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INVESTIGATION OF Fe^{3+}/Fe^{2+} REDOX REACTION BY ELECTROCHEMICAL METHODS IN AQUEOUS SOLUTION

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ABSTRACT

Redox reactions of Fe^{+3}/Fe^{+2} was investigated in the solutions H_2SO_4, $FeSO_4$, $Na_2S_2O_5$, $(NH_4)_2S_2O_8$ and mixture of these compounds by electrochemical nethods (pH = 2.8). For this purpose, current–potential curves were obtained for gold and platinum rotating disc electrodes by cyclic voltammetric and with the dropping mercury electrode by cyclic voltammetric, differential pulse polarography and D.C. polarography methods were used, The rotation rate of the disc electrode was 2200 rpm, the potential sweep rate was 3000 mV/min with the solid electrode, and the potential sweep rate was 6000 mV/min, and one drops per second were selected for the mercury drop electrode.

INTRODUCTION

Fe^{3+}/Fe^{2+} redox reactions were studied in different solutions on various electrodes[1–10]. The standard electrode potentials for the materials in the solution are given below[11].

$$SO_4^{2-} + 2H^+ + 2e^- \rightleftarrows SO_3^{2-} + H_2O \quad E = 0.20\ V \quad (1)$$

$$Fe^{3+} + e^- \rightleftarrows Fe^{2+} \quad E = 0.771\ V \quad (2)$$

$$S_2O_8^{2-} + 2e^- \rightleftarrows 2SO_4^{2-} \quad E = 2.01\ V \quad (3)$$

According to these standard electrode potentials $S_2O_8^{2-}$ oxidizes Fe^{2+} and SO_3^{2-} but Fe^{3+} oxidizes only SO_3^{2-} to SO_4^{2-}. For this reason, the following reaction may occur in $S_2O_8^{2-}$, SO_3^{2-} and Fe^{2+} containing solutions:

$$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-} \quad (4)$$

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \quad (5)$$

$$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^- \quad (6)$$

If the solutions contain only SO_3^{2-} and Fe^{3+} the following reactions can be observed.

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (7)$$

$$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e^- \qquad (8)$$

According to the equations (4–6) SO_4^{2-} and Fe^{3+} are produced in the media containing $(NH_4)_2S_2O_8$, $FeSO_4$ and $Na_2S_2O_5$. If the solutions contain $Na_2S_2O_5$ and $FeSO_4$ no reaction can be observed.

$Na_2S_2O_5$ react with water by following

$$Na_2S_2O_5 + H_2O \rightarrow 2NaHSO_3 \qquad (9)$$

reaction. For this reason, in aqueous solution could be find SO_3^{2-}.

EXPERIMENTAL PROCEDURE

Gold and platinum wire electrodes with a diameter of 1 mm were embedded into epoxy resin and prepared as disc electrodes (Figure 1).

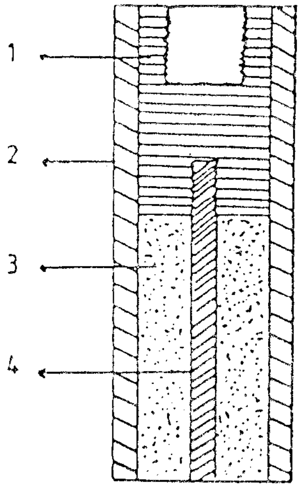

Figure 1. Working electrode (1. Brass 2. Teflon 3. Epoksi 4. Sample).

The studied solutions were prepared with technical $(NH_4)_2S_2O_8$, $Na_2S_2O_5$, $FeSO_4 . 6H_2O$, Merck H_2SO_4 and double distilled water. Experiments were carried out under deareated conditions where the nitrogen was purified of its oxygen using the BASF–RC–11 catalyzer.

Experiments with solid electrodes were carried out using Tacussel PRT–30.01 potentiostat. Tacussel EPL2 recorder and Tacussel EDI rotating disc electrode in the electrolytic cell which is given in Figure 2. The rotation rate of the disc electrode was 2200 rpm, while the potential sweep rate was 3000 mV / min. The working temperature was chosen to be 45 °C.

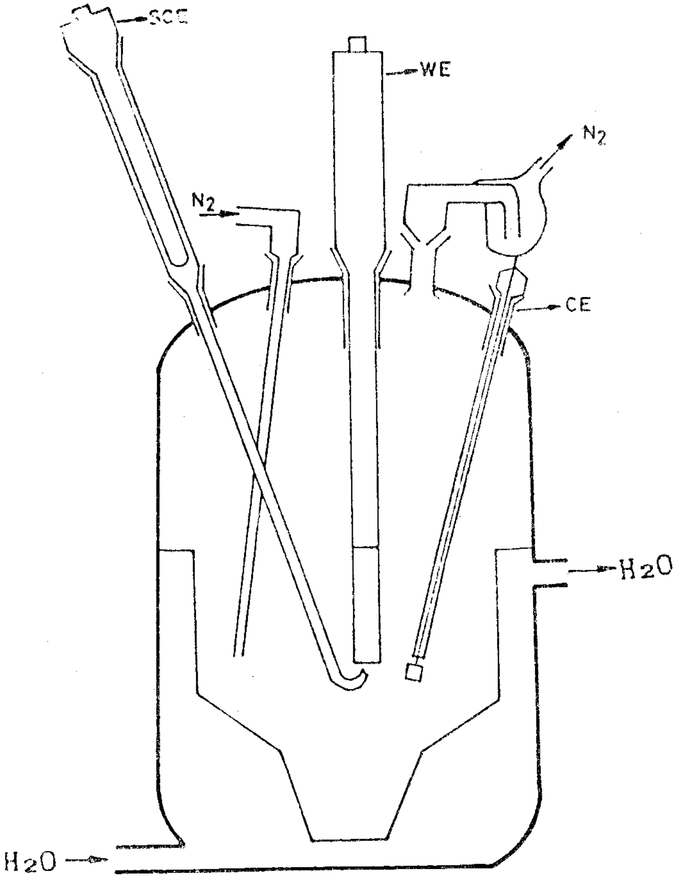

Figure 2. Working cell.

The experiments with the dropping mercury electrode using the cyclic voltammetric, differential pulse polarographic and D.C. polarographic methods were done with the BAS–model 100B polarography equipment. The working temperature was chosen to be 25 °C, the potential sweep rate 6000 mV / min and the drop time one second in this experiment.

All potentials were measured against SCE and referred to the SCE in this paper.

The electrolytes combinations mainly studied are given below (pH = 2.8).

a) H_2SO_4

b) $H_2SO_4 + FeSO_4$

c) $H_2SO_4 + Na_2S_2O_5$

d) $H_2SO_4 + FeSO_4 + Na_2S_2O_5$

e) $H_2SO_4 + (NH_4)_2S_2O_8$

f) $H_2SO_4 + FeSO_4 + (NH_4)_2S_2O_8$

g) $H_2SO_4 + (NH_4)_2S_2O_8 + Na_2S_2O_5$

h) $H_2SO_4 + FeSO_4 + (NH_4)_2S_2O_8 + Na_2S_2O_5$

RESULTS

a) With dropping mercury electrode

The parameters from current–potential curves obtained by cyclic voltammetric, differential pulse polarographic and D.C. polarographic methods between –30 mV and –1030 mV are given in Table 1. These results contain anodic and cathodic peak potentials and currents half-wave poteatials and wawe currents (E_{wave}; I_{wave}). These experiments were carried out in a mixture of 1 cm^3 of the aforesaid solutions and 5 cm^3 of 1M KCl solutions.

b) With solid electrodes

The reduction and oxidation potentials obtained from current–potential curves between –1200 and 1400 mV by cyclic voltammetric method with gold and platinum rotating disc electrode are given in Tables 2 and 3. The experiments were done with carbon electrode, but agreable results could not be obtained, so these results are not given in this paper.

Steady state potentials measured in the studied solutions are given in Table 4. The variation of these potentials with the addition of $Na_2S_2O_5$ in the solution containing $H_2SO_4 + FeSO_4 + (NH_4)_2S_2O_8$ (pH = 2.8)

Table 1. Characteristic Values Obtained With The Dropping Mercury Electrode.

System	Cyclic Voltammetry				Diff. puls polarography		D.C. Polarography	
	Cathodic		Anodic					
	E_{peak} (mV)	I_{peak} (A)	E_{peak} (mV)	I_{paek} (A)	E_{peak} (mV)	I_{peak} (A)	E_{wave} (mV)	I_{wave} (A)
H_2SO_4 + KCl								
H_2SO_4 + $FeSO_4$ + KCl								
H_2SO_4 + $Na_2S_2O_5$ + KCl	-563	1.19 x 10^{-5}	-466	1.37 x 10^{-5}	-480	4.49 x 10^{-7}	-530	9.72 x 10^{-6}
H_2SO_4 + $FeSO_4$ + $Na_2S_2O_5$ + KCl	-570	1.76 x 10^{-5}	-453	2.33 x 10^{-5}	-455	4.36 x 10^{-7}	-505	9.92 x 10^{-6}
H_2SO_4 + $FeSO_4$ + $Na_2S_2O_5$ + $(NH_4)_2$ S_2O_8 + KCl	-590	2.64 x 10^{-5}	-445	3.60 x 10^{-5}	-455	4.40 x 10^{-7}	-505	9.93 x 10^{-6}
H_2SO_4 + $Na_2S_2O_5$ + $(NH_4)_2S_2O_8$ + KCl	-588	2.65 x 10^{-5}	-445	3.55 x 10^{-5}	-455	4.41 x 10^{-7}	-505	9.87 x 10^{-6}

Table 2. The Reduction and Oxidation Potentials on Gold and Platinium Electrode in Studied Solutions (pH = 2.8).

System	pH	E_{red} (mV)	E_{ox} (mV)	Electrodes
H_2SO_4	0.5 0.5	+750 +250	+1050 +50	Au Pt
H_2SO_4 + 28 ppm $FeSO_4$	2.77 2.77	+150 -100	+400 +300	Au Pt
H_2SO_4 + 28 ppm $FeSO_4$ + 6600 ppm $Na_2S_2O_5$	2.83 2.83	-700 -700	-150 -150	Au Pt
H_2SO_4 + 6600 ppm $Na_2S_2O_5$	2.83 2.83	-700 -700	-100 -100	Au Pt
H_2SO_4 + 900 ppm $(NH_4)_2S_2O_8$	2.80 2.80	-650 -650		Au Pt
H_2SO_4 + 6600 ppm $Na_2S_2O_5$ + 900 ppm $(NH_4)_2S_2O_8$	2.82 2.82	-650 -650	-150 -150	Au Pt
H_2SO_4 + 28 ppm $FeSO_4$ + 6600 ppm $Na_2S_2O_5$ + 900 ppm $(NH_4)_2S_2O_8$	2.83 2.83	-700 -650	-100 -100	Au Pt

Table 3. The Rreduction and Oxidation Potentials on Gold and Platinium Electrode in the Solutions Containing Different Values of Fe^{2+} and $Na_2S_2O_5$ (pH = 2.8).

System	pH	E_{red} (mV)	E_{ox} (mV)	Electrodes
H_2SO_4 + 28 ppm $FeSO_4$ + 900 ppm $(NH_4)_2S_2O_8$	2.83 2.83	-400 0.0 and -400	 +200	Au Pt
H_2SO_4 + 112 ppm $FeSO_4$ + 900 ppm $(NH_4)_2S_2O_8$	2.8 2.8	-350 0.0 and -400	 +200	Au Pt
H_2SO_4 + 112 ppm $FeSO_4$ + 360 ppm $Na_2S_2O_5$	2.8 2.8	+100 and -350 0.0	+250 +250	Au Pt
H_2SO_4 + 28 ppm $FeSO_4$ + 95 ppm $Na_2S_2O_5$ + 900 ppm $(NH_4)_2S_2O_8$	2.8 2.8	0.0 and -350 0.0 and -400	+200 -200	Au Pt
112 ppm $FeSO_4$ + 360 ppm $Na_4S_2O_5$ + 900 ppm $(NH_4)_2S_2O_8$ + NaOH	2.8 2.8	+100 and -350 0.0	+250 +250	Au Pt

are given in Table 5 (Figure 3). Steady state potentials measured with the addition of $Na_2S_2O_5$ in the solution containing H_2SO_4 + $(NH_4)_2S_2O_8$ are given in Table 6 (Figure 4).

Table 4. Steady State Potentials Measured Aganist Standart Calomel Electrode (SCE).

System	E_{eq} (mV)	Electrodes
H_2SO_4 + 112 ppm $FeSO_4$	+200 +160	Au Pt
H_2SO_4 + 900 ppm $(NH_4)_2S_2O_8$	+730 +680	Au Pt
H_2SO_4 + 360 ppm $Na_2S_2O_5$	-140 +10	Au Pt
H_2SO_4 + 112 ppm $FeSO_4$ + 360 ppm $Na_2S_2O_5$	+90 -60	Au Pt
H_2SO_4 + 112 ppm $FeSO_4$ + 900 ppm $(NH_4)_2S_2O_8$	+820 +670	Au Pt
112 ppm $FeSO_4$ + 360 ppm $Na_2S_2O_5$ + 900 ppm $(NH_4)_2S_2O_8$ + NaOH	+740 +570	Au Pt

Table 5. Change of Steady State Potentials With the Amount of $Na_2S_2O_5$ Added Into the H_2SO_4 + 112 ppm $FeSO_4$ + 900 ppm $(NH_4)_2S_2O_8$ Solution.

Gold		Platinium	
$Na_2S_2O_5$ (ppm)	E_{eq} (mV)	$Na_2S_2O_5$ (ppm)	E_{eq} (mV)
0	+820	0	+670
210	+750	180	+620
420	+710	360	+460
840	+310	720	+330
1680	-70	1440	+225
3360	-95	2880	+140
6720	-105	5760	+10
		8652	-120
		14442	-120

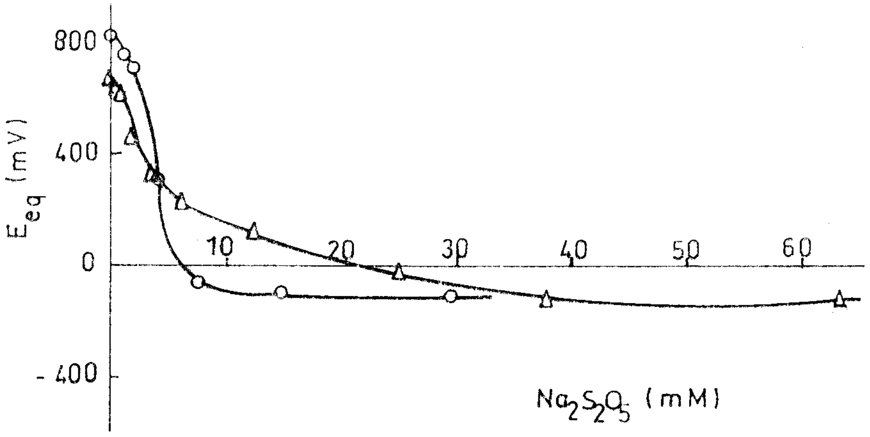

Figure 3. Change of steady state potentials versus of gold (o) and platinium (△) with the amount of $Na_2S_2O_5$ added in the H_2SO_4 + 112 ppm $FeSO_4$ + 900 ppm $(NH_4)_2S_2O_8$ solution.

Table 6. Change of Steady State Potentials With the Amount of $Na_2S_2O_2$ Added Into the H_2SO_2 + 900 ppm $(NH_2)_2S_2O_2$ Solution.

$Na_2S_2O_2$ (ppm)	E_{eq} (mV) Gold	E_{eq} (mV) Platinium
0	+730	+680
180	+230	-30
360	+210	-120
720	+200	-150
1440	+190	-160
2880	+180	-160
5760	+180	-160
8652	+170	-160

DISCUSSION

a) With dropping mercury electrode

It can be seen from Table 1, that only $Na_2S_2O_5$ is reduced and oxidized between studied potentials and media, because, there is only one anodic and cathodic current peak observed from current–potential curves between -30 and -1030 mV. On the other hand, characteristic values E_{wave} and I_{wave} for the reduction reactions are approximately

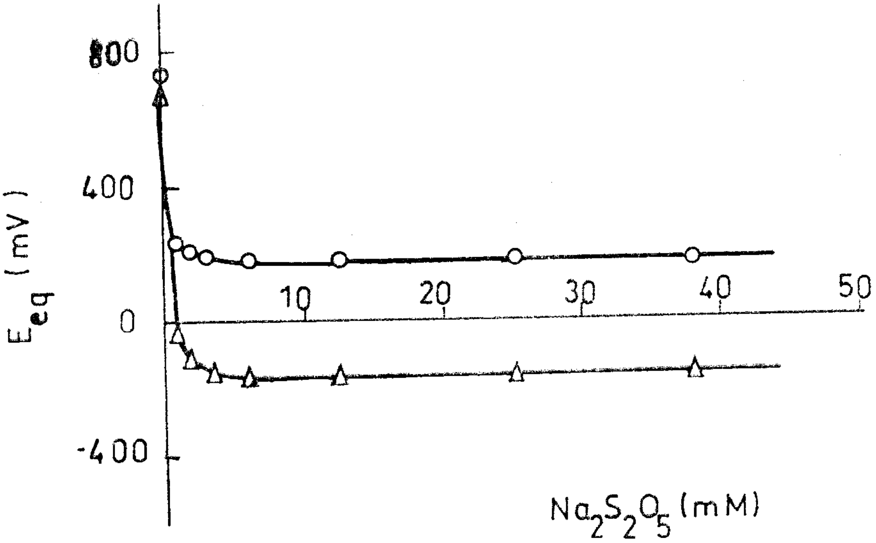

Figure 4. Change of steady state potentials versus of gold (o) and platininium (△) with the amount of $Na_2S_2O_5$ added into the H_2SO_4 + 900 ppm $(NH_4)_2S_2O_8$ solution.

constant in different solutions. These values show that only one compound could react on the mercury electrode in the studied solutions. These could also be seen from current–potential curves obtained by cyclic voltammetric method (peak potentials for reduction between –563 and –590 mV, peak potentials for oxidation between –445 and –466 mV). The variation of peak currents is the result of increasing conductivity and ratio of SO_4^{-2} / SO_3^{-2} with the addition $FeSO_4$ and $(NH_4)_2S_2O_8$ in the solution containing $Na_2S_2O_5$. The peak currents obtained increased from 1.29×10^{-5} A to 2.65×10^{-5} A for the reduction reaction and from 1.37×10^{-5} A to 3.60×10^{-5} A for the oxidation reaction.

The reduction reaction of Fe^{3+} is at –600 mV on the mercury electrode[12]. No current peaks could be observed in H_2SO_4 + $FeSO_4$ solution, because there wasn't enough Fe^{3+} ions in this medium.

b) With the solid electrodes

According to the standard electrode potentials of Fe^{3+} / Fe^{2+}, $S_2O_8^{2-} / SO_4^{2-}$ and SO_4^{2-} / SO_3^{2-}, there can only be Fe^{3+} ions in the solution containing enough $(NH_4)_2S_2O_8$ or Fe^{2+} ions in the solution containing enough $Na_2S_2O_5$.

$Na_2S_2O_5$ was oxidized at –100 mV in the $H_2SO_4 + Na_2S_2O_5$ solution (Table 2). Also Fe^{2+} ions were oxidized to Fe^{3+} ions at +400 mV and Fe^{3+} ions were reduced to Fe^{2+} ions at +150 mV in $H_2SO_4 + FeSO_4$ aqueous medium on the gold electrode (Table 2). These values are approximately agreable with the literature result[10]. These potential values change with the electrode material and composition of the solution.

The reduction reactions were observed at 0,0 and –400 mV in $H_2SO_4 + (NH_4)_2S_2O_8$ solutions. The current value at –400 mV increased with the addition of $FeSO_4$ into the $H_2SO_4 + (NH_4)_2S_2O_8$ solution. For this reason, Fe^{3+} could be reduced to Fe^{2+} at this potential. Steady state potentials were + 820 mV on gold and + 670 mV on platinum in the $H_2SO_4 + FeSO_4 + (NH_4)_2S_2O_8$ aqueous solutions. These potential values show that only Fe^{3+} ions could be present in this medium.

Reduction reactions at + 100 and –350 mV and oxidation reaction at + 250 mV in the aqueous $H_2SO_4 + FeSO_4 + (NH_4)_2S_2O_8 + Na_2S_2O_5$ solutions were observed (Table 3). The steady state potentials were seen to be + 740 mV on gold and + 570 mV on the platinum electrode in these medias (Table 4). This shows why only Fe^{3+} ions could be found in this media. From this result it can be said that Fe^{3+} ions could reduce to Fe^{2+} ions at about –350 mV. Hydrogen gas evolution was observed at the –650 mV in the studied solutions. For this reason electrode protentials must be kept between –200 and –650 m V. if we want the reduction of Fe^{3+} ions to the Fe^{2+} ions without the oxidation of SO_3^{2-}.

Potentials decreased slowly with the addition of $Na_2S_2O_5$ into the aqueous $H_2SO_4 + FeSO_4 + (NH_4)_2S_2O_8$ solution. The inflection point was observed with the addition of a certain amount of $Na_2S_2O_5$ and afterward the potential was seen to stabilize (approximately –100 mV, Figure 3). According to the upper section of Figure 3 must belong to the Fe^{3+} / Fe^{2+} redox system while the section below must belong to the SO_4^{2-} / SO_3^{2-} equilibrium.

The added amount of $Na_2S_2O_5$ (5mM) up to the turning point is equal the total of $(NH_4)_2S_2O_8$ (3.95 mM) and $FeSO_4$ (2mM). This shows that while $Na_2S_2O_5$ reduces Fe^{3+} to Fe^{2+}, the reduced Fe^{2+} with $(NH_4)_2S_2O_8$ oxidized Fe^{3+} at the same time. The steady state potential decrease to the redox potantial of SO_4^{2-} / SO_3^{2-} after the exhaustion of $(NH_4)_2S_2O_8$ and Fe^{3+} in the media.

The equilibrium potentials on gold and platinum were seen to decrease suddenly to the redox potential of SO_4^{2-} / SO_3^{2-} with the addition $Na_2S_2O_5$ to H_2SO_4 + $(NH_4)_2S_2O_8$ aqueous solution (Figure 4). These equilibrium potential values are favorable with the oxidation potential curves (on gold + 200 mV, on platinum –100 mV).

CONCLUSION

1–) Gold is the best electrode for the reduction of Fe^{3+}. This is agreable with the experimental result of Vielstich and et all[6].

2–) Only Fe^{3+} ions are present in the solution containing $(NH_4)_2S_2O_8$.

3–) The electrode potentials must be held between –200 and –650 mV for the reduction of Fe^{3+} ions to Fe^{2+} ions.

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