

Oxidation of hydrosulphide ions on gold

Part I: A cyclic voltammetry study

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The results of an investigation to determine the mechanism(s) of oxidation of sulphide ions on a gold electrode are discussed. The cyclic voltammetry results are presented in Part I and characterization results after various electrochemical pretreatments are to follow in Part II. The cyclic voltammetry studies show that several stages are involved in oxidation of sulphide ions to form elemental sulphur. Initially, sulphide ions undergo underpotential deposition to form chemisorbed sulphur as isolated atoms. As oxidation proceeds, a monolayer of chemisorbed atoms is formed which reacts with sulphide ions in solution to form polysulphides at higher potentials. As the potential for oxidation is further increased elemental sulphur is produced. The reduction of polysulphide to hydrosulphide ions occurs by a 2-electron transfer process whereas the reduction of elemental sulphur occurs by a 1-electron transfer process. The latter reaction involves the formation of an activated complex which is a relatively slow process.

1. Introduction

For many years, there has been considerable interest in investigation of the electrochemical behaviour of sulphur on metals [1-10]. This interest stems from a desire to delineate basic mechanisms in several different technologies. In the processing of crude oil and natural gas, sulphide ions are known to have corrosive effects on iron base alloys [11-13]. In the field of electrocatalysis, it has been observed that adsorbed sulphur significantly enhances the catalytic activity of various metals [14-17]. Since alkali sulphides have been widely used for a long time in the flotation of base metal oxide and sulphide minerals [18-22] a knowledge of the oxidation/reduction reactions involving sulphur species is important.

Differences in the method of formation of sulphur layers, stimulated by diverse interests, have led to apparently conflicting observations regarding their properties. For example, Allen and Hickling [1, 2] concluded that polysulphide species are formed as intermediates in oxidation of sulphide ions to sulphur. In contrast, Wierse *et al.* [3] consider that the sulphide ions are almost completely discharged by a 2-electron process. These authors and Van Huong *et al.* [6] did not consider polysulphides as intermediates in the electrodeposition of sulphur. Furthermore, Wierse *et al.* [3] did not observe polysulphides in electroreduction of sulphur; an observation which conflicts with the studies of Hamilton and Woods [7], and Buckley *et al.* [9] who suggested that polysulphides are formed as intermediates in electroreduction of sulphur to sulphide ions.

The anodic oxidation of sulphur species in aqueous media on noble metals (such as platinum or gold) has

been widely studied with regard to their catalytic effect on the formation (and adsorption) of an oxide layer. Loucka [14, 15], Samec and Weber [16], and Contractor and Lal [17], among other investigators, studied the electrocatalytic effect of sulphur species on the formation and adsorption of oxide layers at a platinum electrode in acidic media. It was found that the oxide layer growth was inhibited due to the competitive surface equilibrium between HS^- and OH^- ions. Similar experiments were carried out in alkaline sulphide solutions by Huang *et al.* [4] and Kapusta *et al.* [10].

On the basis of cathodic reduction of sulphur-containing films, these authors inferred that multi-layer deposition of sulphur must have occurred on the electrode surface. Studies of surface coverage on a gold electrode in alkaline sulphide solutions of pH 13.8 were carried out by Wierse *et al.* [3]. It was observed that the surface coverage depends on potential. The coverage increased linearly with time for about 30 s whereas for longer times (> 50 s), it reached a constant value; (the behaviour at a potential of -0.05 V was an exception). At this potential the coverage continued to increase with time reaching a value of ~ 0.6 V at 300 s. Sulphur adsorbed on the gold electrode did not exceed a monolayer at any deposition potential, however. In addition, from double layer capacity measurements, these authors concluded that the adsorbed sulphur layer at the gold surface between -0.15 and 0.15 V does not conduct electrons. These investigators did not make any distinction between the types of sulphur formed in this potential range and outside it. Such a distinction is important as is demonstrated in this study. These investigators did suggest, however, that the sulphur

layer formed at $E > 0.0$ V was weakly bound, and hence it had no influence on the electrode capacity.

Hamilton and Woods [7, 23] also carried out electrochemical investigations of aqueous sulphur species for neutral and alkaline pH. Based on cyclic voltammetry studies at stationary and rotated gold electrodes, these investigators suggested an underpotential deposition of sulphur at about -0.05 V, depending on the solution pH, and multilayers of sulphur at potentials > 0.1 V. Based on previous work of Allen and Hickling [1, 2] and on thermodynamic equilibrium between sulphur and aqueous sodium sulphide, these authors suggested that sulphur deposition and its reduction occurs through formation of polysulphide intermediates. It was observed that at -0.15 V, for a pH of 6.8 and at -0.25 V, for a pH of 9.2 the surface coverage (θ) did not increase with time but remained constant and below a monolayer coverage ($\theta \sim 0.4$), similar to the observations of Wierse *et al.* [3]. However, sulphur thickness increased to multilayer levels in the potential region of the major anodic peak. Furthermore, it was reported that at these potentials (0.0 – 0.25 V) the growth rate of sulphur deposition decreased once the initial monolayer had been deposited.

This investigation was undertaken with an objective to study the mechanism of oxidation of hydrosulphide ions on gold. The electrochemical behaviour was studied using cyclic voltammetry (the results are discussed in Part I) and the gold/solution interface was characterized by impedance spectroscopy, cathodic reduction and contact angle measurements (these results are discussed in Part II).

2. Experimental details

Cyclic voltammetry measurements were made with an EG & G Princeton Research potentiostat, Model 173 and Apple II microcomputer connected through a Model 276 interface. Both data acquisition and analysis were carried out with the aid of the computer. A three-electrode system was used with gold as the working electrode, a saturated calomel electrode as the reference electrode and two graphite rods as the counter electrodes. The gold electrode used for the cyclic voltammetry was an EG & G electrode with a geometric surface area of 0.07 cm². However, for contact angle measurements a gold electrode of 0.458 cm² geometric surface area was used. The EG & G electrode had a mirror polish and was used as-received. The electrode for contact angle measurements, obtained from Pine Instrument Co., was wet polished gradually using a 600 grit silicon carbide paper followed by 0.3 μ m and 0.05 μ m alumina suspensions. This procedure produced a mirror surface. The real surface of the electrode was determined for the larger electrode by the method of Hamilton and Woods [7] which gave a roughness factor (ratio of real to geometric surface areas) of 1.4. Two different cleaning procedures were tried to clean the gold electrode. In the first procedure the electrode was cleaned

with chromic acid and then thoroughly washed with distilled water before being introduced into the cell. In the second procedure the electrode was subjected to a repetitive triangular potential cycling between -0.75 and 0.4 V at 0.02 V s⁻¹ until a steady state voltammogram was attained (~ 23 cycles). This electrochemical pretreatment was carried out in the borate buffer. Both these treatment procedures gave voltammograms which were similar to those reported by other investigators [7, 9]. The chromic acid cleaning treatment was used in this investigation because a long electrochemical pretreatment might have interfered with sulphur reactions.

Prior to each measurement a 0.1 M sodium tetraborate solution was deoxygenated by bubbling purified nitrogen overnight. The Na₂S stock solution was then added to obtain the desired concentration. The concentration of sulphide ions in the stock solution was determined by titration with a standard solution of lead perchlorate. Care was taken to protect the solution from oxidation by opening the bottle under nitrogen. The electrode was preconditioned at the desired potential for a period of about three hours unless otherwise stated. During the entire experiment, flow of nitrogen at the surface of the solution was continued.

Distilled water of specific resistivity greater than 2 Mohm cm was obtained from a tin-lined Barnstead still (Model 210) equipped with a Q-baffle system for use in this investigation. The experiments were conducted at room temperature (298 ± 1 K).

3. Results and discussions

Voltammograms obtained by stepwise change in the vertex (upper limit of potential) ($E_{s,a}$) are shown in Fig. 1 for scan rate of 5 mV s⁻¹. The upper potential limit of the scan was -0.4 V for the first scan, -0.15 V for the second, 0.04 V for the third, 0.24 V for the fourth and 0.45 V for the fifth scan. Similar voltammograms were obtained at other scan rates also. Although such voltammograms have been observed by previous investigators [7, 9] these are presented in Fig. 1 to facilitate the discussion of the effect of scan rate. The anodic branch of the voltammogram is divided into five regions, marked as a to e. The exact position of various boundaries between regions is based on a.c. impedance and other results which are presented in Part II.

3.1. Underpotential deposition of sulphur

Peak I, observed in Fig. 1 at potentials below $E_{s,a} = -0.45$ V (Region a), is attributed to underpotential deposition (UPD) of sulphur. The current for this peak increased with HS⁻ concentration when the concentration was low ($< \sim 5 \times 10^{-5}$ M) whereas it becomes independent of concentration when the HS⁻ concentration was greater than 8×10^{-5} M. On the basis of these results it is considered that the electro-deposition of sulphur occurs by a two-step process.

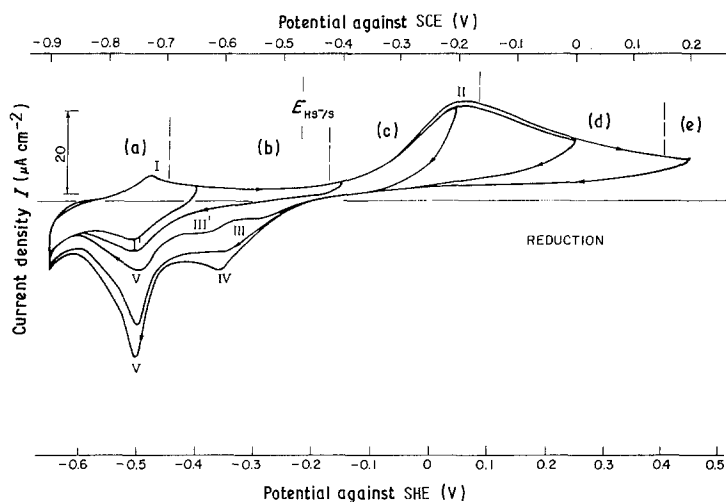
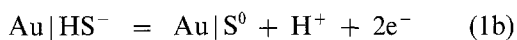


Fig. 1. Voltammograms for a gold electrode in 0.1 M sodium borate and 2×10^{-4} M sodium sulphide solution (pH 9.3) with various potential limits.

Initially, HS^- ions adsorb without a formal change transfer according to the reaction



where $\text{Au}|\text{HS}^-$ represents adsorbed ions. The adsorbed ions undergo oxidation according to the reaction.



where $\text{Au}|S^0$ represents chemisorbed S^0 . The chemisorbed sulphur is considered to be in atomic state instead of the more stable S_8 -ring allotrope. Reaction 1b occurs at potentials considerably below the thermodynamic potential for oxidation of HS^- to elemental sulphur. The coverage of gold by atomic sulphur was below a monolayer in Region a. Similar observations have been made by Hamilton and Woods [7]. The oxidation product formed during the anodic process represented by Reaction 1b was reduced in a single cathodic peak I' for which the peak potential, $E_{p,I'} = -0.51$ V. The dependence of current for peak I' on HS^- concentration was similar to that of peak I. The cathodic process can be written as reverse of Reaction 1b. The peak potentials for peaks I and I' were independent of scan rate as shown in Fig. 2. In addition, the peak current, $I_{p,I}$ varied linearly with

square root of scan rate as shown in Fig. 3. Furthermore, a difference between $E_{p,I}$ and $E_{p,I'}$ of 0.03 V was found. On the basis of these observations it is suggested that Reaction 1b is a 2-electron transfer, reversible process which gives rise to peaks I and I' in cyclic voltammetry when the scan range is -0.65 to -0.45 V. Hamilton and Woods [7] have shown that these peaks are unaffected by the rotation of the electrode which further confirms the hypothesis that surface reactions rather than diffusion processes control the peaks I and I'. The behaviour of the electrode outside this scanning range is discussed in the next section.

3.2. Monolayer formation of chemisorbed sulphur

When the vertex potential, $E_{s,a}$, was increased such that the potential extended into Region b (Fig. 1), the surface coverage by chemisorbed sulphur approached a monolayer, as determined by cathodic charge transfer. Although Peak I continues to satisfy the criterion for a reversible process ($E_{p,I}$ being independent of scan rate as shown in Fig. 4) the criterion of reversibility is no longer valid for peak I'. From these results it is postulated that the electroreduction of chemisorbed sulphur becomes more difficult when $E_{s,a}$ is taken to -0.15 V or higher. A gradual structural change of the chemisorbed sulphur could contribute

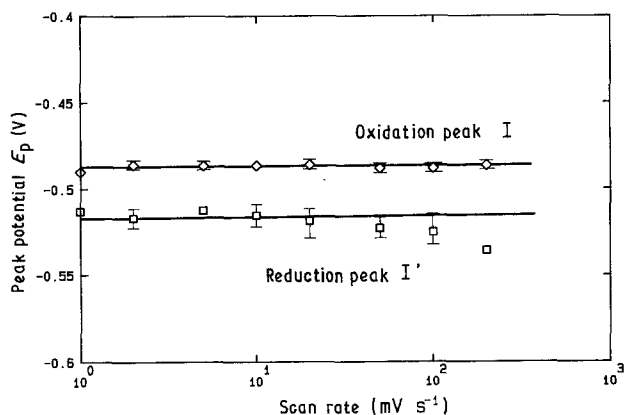


Fig. 2. Dependence of the anodic ($E_{p,I}$) and cathodic ($E_{p,I'}$) peak potentials of the peaks I and I', respectively, on logarithm of the scan rate. Scanning range: -0.065 to -0.4 V. Solution composition same as in Fig. 1.

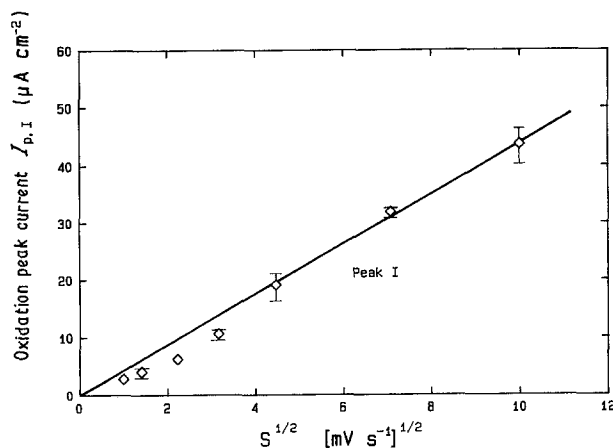


Fig. 3. Dependence of the anodic ($I_{p,I}$) peak current density of the peak I on square root of the scan rate. Scanning range: -0.65 to -0.4 V. Solution composition same as in Fig. 1.

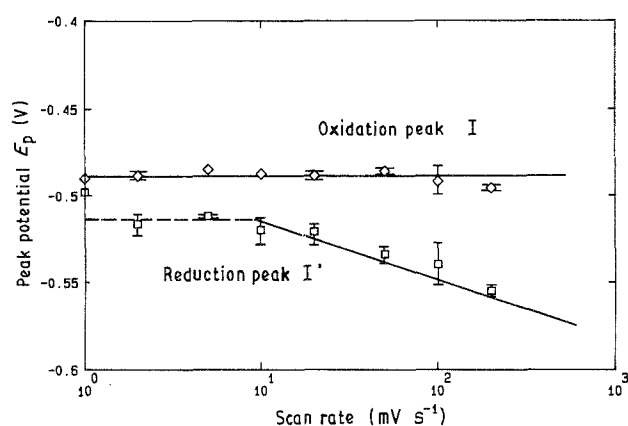
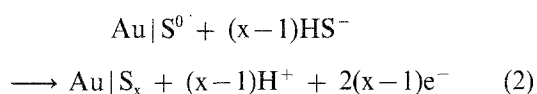


Fig. 4. Dependence of the anodic ($E_{p,I}$) and cathodic ($E_{p,I'}$) peak potentials of the peaks I and I', respectively, on logarithm of the scan rate. Scanning range: -0.65 to -0.15 V. Solution composition same as in Fig. 1.

to this behaviour. From these results it is proposed that the nature of the surface changes in Region b. Passivation of gold occurs in this region through growth of a 2-dimensional layer, which may be written as Au|S_x . The following reaction is proposed.



a.c. impedance spectroscopy results presented in Part II confirm passivation of gold in this region. Furthermore, it is seen in Fig. 4 that $E_{p,I'}$ varied with $\log v$, and the slope

$$\frac{\partial E_{p,I'}}{\partial \log v} = 0.03 \text{ V per decade} \quad (3)$$

which is the expected value for a totally irreversible system. Since $(\partial E_p / \partial \log v) = 30/\alpha n$, $n = 2$ if $\alpha = 0.5$.

3.3. Formation of polysulphide intermediates

When the vertex potential $E_{s,a}$, was increased such that the potential was in Region c, two additional cathodic peaks marked as III and III', were observed. These peaks were associated with reactions involving polysulphides which were deposited when the potential was in this region. Polysulphides were formed in this potential range by a combination of Reactions 1 and 2 with the following chemical reaction:



This mechanism is similar to that proposed by Allen and Hickling [2] who suggested that adsorption of polysulphides could occur through interaction between the electrodeposited sulphur film and sulphide ions. Rotating ring-disc (RRDE) studies of the sulphur (-II)/sulphur (0) system on gold carried out by Buckley *et al.* [9] seem to corroborate this mechanism. The polysulphide formed in the anodic Region c could be reduced through charge transfer reactions of the type

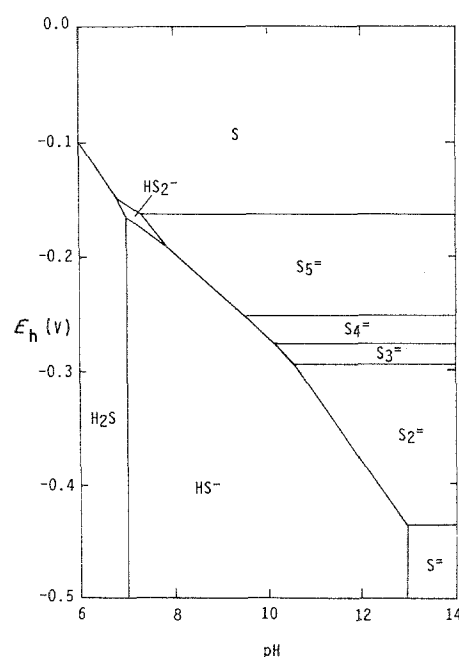
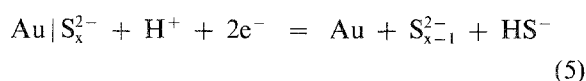
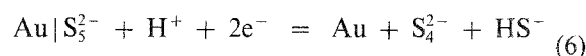
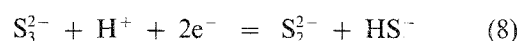


Fig. 5. E_h -pH diagram for the sulphur-water system at 25°C with concentrations of 2×10^{-4} M for sulphur (-II) species and 10^{-6} M for polysulphide species [7].

Several polysulphides can form as intermediates depending upon the value of x . Their stability domains are shown in the E_h -pH diagram in Fig. 5. The potential range in which polysulphides are expected is in reasonable agreement with the experimental data. As seen in Fig. 1, the cathodic peak III commences close to the reversible potential of -0.25 V for the $\text{S}_5^{2-}/\text{S}_4^{2-}$ redox couple. The corresponding reaction may be written as



S_3^{2-} and S_2^{2-} species could also form, through reactions of the type



when the negative-going scan is taken to potentials less than -0.32 V (Peak III'). The reversible potentials of the $\text{S}_4^{2-}/\text{S}_3^{2-}$ and $\text{S}_3^{2-}/\text{S}_2^{2-}$ redox couples are about -0.27 and -0.29 V, respectively, as can be seen in Fig. 5. Because the difference between these potentials is very small (~ 0.02 V), it was assumed that the peak potentials of the Reactions 7 and 8 overlap.

Through the RRDE studies Buckley *et al.* [9] demonstrated that the polysulphide intermediates formed at pH 9.2 contained an average of 3.3 sulphur atoms which is consistent with the above mechanism. The effect of scan rate is shown in Fig. 6. The potential for peaks I and III are independent of scan rate indicating a reversible surface process. On the other hand, the potential for peaks III' and V vary with scan rate (for $v \geq \sim 0.5$ mV s^{-1}). The change in potentials are given by

$$\frac{\partial E_{p,III}}{\partial \log v} = 0.03 \text{ V per decade} \quad (9)$$

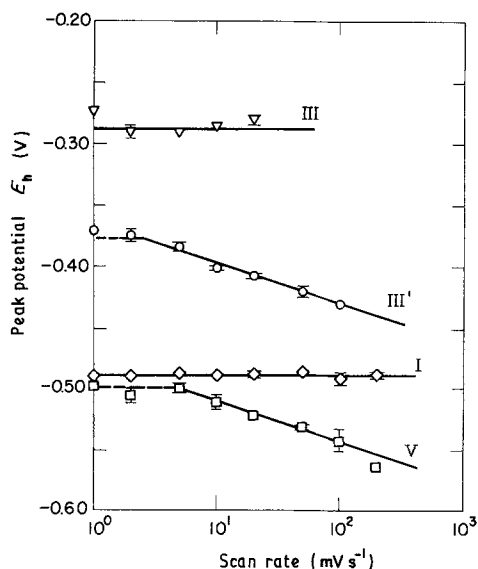
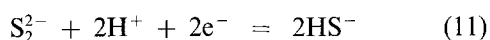


Fig. 6. Dependence of the anodic ($E_{p,I}$) and various cathodic ($E_{p,III}$, $E_{p,III'}$, and $E_{p,V}$) peak potentials, on logarithm of the scan rate. Scanning range: -0.65 to 0.04 V. Solution composition same as in Fig. 1.

$$\frac{\partial E_{p,V}}{\partial \log v} = 0.03 \text{ V per decade} \quad (10)$$

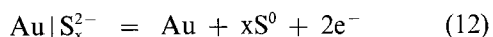
which are the expected values for totally irreversible systems. Peak V represents electroreduction of S_2^{2-} ions to HS^- ions, according to the reaction



The current in peak V depends upon the rate of stirring, a behaviour which was also observed by Hamilton and Woods [7]. These findings suggest that diffusion of H^+ was rate determining for the process corresponding to peak V.

3.4. Multilayer deposition of sulphur

When the anodic scan was taken to potentials more positive than $E_{s,a} = 0.08$ V (marked as Region d in Fig. 1), elemental sulphur was formed according to the reaction



Peaks IV and V were observed when the elemental sulphur was reduced in the cathodic scan from Region d. The change in peak potential is given by

$$\frac{\partial E_{p,IV}}{\partial \log v} = 0.06 \text{ V per decade} \quad (13)$$

for peak IV, and

$$\frac{\partial E_{p,V}}{\partial \log v} = 0.03 \text{ V per decade} \quad (14)$$

for peak V as seen in Fig. 7.

On the basis of these results it is concluded that peak IV corresponds to a 1-electron process whereas peak V corresponds to a 2-electron process. It was also observed that the charge associated with peak IV was always less than that corresponding to a monolayer and its value did not change significantly with either

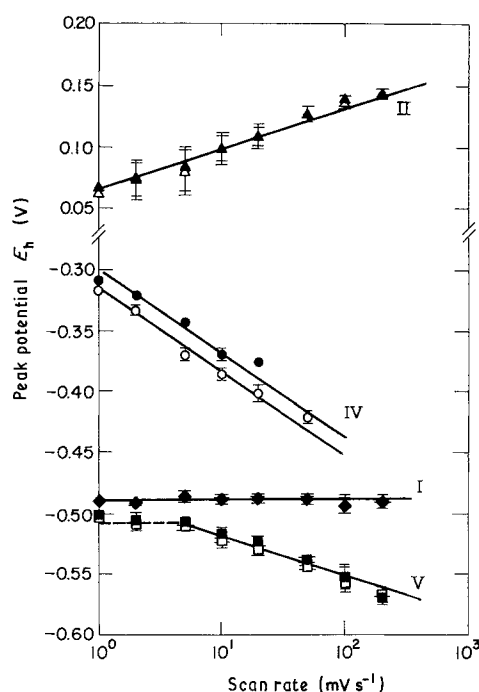
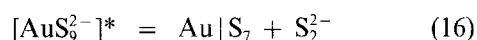
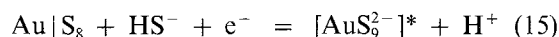
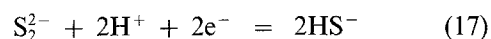


Fig. 7. Dependence of the peak potentials of various anodic ($E_{p,I}$ and $E_{p,II}$) and cathodic ($E_{p,IV}$ and $E_{p,V}$) peaks, on logarithm of the scan rate. Scanning range: -0.65 to 0.24 or 0.44 V, represented, respectively, by solid and empty symbols. Solution composition same as in Fig. 1.

the scan rate or the vertex potential. We postulate that the reduction of elemental sulphur occurs through a 1-electron process with an activated complex, $[AuS_9^{2-}]^*$, as an intermediate. The reaction might be written as



which gives rise to the reduction peak IV. $Au|S_7$ represents a chemisorbed form of S which can undergo further decomposition reactions. Reduction of S_2^{2-} species occurred thus



giving rise to peak V. These observations show that polysulphides can be reduced readily, but the reduction of elemental sulphur is slow.

These results are consistent with previous findings in which it was suggested that reactions involving elemental sulphur are generally slow. Most likely Reaction 15 is the rate-determining step for the electroreduction of elemental sulphur. The reaction product, S_2^{2-} underwent reduction at about -0.5 V to give rise to Peak V in the cathodic scan. From Fig. 7 it can be seen that when $E_{s,a}$ exceeded 0.04 V (Region d), Peak I was controlled by reversible surface process, while Peak V is influenced by mass transport [7, 9]. In quiescent solution, the polysulphide intermediates formed during sulphur reduction remained at the electrode surface and were reduced further to HS^- ions. The diffusion controlled process responsible for Peak V is also confirmed by the shift of $E_{p,V}$ to more negative potentials. The slope of $RT/2F = 0.03$ V per

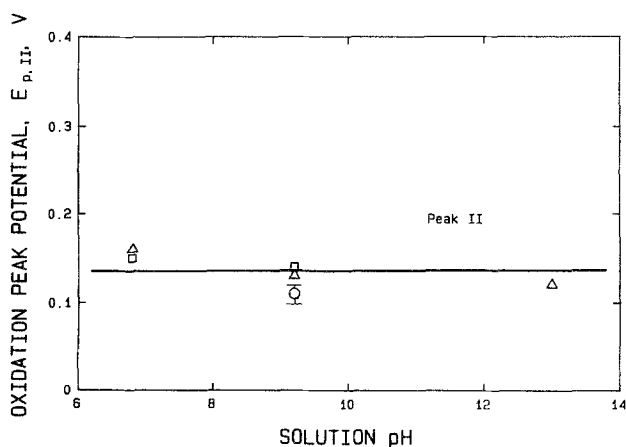


Fig. 8. Dependence of the anodic ($E_{p,II}$) peak potential of the Peak I on pH. Scan rate = 20 mV s^{-1} . Scanning range: 0.5 to 0.44 V. Solution composition same as in Fig. 1. \circ Present work. Data taken from the literature are also represented (\square Hamilton and Woods, 1983; \triangle Buckley *et al.*, 1987).

decade confirms a 2-electron transfer process as shown by Reaction 17. Similarly, it is observed in Fig. 7 that the peak potential ($E_{p,III}$) for Reaction 12 increases, as expected, by $0.03 \text{ V} (R/2F)$ per decade increase in scan rate.

The data of Hamilton and Woods [7] and Buckley *et al.* [9] are presented in Fig. 8 together with the results obtained as part of this investigation. As seen in Fig. 8, $E_{p,II}$ was independent of pH as expected for Reaction 12. The peak potential $E_{p,IV}$, in Fig. 7 shifted to more negative potentials suggesting that electro-reduction of sulphur film became difficult as a result of more oxidation charge being passed. This behaviour would be expected for a resistive film of sulphur.

4. Summary

As the potential was gradually raised, stagewise oxidation of sulphide ions occurred. Underpotential deposition of sulphide ion to form chemisorbed sulphur occurred by a 2-electron change transfer process in the potential range of -0.60 to -0.45 V . The sulphur layer grew to a 2-dimensional layer in the potential range of -0.45 to -0.15 V . In the potential range of -0.15 to 0.08 V polysulphide ions were formed through reactions between chemisorbed sulphur atoms and hydrosulphide ions in solution. The polysulphide ions could be reduced to hydrosulphide ions by a 2-electron transfer reaction.

Elemental sulphur was produced if oxidation was carried out in the potential range of 0.08 to 0.4 V . The oxidation reaction was also a 2-electron transfer process. The reduction of elemental sulphur, however, occurred by a 1-electron transfer process. It is postulated that once the stable S_8 allotrope of sulphur is formed, its reduction takes place through the formation of an activated complex. The activated complex, which is hypothesized to contain 9-sulphur atoms, is formed by a 1-electron charge transfer process. The

activated complex decomposed to form hydrosulphide ions in solution. These results explain the previous findings that once elemental sulphur is formed its reactions are generally slow. Since the reactions of sulphide ions, and the products of reactions are very sensitive to the potential at which the reaction is carried out, it is important that *ex situ* surface characterization studies designed to identify the reaction products be carried out after products were formed under well-defined conditions. *In situ* surface characterization methods have a distinct advantage in these types of systems. The results of some *in situ* characterization studies are reported in Part II of this investigation.

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