text{SCN})_3^-$, is formed as a relatively stable product during the first oxidation process. The potential range of $(\text{SCN})_3^-$ formation increases with increase in concentration of SCN^- , and it is exclusively produced in the potential range of 0.550 to 1.40 V versus SCE with 1.0 M NH_4SCN solution. The second oxidation process does not produce any stable product, and the products of second oxidation passivate the electrode surface.

Keywords Electrochemical oxidation · Thiocyanate · Trithiocyanate · Thiocyanogen · Cyclic voltammetry · Rotating ring-disc electrode voltammetry · Spectroelectrochemistry

Introduction

Thiocyano derivatives are valuable intermediates in organic synthesis, especially for the preparation of nitrogen and

sulfur containing heterocycles [1–3]. Thiocyanogen, $(\text{SCN})_2$, is generally used as the electrophilic reagent for the preparation of thiocyano compounds [3]. $(\text{SCN})_2$ can be prepared either by chemical oxidation of thiocyanate (SCN^-) using various oxidizing agents like chlorine, bromine [3], iodine/methanol [2], ceric ammonium nitrate [4], etc. as the oxidizing agents or by electrochemical oxidation under suitable conditions [5]. Electrochemical preparation of $(\text{SCN})_2$ is clean when compared with the chemical method where handling of hazardous oxidizing agents, formation of side products, low yield etc. are the disadvantages. Because $(\text{SCN})_2$ is reported to be highly unstable in the aqueous medium [6], preparations dealing with $(\text{SCN})_2$ are normally carried out in the nonaqueous medium. However, Weltcher et al. [7] have prepared $(\text{SCN})_2$ by oxidizing SCN^- using chlorine in a two-phase mixture containing aqueous solution of sodium thiocyanate and the nonaqueous solvent toluene. Electrochemical synthesis in such a two-phase electrolyte is highly desirable when compared with electrolysis in nonaqueous solvents. The two-phase electrolysis does not require expensive supporting electrolytes; water is available for counter electrode reaction, and ohmic resistance is less [8]. Earlier, we have demonstrated that electrochemical thiocyanation can be carried out in a two-phase electrolytic medium [8, 9]. An electrolytic mixture of 1.0 M NH_4SCN in 0.25 M H_2SO_4 +dichloromethane was used for the two-phase electrolysis. The thiocyanating species generated in the aqueous phase by the electrooxidation of SCN^- was getting extracted into the nonaqueous solvent, thereby, avoiding its decomposition in the aqueous electrolyte. However, the identity of thiocyanating species produced in the two-phase electrolysis was not known. Current efficiency for the process was highly influenced by the concentration of SCN^- in the aqueous phase. Hence, the author was interested to establish the identity of thiocyanating species generated in the two-phase electrolysis, as well as to

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understand the effect of concentration in the electrochemical oxidation of SCN^- in the acidic medium.

A few studies on the electrochemical oxidation of SCN^- in aqueous medium have been reported in the literature [10–13]. Nicholson [10] has reported the formation of $(\text{SCN})_2$ as the result of SCN^- electrooxidation. Holtzen and Allen [11] have reported cyanide, sulfate, and a polymeric substance as the products of SCN^- electrooxidation. Loucka and Janos [12] have concluded that SCN^- electrooxidation occurs via chemisorption on platinum (Pt), and it is ultimately oxidized to sulfate involving six electrons. The above authors have not reported the formation of any stable, soluble product as the result of electrooxidation of SCN^- in aqueous medium. However, Itabashi [13] has confirmed the formation of soluble trithiocyanate, $(\text{SCN})_3^-$, during the electrooxidation of 0.10 M NaSCN in 0.10 M HClO_4 on gold electrode by the combined use of voltammetric and spectroelectrochemical methods. Experiments in the above study were carried out with 0.10 M NaSCN within a potential range of 0 to 0.550 V versus saturated calomel electrode (SCE). The effect of SCN^- concentration, as well as of the extended potential window on the oxidation process, was not reported. The survey of published reports indicates a definite literature gap regarding the detailed mechanism of SCN^- electrooxidation as well as the effect of SCN^- concentration under different conditions. In view of the above, experiments were carried out employing cyclic voltammetry (CV), in situ UV-visible absorption measurement, rotating ring-disc electrode (RRDE) voltammetry, and electrical impedance spectroscopy (EIS) with the aim to understand the electrooxidation mechanism of SCN^- on Pt electrode, to identify the species formed during the process, and to study the effect of SCN^- concentration. The experimental details and the results are discussed in the present communication.

Experimental

Chemicals and reagents

Ammonium thiocyanate (NH_4SCN ; Sigma Aldrich) was used as received. Analytical grade sulfuric acid (H_2SO_4 ; Merck) was distilled and used. Aqueous solutions were prepared with double distilled water. All the experiments were carried out in 0.5 M H_2SO_4 medium.

Electrochemical studies

The Pt working electrodes were pretreated by keeping in chromic acid for 15 min. Then, they were electrochemically cleaned by employing the current density of 10 mA cm^{-2} in 0.50 M H_2SO_4 , first cathodic followed by anodic polariza-

tion for the duration of 10 min each. Afterwards, the electrode potential was cycled at 0.5 V s^{-1} between -0.23 to 1.2 V versus SCE in 0.50 M H_2SO_4 until a stable and reproducible cyclic voltammogram was obtained. All the reported potential values are with respect to the saturated calomel reference electrode. The solutions were de-aerated by bubbling nitrogen for at least 10 min before the experiments. A blanket of nitrogen was maintained over the solution while carrying out the experiments. The temperature of the experimental cell was maintained at a specified value using a thermostated immersion circulator. The experiments were carried out at 0 to 2 °C unless or otherwise specified.

Cyclic voltammetry

The cyclic voltammetric experiments were carried out in a conventional three-electrode electrochemical cell (100-ml capacity). A Pt disc electrode of geometrical area (0.1256 cm^2) received from PAR Electrochemical Systems, USA, was used as the working electrode, and a Pt spiral of relatively large area was used as the counter electrode. SCE was the reference electrode unless or otherwise specified. The reference electrode was separated from the sample solution by a Luggin capillary fitted with a porous Vycor™ tip. The experiments were carried out with a multistat (1480, Solartron Analytical, USA) interfaced to the computer. Experimental control and data analysis were carried out using the CorrWare™ software (version 2.8 Scribner Associates).

RRDE voltammetry

RRDE experiments were carried out in a three-compartment cylindrical cell using Pt-ring, Pt-disc (theoretical collection efficiency 0.20) electrodes obtained from Pine Instruments, USA. A platinum spiral placed in a glass compartment separated from the sample solution by a porous glass frit was used as the counter electrode. The arrangement for the SCE reference electrode was same as described for CV studies. The potential of both disc and ring electrode was controlled independently of each other with a bi-potentiostat (AFCBP1, Pine Instruments, USA) interfaced to a computer. Control of the experiments as well as data analysis were carried out using PineChem™ software from Pine Instruments, USA.

Electrical impedance spectroscopy

All impedance measurements were recorded between 10 kHz and 1 Hz with an AC amplitude of 5 mV, using a Solartron 1260 gain phase analyzer interfaced to Solartron 1480 multistat. The experiments under various conditions

were carried out using Zplot™ (version 2.8, Scribner Associates) software.

Results and discussion

Cyclic voltammetry

When the experiments were carried out at 25 °C, a yellowish polymeric mass was generated especially in concentrated solutions and settled at the bottom of the voltammetric cell. Polymer formation could be largely avoided by conducting the experiments at low temperature. Hence, voltammetric experiments were carried out in the temperature range 0 to 2 °C. CVs recorded with clean Pt electrode in 0.5 M H₂SO₄ and that in the presence of 5×10^{-5} M NH₄SCN in the potential range -0.23 to 1.20 V are given in Fig. 1. The CV recorded in 0.5 M H₂SO₄ shows characteristic peaks for hydrogen adsorption and its oxidative desorption. Platinum oxide (PtO) formation occurs beyond 0.500 V during the forward sweep, and its reduction peak appears around 0.500 V during the reverse sweep. The CV recorded in the presence of NH₄SCN shows complete inhibition of hydrogen adsorption and its oxidative desorption peaks even with extremely low concentration of 5×10^{-5} M NH₄SCN. The oxidation of SCN⁻ occurs beyond 0.550 V, and two oxidation processes (I_a^i, I_a^{ii}) are observed during the forward sweep. A small hump around 0.500 V during the reverse sweep is due to the reduction of PtO formed during the forward sweep. However, PtO reduction peak is totally absent in the CV if the NH₄SCN concentration is above 1×10^{-3} M (discussed later). The above CVs reveal strong affinity of SCN⁻ anion for

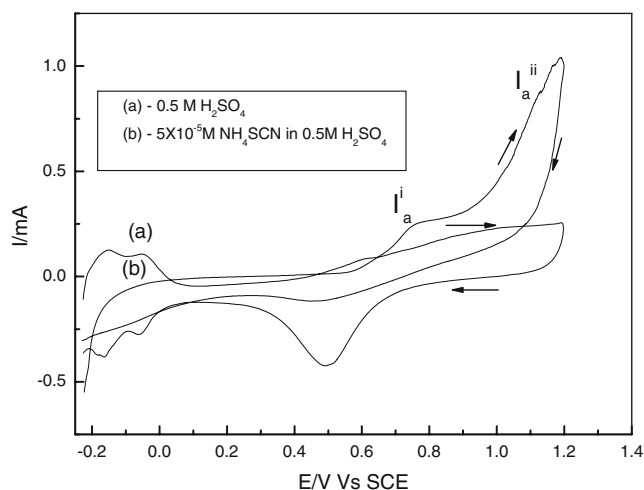


Fig. 1 Cyclic voltammogram of clean platinum electrode in **a** 0.5 M H₂SO₄, **b** 5×10^{-5} M NH₄SCN in 0.5 M H₂SO₄; scan rate, 0.100 V s⁻¹; temperature, 2 °C

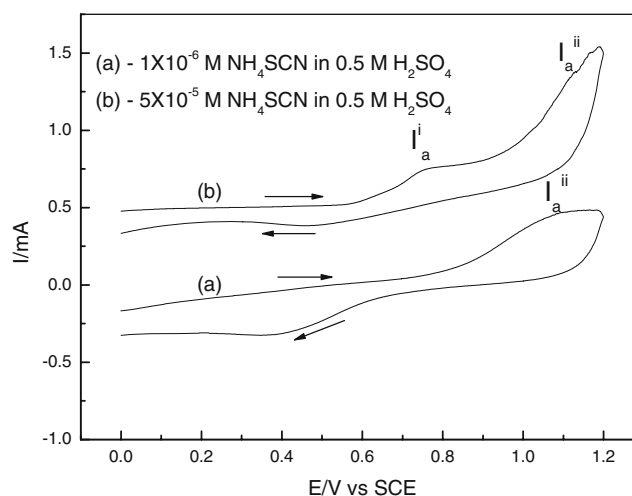


Fig. 2 Cyclic voltammograms of thiocyanate oxidation at different concentrations (*i*): **a** 1×10^{-6} M NH₄SCN; **b** 5×10^{-5} M NH₄SCN; scan rate, 0.100 V s⁻¹; temperature, 2 °C

chemisorption onto platinum electrode and almost complete inhibition of hydrogen adsorption and PtO formation even under extremely dilute conditions.

CVs recorded with different concentrations of NH₄SCN are given in Fig. 2. At a very low concentration of 1×10^{-6} M NH₄SCN (Fig. 2a), only second oxidation wave (I_a^{ii}), beginning around 0.900 V, is observed in the CV. However, on increasing the concentration to 5×10^{-5} M NH₄SCN (Fig. 2b), two oxidation processes are distinctly observed in the CV. In the electrode reactions of species that can specifically adsorb on electrode surface, the adsorbed species normally reacts at higher potential due to its stabilization on the electrode surface [14]. Hence, the second oxidation wave (I_a^{ii}) is due to the oxidation of adsorbed SCN⁻. Because the peak parameters of the first oxidation process (I_a^i) could not be analyzed due to its overlapping nature, it is not clear whether the (I_a^i) oxidation process is due to the oxidation of SCN⁻ from the solution or the weakly adsorbed SCN⁻. The absence of first wave in Fig. 2a means that, at extremely low concentration of 1×10^{-6} M NH₄SCN, the oxidation current is mainly due to the chemisorbed SCN⁻ that gives only the second oxidation wave (I_a^{ii}). To confirm the higher oxidation potential of adsorbed SCN⁻, clean Pt electrode was immersed in 0.010 M NH₄SCN solution for 5 min, removed from the solution, and cleaned with demineralized (DM) water; its CV recorded in 0.5 M H₂SO₄ within the potential range of -0.20 to 1.20 V, and the resulting voltammogram is presented in Fig. 3. The voltammogram clearly shows that the oxidation of adsorbed SCN⁻ occurs beyond 0.900 V, and this potential value is in the range of the second oxidation wave in the voltammograms of Figs. 1 and 2, thus, providing direct evidence for the higher oxidation potential of chemisorbed SCN⁻.

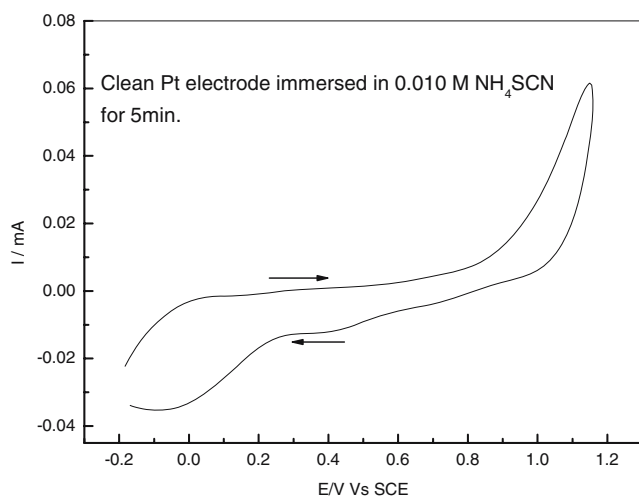


Fig. 3 Cyclic voltammogram of chemisorbed thiocyanate on platinum electrode in 0.5 M H_2SO_4 ; condition for chemisorption, immersed in 0.010 M NH_4SCN for 5 min; scan rate, 0.100 V s^{-1} ; temperature, 2°C

The above observations contradict the conclusions arrived by Loucka and Janos [12] who have reported same oxidation potential for the dissolved as well as chemisorbed SCN^- . In the author's opinion, the earlier workers might have assigned the PtO formation wave that begins at 0.500 V during the forward sweep to SCN^- oxidation. The difficulty here is mainly due to the comparable current magnitudes of PtO formation, as well as the adsorbed thiocyanate oxidation. During the oxidation studies of adsorbed SCN^- on Pt, Loucka and Janos [12] have initially applied a negative potential sweep from 0.400 to 0.0 V before beginning the positive sweep. There may be a possibility of SCN^- desorption during the negative sweep that may result into the generation of fresh Pt surface that will subsequently undergo oxidation during the forward sweep beyond 0.500 V. In fact, PtO formation will be completely inhibited only if the electrode surface is totally covered with SCN^- . In a partially covered electrode, PtO formation also will begin around 0.500 V, and the Pt oxidation current may overlap with the SCN^- oxidation current. To get further evidence in support of this view, clean Pt electrode was immersed in 0.010 M NH_4SCN for 5 min, removed from the solution, cleaned with DM water, and multiple CVs of it were recorded in 0.5 M H_2SO_4 and shown in Fig. 4. The potential has to be cycled many times to completely remove the chemisorbed SCN^- or its oxidation products as described by the earlier workers [12]. Because the electrode surface will be completely covered with chemisorbed SCN^- in the beginning, PtO formation is totally blocked during the first cycle and the oxidation of chemisorbed SCN^- begins around 0.900 V. With increase in the number of cycles, the onset of oxidation is gradually shifted towards less positive potentials due to the PtO formation current and oxidation wave

begins around 0.500 V after five cycles. The PtO reduction peak is also shifted towards more negative potentials initially and gradually shifting towards its original position (0.500 V) with increase in the number of cycles. Kapusta et al. [15] have reported the formation of platinum (IV) sulfide during the anodic oxidation of sulfide species on Pt electrode that passivates the electrode and inhibits PtO formation. There is also a possibility of such platinum (IV) sulfide formation in the present system.

The CV of 0.010 M NH_4SCN within the potential range of the first wave (0.0 to 0.650 V) is given in Fig. 5. The appearance of a reduction wave (I_c^i) around 0.500 V during the reverse sweep shows the formation of a relatively stable product during the first oxidation process I_a^i , which could be detected at the electrode during the reverse sweep. Itabashi [13] has already reported the formation of trithiocyanate ($\text{SCN})_3^-$ on gold minigrad electrode in the potential range 0 to 0.550 V. Hence, ($\text{SCN})_3^-$ could be the relatively stable species formed during the first oxidation process. To confirm the ($\text{SCN})_3^-$ formation, constant potential electrolysis was carried out by maintaining the potential at 0.650 V for 30 min; UV-visible absorption of electrolyzed as well as the original solutions were checked. The electrolyzed solution showed a new absorption peak with maximum absorbance (λ_{max}) at 305 nm. Barnett and Stanbury [16] have reported a λ_{max} value of 305 nm for ($\text{SCN})_3^-$, formed during chemical oxidation of SCN^- in the aqueous medium using chlorine gas as the oxidizing agent. Because the λ_{max} value of 305 nm observed in the present study exactly matches with the reported value for ($\text{SCN})_3^-$ [16], we could clearly establish the formation of ($\text{SCN})_3^-$ during the first oxidation process (I_a^i).

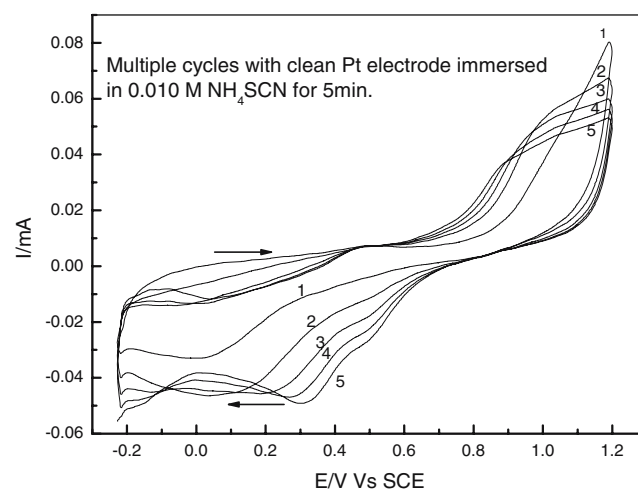


Fig. 4 Multiple cyclic voltammograms of chemisorbed thiocyanate on platinum electrode in 0.5 M H_2SO_4 ; condition for chemisorption, immersed in 0.010 M NH_4SCN for 5 min; scan rate, 0.100 V s^{-1} ; temperature, 2°C

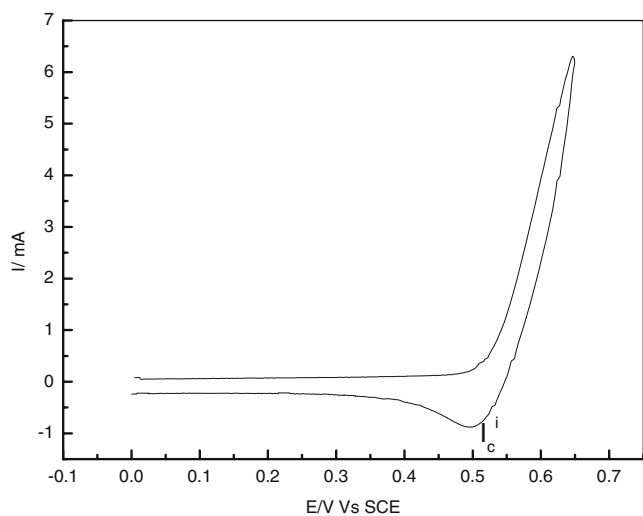


Fig. 5 Cyclic voltammogram of 0.010 M NH₄SCN in the potential range 0 to 0.650 V; scan rate, 0.500 V s⁻¹; temperature, 2 °C

Cyclic voltammogram recorded with 0.010 M NH₄SCN within the potential range of 0 to 1.30 V at the scan rate of 0.100 V s⁻¹ is shown in Fig. 6. Two waves are completely overlapped; due to which, peak current for the first wave could not be accurately determined. The absence of (SCN)₃⁻ reduction peak during reverse sweep indicates that (SCN)₃⁻ does not remain stable enough to be detected during the reverse sweep at the sweep rate of 0.100 V s⁻¹. The PtO formation during the forward potential sweep is totally inhibited, and hence, PtO reduction peak is not observed during the reverse sweep. The broad nature of CV and the extensive tailing of the reverse voltammogram show severe electrode poisoning. Even then, overall current density values were reasonably reproducible with scrupulously cleaned electrode, and it increased with the increase in sweep rate. Nicholson [10] has reported that SCN⁻ oxidation is a diffusion-controlled process where the first oxidation wave was not identified; only the second oxidation wave was discussed. Peak current, *I_p*, for a diffusion-controlled irreversible electrode process can be calculated using the following equation [14]:

$$I_p = (2.99 \times 10^5) n(\alpha n_a)^{1/2} AC^* D^{1/2} \nu^{1/2}$$

where *n* is the total number of electrons transferred, α the transfer coefficient, *n_a* is the number of electrons transferred in the rate controlling step, *A* the electrode area (cm²), *C** the bulk concentration (mol/cm³), *D* the diffusion coefficient (cm² s⁻¹). The actual surface area of the electrode was calculated from the charge corresponding to the hydrogen adsorption peaks (210 μC cm⁻²). The *I_p* value for 0.010 M solution at the sweep rate of 0.100 V s⁻¹ was calculated by substituting the *D* value of 1 × 10⁻⁵ cm² s⁻¹, a commonly used value for dilute aqueous solutions [17], *n* = 2, αn_a = 0.50, and the respective values of other parameters. The calculated

I_p value of 4.72 mA is very much lower than the experimentally observed peak currents in Fig. 6. The error due to assumed values of transfer coefficient (0.50) and diffusion coefficient (1 × 10⁻⁵ cm² s⁻¹) alone are not responsible for such a large variation in peak current. It is reported that the removal of sulfur species from the electrode surface involves the formation of polysulfides [18]. The experimentally observed higher peak current is due to such further reactions of the sulfur species adsorbed on the electrode surface. Coulombic charge density corresponding to (*I_aⁱ*), (*I_aⁱⁱ*) oxidation processes were determined by the integration of CV presented in Fig. 6 and found to be 5,069, 8,867 μC cm⁻², respectively. On dividing the charge density of (*I_aⁱⁱ*) wave, 8,867 μC cm⁻², by the value 210 μC cm⁻² (corresponding to one electron per one H-adsorbing site, e.p.s.), the value of oxidation charge in e.p.s. unit was estimated as 42.22. The very high e.p.s. value of 42.22 shows that the second oxidation process is not solely due to chemisorbed SCN⁻, and the two oxidation waves are overlapped.

As discussed in the earlier studies and re-confirmed in the present investigation, (SCN)₃⁻ is the species formed during the first oxidation process [13]. It has been well established that (SCN)₃⁻ formation occurs via thiocyanato radical anion (SCN)₂⁻ [19]. The formation of (SCN)₂⁻ is highly dependent on the concentration of SCN⁻ in the solution [19]. The concentration of SCN⁻ near the electrode will be high in the beginning of SCN⁻ oxidation, and hence, effective formation of (SCN)₂⁻ is possible by the combination of SCN⁻ with the thiocyanato radical (SCN[•]). The (SCN)₂⁻ is supposed to undergo a second order decomposition reaction to produce (SCN)₃⁻ [19]. With continuation of potential scan, the concentration of SCN⁻ near the electrode will drop. At the potential value corresponding to the first oxidation wave, the concentration of SCN⁻ near the electrode surface is not sufficient

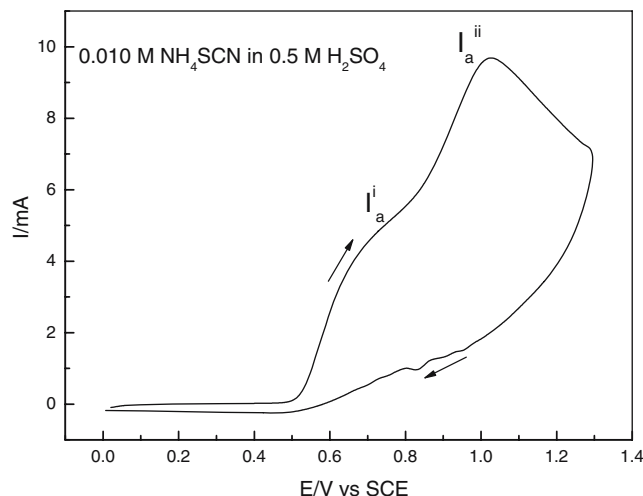


Fig. 6 Cyclic voltammogram of 0.010 M NH₄SCN in the potential range 0 to 1.20 V; scan rate, 0.100 V s⁻¹; temperature, 2 °C

enough to combine with SCN^- for effective $(\text{SCN})_2^-$ formation. As the result, SCN^- radicals may coat the electrode surface, thus, generating the first wave (I_a^i). Hence, beyond the first wave, $(\text{SCN})_3^-$ formation is not possible but oxidation of dissolved SCN^- will continue to occur along with adsorbed SCN^- , and the primary SCN^- radicals may be ultimately oxidized to SO_4^{2-} , thus, generating large currents during the second oxidation process. It is not clear whether SCN^- oxidation to SO_4^{2-} also occurs during the first oxidation process. The potential range of the first oxidation wave [potential range of $(\text{SCN})_3^-$ formation] increases with increase in concentration of SCN^- , and the second wave (I_a^{ii}) becomes almost insignificant at higher concentrations. For 1.0 M NH_4SCN , only the first wave (I_a^i) is observed in the entire potential range of 0.550 to 1.40 V (not shown here).

RRDE voltammetric studies

Rotating ring-disc voltammetric experiments were carried out to study the effect of SCN^- concentration on $(\text{SCN})_3^-$ formation. The potential of the disc electrode was anodically scanned within the potential range of 0.400 to 1.200 V at the scan rate of 0.005 V s^{-1} . The ring potential was maintained at 0.200 V. The disc and ring currents were plotted as the function of disc potential, and the plots for 0.001 and 0.010 M NH_4SCN are given in Fig. 7.

The nature of the current potential curve of the disc electrode is similar to the forward potential sweep of CVs. The $(\text{SCN})_3^-$ formed at the disc electrode due to the oxidation of dissolved SCN^- during the first oxidation process (I_a^i) gets transported across the gap and undergoes reduction at the ring electrode-generating ring current that clearly establishes the soluble nature of $(\text{SCN})_3^-$. For the 0.001 M NH_4SCN solution (Fig. 7a), the ring current continuously increased till the disc potential reached 0.700 V and decreased slowly on continuing the disc electrode potential scan beyond 0.700 V. This experiment means that the effective formation of $(\text{SCN})_3^-$ at the disc electrode can happen only up to 0.700 V in 0.001 M NH_4SCN solution. However, the ring current has not abruptly dropped to zero on continuing the disc potential sweep beyond 0.700 V, instead, gradually getting reduced and becomes zero when the disc potential reached 1.0 V. At potential values higher than 0.700 V, the concentration of 0.001 M NH_4SCN is not sufficient enough for the formation of $(\text{SCN})_3^-$ at the maximum rate but $(\text{SCN})_3^-$ formation continuous to happen, although at a lesser rate, until the disc potential reached 1.0 V. On increasing the SCN^- concentration to 0.01 M NH_4SCN , the potential range of $(\text{SCN})_3^-$ formation at the disc electrode has increased, which also manifested itself in the current potential curve of the ring electrode. In this case, the ring

current started to decrease only when the disc potential reached 0.900 V. Thus, by increasing the SCN^- concentration from 0.001 M NH_4SCN to 0.010 M NH_4SCN , the potential range of effective $(\text{SCN})_3^-$ formation at the disc electrode was extended by 0.200 V. The RRDE studies provided direct evidence of the SCN^- concentration effect on $(\text{SCN})_3^-$ formation. Another inference from the RRDE studies was that the peak shape polarization curve obtained for the disc electrode indicates extensive electrode poisoning during the second oxidation process. Peaks, instead of limiting current plateau in the polarization curves with rotating electrodes, are reported to be due to the blocking of the electrode surface by the products of electrode reaction [20].

Electrical impedance spectroscopy

The EIS studies were carried out to understand the chemisorption behaviour of SCN^- or its oxidation products

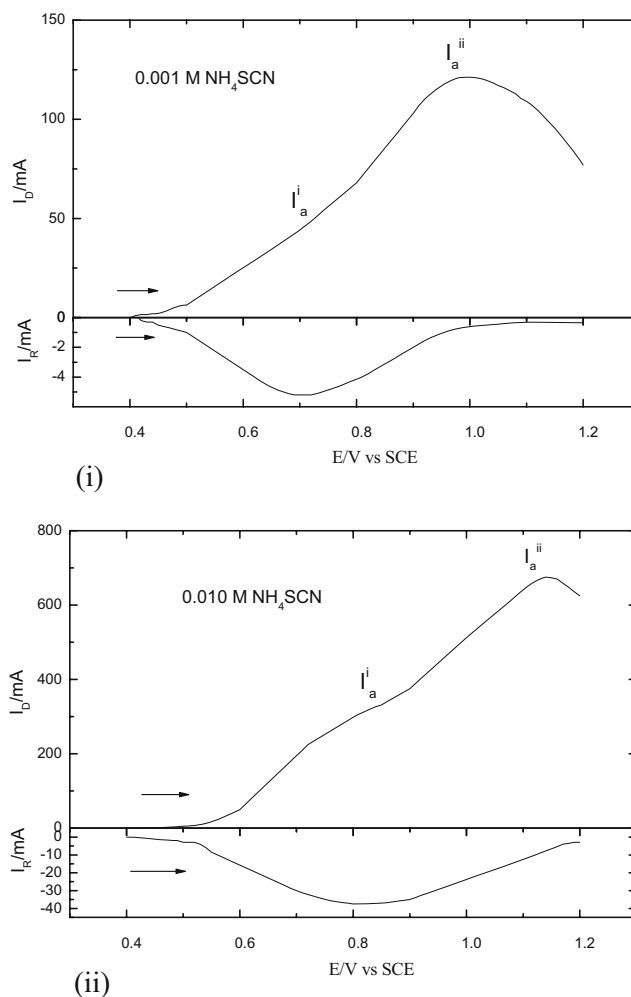


Fig. 7 RRDE experiments at different concentrations of thiocyanate. *i* 0.001 M NH_4SCN ; *ii* 0.010 M NH_4SCN ; rotation rate, 1,000 rpm; disc potential sweep rate, 0.005 V s^{-1} ; ring potential, 0.200 V; temperature, $2 \text{ }^\circ\text{C}$

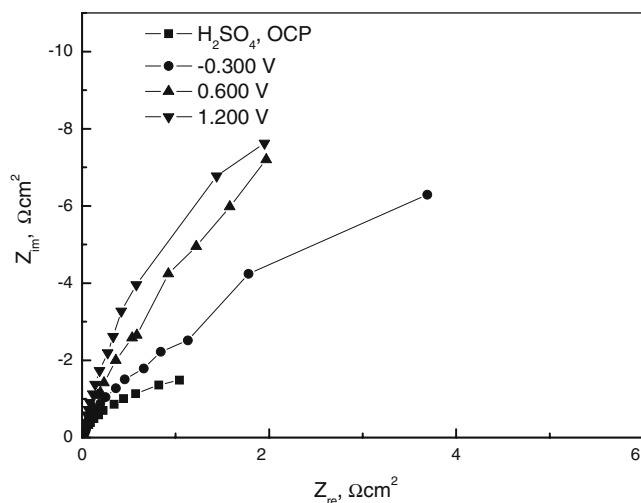


Fig. 8 Nyquist plot of impedance data for Pt electrode at different potentials; concentration, 0.001 M NH₄SCN; temperature, 2 °C

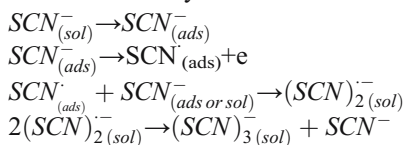
at different potentials. The impedance data recorded at different potentials from -0.300 to 1.200 V are presented in the form of Nyquist plot in Fig. 8. The impedance plots show capacitive behavior; impedance in the presence of SCN⁻ has increased to a large extent when compared with the impedance spectrum of 0.50 M H₂SO₄. The impedance value increase on moving the measurement potential from -0.300 toward 1.200 V. The increased impedance on moving toward higher anodic potential values is due to the enhanced adsorption of thiocyanate or its oxidation products at higher anodic potential values [21]. The broad nature of CV curves and peak-shaped RRDE disk voltammogram [20] are also indication of extensive electrode passivation. Hence, it can be concluded that the electrode surface is mainly coated with the products of oxidation at higher potentials during the second oxidation process.

Probable mechanism for thiocyanate oxidation on platinum electrode in acidic medium

The following mechanistic scheme is proposed for the electrochemical oxidation of SCN⁻ in the acidic medium on Pt electrode based on the results of the present investigation as well as the existing literature.

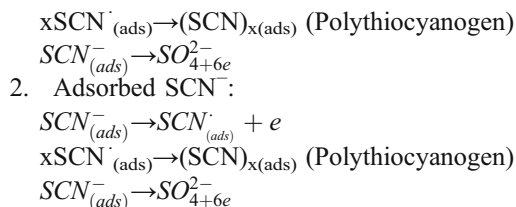
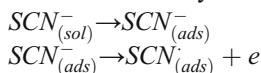
First oxidation process

Dissolved/weakly adsorbed SCN⁻



Second oxidation process

1. Dissolved/weakly adsorbed SCN⁻:



No stable product corresponding to the second oxidation process could be identified during this study. However, CV, RRDE, and EIS studies all confirm the passivation of electrode surface with the products of oxidation at high anodic potentials. In fact Pucciarelli et al. [22] have studied the electrooxidation of SCN⁻ in the molten KSCN–NaSCN eutectic mixture and have reported that (SCN)₃⁻ is formed at low current densities due to the interaction of SCN⁻ radicals with SCN⁻ present in the solution. At higher current densities, SCN radicals polymerize to form polythiocyanogen film on the electrode surface. The polythiocyanogen is a photoactive conducting polymer and construction of a photoactive device based on polythiocyanogen has been recently reported [23]. These authors have prepared polythiocyanogen by the electrolysis of KSCN in polycarbonate at 90 °C.

Conclusions

Electrochemical oxidation of thiocyanate (SCN⁻) was studied using various electrochemical techniques. Thiocyanate anion has very strong affinity to chemisorb on the platinum electrode, even under extremely dilute concentration of 1 × 10⁻⁶ M. The adsorbed SCN⁻ undergoes oxidation at potentials higher than 0.900 V versus SCE.

Two oxidation processes (*I_aⁱ*, *I_aⁱⁱ*) are involved in the overall SCN⁻ oxidation, and trithiocyanate (SCN)₃⁻ is produced as a relatively stable species during the first oxidation process. The potential range of (SCN)₃⁻ formation increases with the increase in the concentration of SCN⁻, and it is exclusively produced in the whole potential range of 0.550 to 1.400 V with 1.0 M NH₄SCN. The electrolytic method in the presence of high concentration of SCN⁻ can be employed for the preparation of (SCN)₃⁻ for preparative organic chemistry purposes. However, to avoid its decomposition in the aqueous electrolyte, it has to be consumed as soon as it is formed or continuously extracted into a nonaqueous solvent.

The second oxidation does not produce any stable product, and the electrode surface is passivated during this process. A probable mechanism for SCN⁻ oxidation in aqueous medium has been proposed.

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