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Spectroelectrochemical Characterization of Iron(III)-Thiocyanate Complexes in Acidic Thiocyanate Solutions at an Optically Transparent Thin-Layer-Electrode Cell

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The reduction-oxidation process of the couple Fe(III)/Fe(II) in acidic thiocyanate solutions was investigated by voltammetric and spectroelectrochemical techniques by using a gold-minigrid optically transparent thin-layer-electrode cell. The thin-layer cyclic voltammogram of Fe(III) in acidic thiocyanate solution exhibits two unresolved cathodic peaks and an anodic wave with a shoulder followed by a rising current. Spectroelectrochemical data indicate that the oxidation of SCN^- by Fe(III) as well as the electrooxidation of SCN^- in acidic thiocyanate solution gives the same species such as $(SCN)_3^-$ with an absorption peak at 320 nm and that $Fe(NCS)_2^+$ with an absorption peak at 475 nm and $(SCN)_3^-$ at 320 nm are reduced at potentials near +0.28 and +0.33 V vs. SCE, respectively. It has been proposed that the formation of $(SCN)_3^-$ proceeds through the anion radical $(SCN)_2^{-}\cdot$ produced by the oxidation of SCN^- by Fe(III) and is followed by the disproportionation of $(SCN)_2^{-}\cdot$ into $(SCN)_3^-$ and SCN^-. The formal redox potential of the couple $SCN^-/(SCN)_3^-$ was estimated to be +0.44 V vs. SCE.

Introduction

Thiocyanate ions are readily oxidized by a variety of inorganic reagents in aqueous solutions.[1-5] It seems generally accepted that the chemical oxidation of SCN^- in aqueous solutions proceeds through the formation of thiocyanogen $(SCN)_2$ as a reaction intermediate, which undergoes hydrolysis to yield sulfate and cyanide ions as the main products, although the actual hydrolysis mechanism of $(SCN)_2$ is controversial.[6,7] The problem is complicated by the necessarily large number of intermediates.

It was recently reported that SCN^- in acidic solutions was electrochemically oxidized to give trithiocyanate ion, $(SCN)_3^-$, which was moderately stable and was reduced to SCN^- with a high reduction efficiency of above 95%.[8] It is the purpose of this paper to clarify the oxidation products of SCN^- by inorganic reagents, using for an example the oxidation of SCN^- by Fe(III). The blood red color of the Fe(III)-thiocyanate complex has been known to fade spontaneously. It has been proposed that the fading is due to the reduction of Fe(III) by SCN^- with the formation of Fe(II) and $(SCN)_2$.[1,9] However, very little work has been reported on the identification of the oxidation products of SCN^- by Fe(III).[9,10] This paper presents direct evidence for the reaction intermediate of the oxidation of SCN^- by Fe(III) with the combined use of voltammetric and spectroelectrochemical methods at an optically transparent thin-layer-electrode cell.

Experimental Section

All electrochemical and spectroelectrochemical measurements were made with a potentiostat (Fuso, Co., Model 311), a function generator (Fuso Co., Model 321), and a digital coulometer (Nikko Keisoku, Model NDCM-2). The UV-vis spectra were obtained with a Hitachi 556 spectrophotometer. Thin-layer cyclic voltammograms and absorbance-potential and absorbance-time curves were recorded with Model F-43P and/or Model F-42C recorder (Riken Denshi Co.). The gold-minigrid optically transparent thin-layer-electrode (OTTLE) cell was constructed by clamping a gold minigrid (Buckbee-Mears Co., St. Paul, MN; 500 lines/in.) and a Teflon tape (Dielectric Corp., Famingdale, NY) between two quartz slides, as described previously.[11] The OTTLE had a cell thickness of 0.017 cm. The auxiliary electrode was a platinum wire, and the potential of the working electrode was measured against a saturated calomel electrode (SCE).

Iron(III) perchlorate and other chemicals were of analytical reagent grade and were used without further purification. All solutions were made up with twice distilled water and were deaerated with water-pumped nitrogen. All experiments were carried out at room temperature near 18 ± 2 °C.

Results and Discussion

Electrochemical Study. Typical thin-layer cyclic voltammograms in acidic thiocyanate solutions in the presence and absence of iron ion are shown in Figure 1. In the presence of Fe(III), Fe(III) in the OTTLE cell was previously reduced to Fe(II) at 0.00 V while the absorbance at 475 nm assigned to the Fe(III)-NCS^- complex and the current level were monitored. When both the absorbance at 475 nm and the current level at 0.00 V had fallen to essentially zero, the cyclic voltammogram of the solution in the OTTLE cell was recorded. On the initial positive scan, the cyclic voltammogram exhibits an anodic wave with a shoulder, followed by a rising current up to the anodic switching potential, and a cathodic wave with two unresolved peaks near +0.33 and +0.28 V on the reverse scan, as shown in Figure 1A. When iron ion in the OTTLE cell was present as Fe(III), the initial scan was started from ca. +0.44 V toward negative potentials. The resulting cathodic wave was similar in shape and position to that shown in Figure 1A, but the cathodic wave decreased in size. Figure 1B shows the voltammograms in acidic thiocyanate solution in the absence of iron ion. The anodic current corresponding to the oxidation of SCN^- increases up to the anodic switching potential since a high concentration of SCN^- is employed. The cathodic wave gives a peak near +0.27 V on the reverse scan.

The charges for the oxidation and reduction processes under thin-layer cyclic voltammetric conditions as a function of the concentration of Fe(III) are plotted in Figure 2. In the presence of Fe(III), Fe(III) was previously reduced to Fe(II) at 0.00 V, and then cyclic voltammetric experiments were carried out on this solution. The anodic and cathodic charges are approximately proportional to the concentration of Fe(III), and the charges determined by extrapolating the plot of Q vs. [Fe(III)] to the zero point of iron concentration are nearly the same as those determined independently in acidic thiocyanate solution in the absence of iron. This result suggests that there is no appreciable interaction between the oxidized species of SCN^- and Fe(III) under the experimental conditions. The reduction efficiency of the oxidized species decreases as the anodic switching potential becomes more positive. This seems to be due to the decomposition of the oxidized species of SCN^- during the negative scan.

The effect of hydrogen ion concentration on the thin-layer cyclic voltammograms is shown in Figure 3. The ionic strength of the

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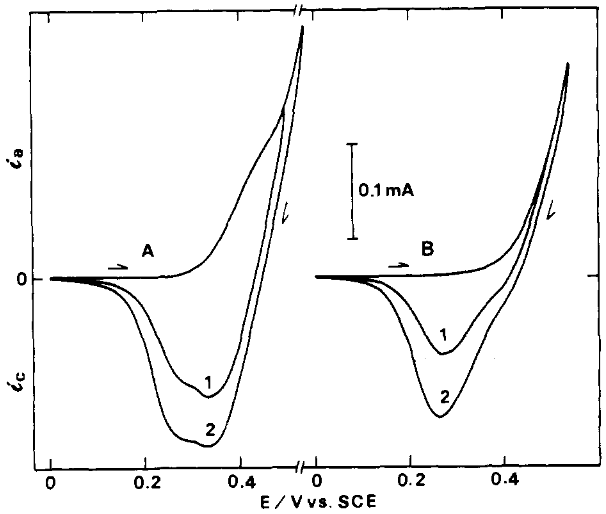

Figure 1. Thin-layer cyclic voltammograms in 0.1 M NaSCN and 0.1 M $HClO_4$ solutions with (A) and without (B) 2 mM Fe(III) present (sweep rate 2 mV s^{-1}). Anodic switching potential: (1) +0.500; (2) +0.540 V.

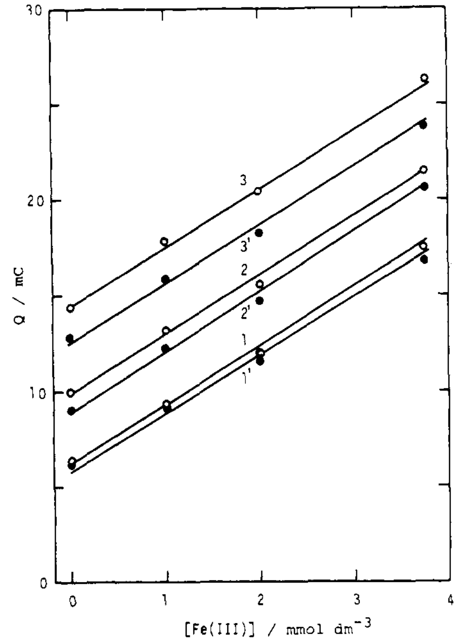

Figure 2. Effect of concentration of Fe(III) on the anodic (○) and cathodic (●) charges for the oxidation and reduction processes in 0.1 M NaSCN and 0.1 M $HClO_4$ (sweep rate 2 mV s^{-1}). Anodic switching potential: (1, 1′) +0.500; (2, 2′) +0.520; (3, 3′) +0.540 V.

solution at the concentration of $HClO_4$ below 0.04 M (M = mol dm^{-3}) was kept constant at 0.2 M by adding $NaClO_4$. The broken lines show the cyclic voltammograms of supporting electrolyte. This result indicates that the oxidation processes of Fe(II) and SCN^- as well as the reduction processes of Fe(III) and the oxidized species of SCN^- take place at almost same potential regions.

The ratios of the cathodic charge Q_c to the anodic charge Q_a measured under thin-layer cyclic voltammetric conditions are summarized in Table I. $Q_cQ_a^{-1}$ was greater than 90% at the concentrations of both NaSCN and $HClO_4$ above 0.1 M. $Q_cQ_a^{-1}$ decreases drastically with decrease in hydrogen ion concentration below 0.04 M.

Spectroelectrochemical Study. Figure 4 shows the absorption spectra of iron(III)–thiocyanate solutions before and after the controlled-potential electrolysis. Curve a in Figure 4 is a typical spectrum of iron(III)–thiocyanate solutions with characteristic peaks at 475 and 320 nm. Miyake[12] proposed that the peak at 320 nm was due to the formation of Fe(III)–Cl^- complex; however, this peak also appears in the iron(III)–thiocyanate solution without chloride ions present. The absorption peaks at 475 and 320 nm disappear completely upon the electroreduction of Fe(III) carried out at 0.00 V, as shown in curve b of Figure 4. Curve c presents the spectrum obtained after the reoxidation of Fe(II) under controlled-potential step from 0.00 to +0.50 V. The anodic current during the controlled-potential oxidation at +0.50 V did not reach a constant value, since the electrooxidation of SCN^- also took place at the same potential. Curve c was recorded under conditions where the total number of coulombs passed during the controlled-potential oxidation at +0.50 V was approximately 2.5 times the number of coulombs needed for the one-electron oxidation process of Fe(II). The electrooxidized thiocyanate solution containing iron ion also exhibits an absorption spectrum with peaks at 475 and 320 nm. These absorption peaks are greater than those observed for the iron(III)–thiocyanate solution before the elec-

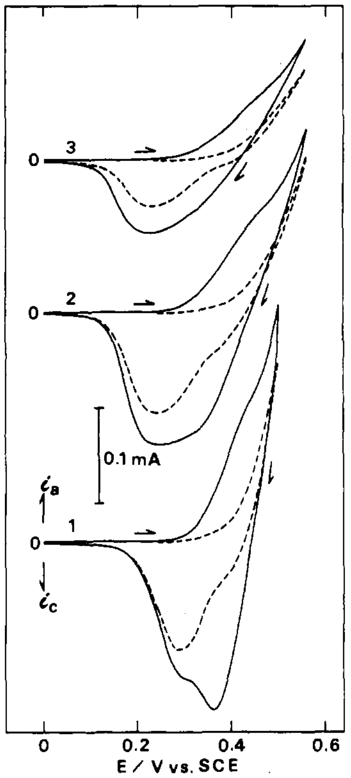

Figure 3. Effect of concentration of $HClO_4$ on the thin-layer cyclic voltammograms in 0.1 M NaSCN solutions with (solid line) and without (broken line) 2 mM Fe(III) present (sweep rate 2 mV s^{-1}). [$HClO_4$]: (1) 0.2; (2) 0.04; (3) 8 × 10^{-3} M.

Table I. Effect of Electrolyte and Anodic Switching Potential on the Electroreduction Efficiencies Measured under Cyclic Voltammetric Conditions[a]

electrolyte	[Fe(III)]/ mM	$Q_cQ_a^{-1}$/%[b]
0.5 M NaSCN, 0.1 M $HClO_4$	0	96 (+0.40), 93 (+0.42)
0.5 M NaSCN, 0.1 M $HClO_4$	2	98 (+0.40), 95 (+0.42)
0.1 M NaSCN, 0.2 M $HClO_4$	0	96 (+0.48), 94 (+0.50)
0.1 M NaSCN, 0.2 M $HClO_4$	2	97 (+0.48), 94 (+0.50)
0.1 M NaSCN, 0.1 M $HClO_4$	0	96 (+0.50), 92 (+0.54)
0.1 M NaSCN, 0.1 M $HClO_4$	2	96 (+0.50), 90 (+0.54)
0.1 M NaSCN, 0.04 M $HClO_4$, 0.06 M $NaClO_4$	0	85 (+0.52), 78 (+0.56)
0.1 M NaSCN, 0.04 M $HClO_4$, 0.06 M $NaClO_4$	2	89 (+0.52), 83 (+0.56)
0.1 M NaSCN, 8 mM $HClO_4$, 0.1 M $NaClO_4$	0	58 (+0.54), 54 (+0.56)
0.1 M NaSCN, 8 mM $HClO_4$, 0.1 M $NaClO_4$	2	74 (+0.54), 65 (+0.56)

[a] Sweep rate = 2 mV s^{-1}. [b] The values in parentheses indicate the anodic switching potential (V vs. SCE) on the cyclic voltammograms.

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(12) Miyake, C. *Bull. Chem. Soc. Jpn.* **1960**, *33*, 867–871.

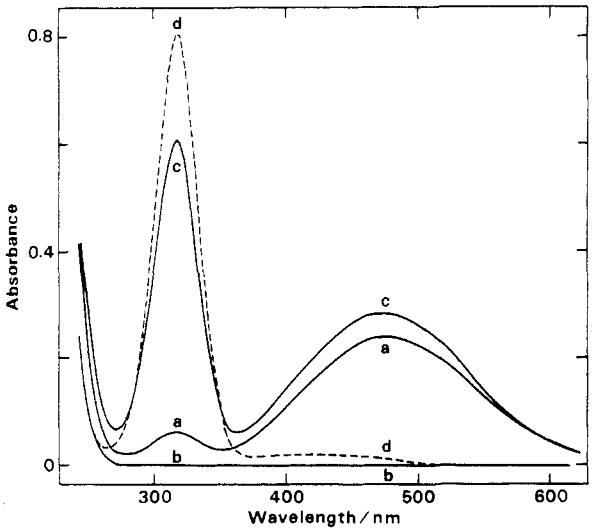

Figure 4. Thin-layer absorption spectra before and after the electrolysis in 0.1 M NaSCN and 0.1 M $HClO_4$ solutions with (a–c) and without (d) 2 mM Fe(III) present (cell thickness 0.017 cm): (a) before electrolysis; (b) after reduction of Fe(III) at 0.00 V and cathodic charge of 8.1 mC; (c) after reoxidation of Fe(II) at +0.50 V and anodic charge of ca. 20 mC; (d) after oxidation of SCN^- at +0.50 V and anodic charge of ca. 20 mC.

trolysis. A slight increase in absorbance at 475 nm could arise from the fact that the iron(III)–thiocyanate solution has already faded partially. A large increase in absorbance at 320 nm is due to the electroreduction of SCN^-. Curve d in Figure 4 shows the spectrum for the electrooxidized thiocyanate solution in the absence of iron ion. The electrooxidized thiocyanate solution exhibits a symmetrical peak at 320 nm and a small and broad peak at 420 ± 5 nm.[8] These peaks also disappear upon the electroreduction of the solution at 0.00 V, and the resulting spectrum is the same as that of curve b in Figure 4.

Figure 5 presents the absorbance–potential curves in acidic thiocyanate solutions with and without iron ion present. These spectroelectrochemical experiments were carried out with the same conditions as Figure 1. The broken lines show the absorbance changes monitored at 475 and 320 nm in acidic thiocyanate solution in the absence of iron ion. The absorbance monitored at 320 nm (Figure 5B′) increases as the anodic switching potential becomes more positive, reaches a maximum during the negative scan at potential near the zero-current axis on the thin-layer cyclic voltammogram, then decreases as the applied potential becomes less positive, and falls to zero upon which the cathodic current drops to an almost zero level. No detectable change is observed on the absorbance monitored at 475 nm in acidic thiocyanate solution in the absence of iron ion, as shown in Figure 5A′.

The solid lines in Figure 5 present the absorbance changes monitored at 475 and 320 nm in acidic thiocyanate solution containing iron ion. In the presence of Fe(III), Fe(III) in the OTTLE cell was previously reduced to Fe(II) at 0.00 V, and then the absorbance–potential curves were recorded from 0.00 V to positive potentials. On the initial positive scan, Fe(II) is oxidized to Fe(III), the absorbance at 475 nm increases and gives a broad peak during the negative scan, and then Fe(III) is reduced to Fe(II) with an absorbance "half-wave potential" of +0.32 V, where the absorbance "half-wave potential" means the potential at which an absorbance is equal to one-half of the maximum absorbance on the absorbance–potential curve observed during the negative scan. The absorbance monitored at 320 nm exhibits a sharp peak during the negative scan, and the oxidized species are totally reduced in a relatively narrow potential region (approximately 160 mV) with an absorbance "half-wave potential" of +0.38 V. Although the absorbance–potential curves monitored at 320 nm in acidic thiocyanate solutions with and without iron ion present display an identical shape with a sharp peak, as shown in Figure 5 B, B′, they are clearly different. The electrooxidized thiocyanate solution in the absence of iron ion is reduced in a wide potential region (approximately 250 mV) with an absorbance "half-wave potential" of +0.34 V.

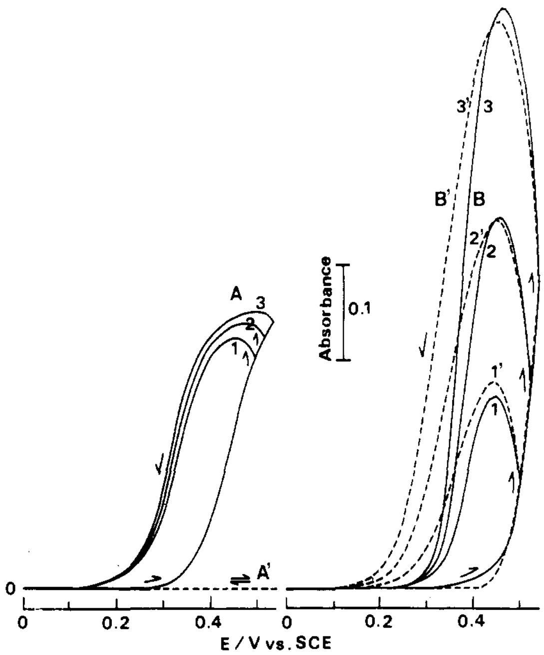

Figure 5. Absorbance–potential curves in 0.1 M NaSCN and 0.1 M $HClO_4$ solutions with (A, B) and without (A′, B′) 2 mM Fe(III) present (cell thickness 0.017 cm; sweep rate 2 mV s^{-1}). Wavelength monitored: (A, A′) 475; (B, B′) 320 nm. Anodic switching potential: (1, 1′) +0.500; (2, 2′) +0.520; (3, 3′) +0.540 V.

If the absorption peaks at 475 and 320 nm for the acidic iron(III)–thiocyanate solution are assigned to the same species, it could be expected that the absorbance–potential curves monitored at both 475 and 320 nm give the same absorbance "half-wave potential".

The absorbance–potential curves monitored at 475 and 320 nm for the acidic iron(III)–thiocyanate solution exhibit the absorbance "half-wave potential" of +0.32 and +0.38 V, respectively. Furthermore, the thin-layer cyclic voltammogram for the same solution gives two cathodic peaks at +0.28 and +0.33 V, as shown in Figure 1. These results indicate that the absorption peak at 475 nm is related to the Fe(III)–NCS^- complex, which is reduced at +0.28 V in the OTTLE cell, and the peak at 320 nm is associated with the oxidized species of SCN^-, which is reduced at +0.33 V in the same cell.

Cauquis and Pierre[13] followed the absorption spectrum of the acetonitrile solution containing the electrooxidation products of SCN^- and observed two peaks at 320 and 283 nm, which were assigned to trithiocyanate ion, $(SCN)_3^-$, and thiocyanogen, $(SCN)_2$, respectively. Provided the assignment of the absorption of $(SCN)_3^-$ is correct, the oxidized species of SCN^- in acidic thiocyanate solution could be assigned to $(SCN)_3^-$. The fact that the acidic iron(III)–thiocyanate solution exhibits an absorption spectrum with peaks at 475 and 320 nm indicates that both the Fe(III)–NCS^- complex and small amounts of $(SCN)_3^-$ are present in acidic iron(III)–thiocyanate solution. It is reasonable to suppose that a small proportion of SCN^- is oxidized by Fe(III) to yield $(SCN)_3^-$ in an acidic iron(III)–thiocyanate solution.

The absorbance–time curves monitored at 475 and 320 nm under controlled-potential step from 0.00 to +0.50 V are shown in Figures 6 and 7, respectively. The absorbance at 475 nm increases rapidly until all of Fe(II) in the thin layer is oxidized. The absorbance, measured by extrapolating the linear portion of the curve to zero time as indicated in curve 2 of Figure 6, is proportional to the iron(III) concentration. The molar absorptibility of the Fe(III)–NCS^- complex determined from the absorbance at the zero time on the absorbance–time curves was found

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[13] Cauquis, G.; Pierre, G. *Bull. Soc. Chim. Fr.* **1972**, 2244.

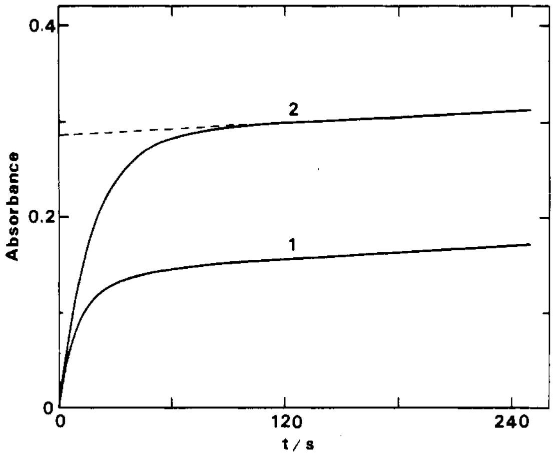

Figure 6. Variation of absorbance at 475 nm with the electrolysis time in 0.1 M NaSCN and 0.1 M $HClO_4$ at +0.500 V (cell thickness 0.017 cm). [Fe(II)]: (1) 1; (2) 2 mM.

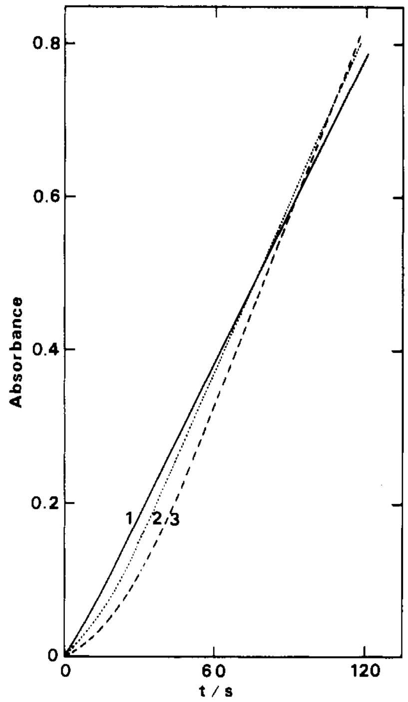

Figure 7. Variation of absorbance at 320 nm with the electrolysis time in 0.1 M NaSCN and 0.1 M $HClO_4$ at +0.500 V (cell thickness 0.017 cm). (cell thickness 0.017 cm).

to be 8.2×10^3 M^{-1} cm^{-1} in 0.1 M NaSCN and 0.1 M $HClO_4$ solution. It seems likely that Fe(III) under present experimental conditions exists predominantly as $Fe(NCS)_2^+$ rather than $Fe(NCS)^{2+}$. Perrin[14] followed the absorption spectra of Fe(III) in acidic solution containing thiocyanate ions of the order of 0.1 M and found that $Fe(NCS)_2^+$ gave an absorption peak at 485 nm with a molar absorptivity of 9.8×10^3 M^{-1} cm^{-1}.

On the other hand, the absorbance at 320 nm increases with increase in electrolysis time since a high concentration of SCN^- is employed as a supporting electrolyte, as shown in Figure 7. The absorbance–time curves in the presence of iron ion display upward curvature at the beginning of the electrolysis; however, the absorbance after passing the curvature rises more rapidly than that observed in the absence of iron ion. This result seems to indicate that Fe(II) is oxidized to Fe(III) in preference to thiocyanate ion at +0.50 V and that $(SCN)_3^-$ produced is stabilized by Fe(III) with the formation of an ion pair. The concentration of $(SCN)_3^-$ at ca. 30 min after the preparation of solution containing 2×10^{-3} M $Fe(ClO_4)_3$, 0.1 M NaSCN, and 0.1 M $HClO_4$ was evaluated as 1.7×10^{-4} M, by use of a molar absorptivity for $(SCN)_3^-$ of 2.2×10^4 M^{-1} cm^{-1} at 320 nm.[8]

The formation of $(SCN)_3^-$ in acidic iron(III)–thiocyanate solution could be explained by the reactions

$$Fe(NCS)_2^+ \xrightarrow[\text{slow}]{} Fe(II) + (SCN)_2^{-}\cdot \qquad (1)$$

$$2(SCN)_2^{-}\cdot \xrightarrow[\text{fast}]{} (SCN)_3^- + SCN^- \qquad (2)$$

The anion radical $(SCN)_2^{-}\cdot$ was first identified in pulse radiolysis of aqueous thiocyanate solution[15] and then was postulated as an intermediate in the chemical oxidation of SCN^- by a variety of reagents.[3-5] The anion radical, which exhibits a transient absorption spectrum at 470 nm with a molar absorptivity of 7.6×10^3 M^{-1} cm^{-1}, has been shown to decay in a diffusion-controlled process following a second-order rate law with the disproportionation rate constant on the order of 10^9 M^{-1} s^{-1}.[15,16] The decay of $(SCN)_2^{-}\cdot$ has been attributed to the reaction

$$2(SCN)_2^{-}\cdot \rightarrow (SCN)_2 + 2SCN^- \qquad (3)$$

Thiocyanogen $(SCN)_2$ is stable in anhydrous solvents such as acetonitrile[13] and acetic acid,[17] and it is rapidly hydrolyzed in aqueous solutions to yield sulfate and cyanide ions as the main products.[2,4] However, this study has not provided any conclusive evidence as to the decomposition products of $(SCN)_3^-$.

Conclusion

The absorption spectrum of the acidic iron(III)–thiocyanate solution consists of two peaks at 475 and 320 nm. The voltammetric and spectroelectrochemical data from this work indicate that the oxidation of SCN^- by Fe(III) as well as the electrooxidation of SCN^- in acidic thiocyanate solutions yields the same species, such as $(SCN)_3^-$ with an absorption peak at 320 nm, and that $Fe(NCS)_2^+$ at 475 nm and $(SCN)_3^-$ at 320 nm are reduced at potentials near +0.28 and +0.33 V, respectively. Trithiocyanate ion is moderately stable in acidic thiocyanate solutions containing Fe(III) and large excess of hydrogen ions. Presumably, this arises from the formation of ion pairs between $(SCN)_3^-$ and Fe(III) and/or the formation of an acid molecule such as $H(SCN)_3$.

It seems likely that the thermal fading of the blood red of iron(III)–thiocyanate solution proceeds by the reduction of Fe(III) by SCN^- with the formation of Fe(II) and $(SCN)_3^-$.

The formal redox potential of the couple $SCN^-/(SCN)_2^{-}\cdot$ has been estimated to be 1.29–1.33 V vs. NHE.[4,5] If this is really the case, a simple electron transfer from SCN^- to Fe(III) is not favored thermodynamically since the standard potential for the couple Fe(III)/Fe(II) is +0.77 V vs. NHE.[18] However, it is apparent from this work that the experimental redox potential for the couple $SCN^-/(SCN)_3^-$ is close to +0.68 V vs. NHE, at which the mixed current associated with the oxidation of SCN^- and the reduction of $(SCN)_3^-$ is observed. This value is close to +0.77 V vs. NHE for the couple of $SCN^-/(SCN)_2$.[18]

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Registry No. $Fe(NCS)_2^+$, 98720-90-2; NaSCN, 540-72-7; SCN^-, 302-04-5; $(SCN)_3^-$, 37234-25-6; Fe, 7439-89-6; Au, 7440-57-5.

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