Reduction of Sulphur Dioxide in Molten Amides - Voltammetry at Slow Sweep Rates and Illumination

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Electrochemical reduction of sulphur dioxide in different molten amides - (i) ambient temperature ternary mixtures of acetamide + urea + nitrates and (ii) molten acetamide at 85°C - occurs in two one electron steps when slow sweep rates are employed. The second step is inferred to be due to a highly irreversible reduction of $SO_2^{\cdot-}$ to SO_2^{2-}. Illumination of the electrode - electrolyte interface increased the reduction currents and shifted the peak potentials in the positive direction. In contrast to the behaviour at glassy carbon electrodes, a surface process involving $SO_2^{\cdot-}$ is present with mercury electrodes.

Electrochemical reduction of sulphur dioxide has been widely investigated from two points of view - (i) atmospheric pollution and (ii) utilization of SO_2 as a cathodic material in high power density batteries [1-11]. Reduction of sulphur dioxide at various electrodes like platinum, mercury and carbon in solvents like water [1-4], DMF [5,6], DMSO [7,8], PC [9,10] and AN [11] have been reported. A few reports on the reduction of SO_2 in molten solvents are also available [12,13]. Electrochemical reduction of SO_2 in ambient temperature amide melts at mercury, platinum, semiconductor and glassy carbon electrodes have been reported from this laboratory [13,14]. It has been shown that SO_2 undergoes a one-electron reduction to form $SO_2^{\cdot-}$, which subsequently dimerises to dithionite ($S_2O_4^{2-}$). On illuminating the electrode-electrolyte interface (glassy carbon, mercury and semiconductors but not platinum electrode), the reduction current has been found to increase by 80-100% over the dark current [15,16].

In the present paper the results of a cyclic voltammetric study employing very low sweep rates is described and discussed. The influence of light on the reduction process under these conditions is also examined.

EXPERIMENTAL

Preparation of the amide melts and electrodes are the same as described earlier [13-17]. All potentials are referred to the electrode Ag/AgCl,Cl^- (saturated in the melt). Electrochemical studies are performed with a BAS 100 A electrochemical analyser with built-in IR compensation. Illumination of the electrode / electrolyte interface is carried out with a tungsten - halogen lamp (100 W, Spindler and Hoyer, Gottingen, Germany).

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RESULTS AND DISCUSSION

Glassy Carbon Electrode

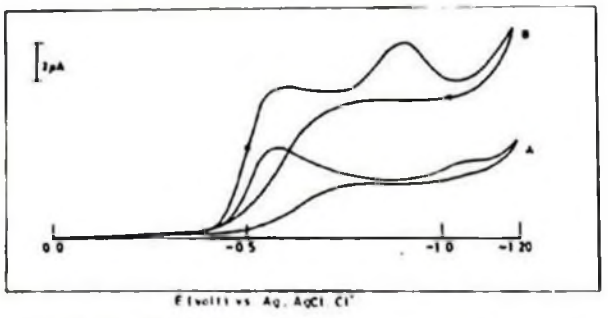


Fig1 Cyclic Voltammograms for SO_2 Reduction Electrode GCE;
Medium Amide Melt; T = 25°C;
$[SO_2]$ = 6.2 x 10^{-3} M/l;
Scan rate 0.002 V/sec
(A) dark (B) Illuminated

When very slow sweep rates are employed (< 0.005 V/sec), two reduction steps are observed for the reduction of SO_2 at 25°C (Fig. 1). The first reduction peak corresponds to the one-electron reduction of SO_2 to $SO_2^{\cdot-}$ [13]. The second cathodic peak potential (E_{pc2}) is found to be highly dependent on sweep rate. It shifts in the negative direction with increasing sweep rates. When the sweep rate exceeds a limit, the second reduction probably occurs outside the electrochemical window. Table 1 shows the maximum sweep rates for observing the second reduction step at various temperatures.

Table 1

Maximum Sweep rate at which the second Cathodic step can be observed.

Temp t/°c	< — Maximum Sweep rate V/sec — > Ternary melt	Molten acetamide
25	0.003	-
45	0.005	-
65	0.01	-
75	0.015	-
85	0.02	0.025

The reduction current of the second peak (I_{pc2}) is only about 1/10th of I_{pc1}. An anodic step is seen, if the sweep is reversed at the end of the first reduction step, but not if reversed beyond the second step. SO_2 is known to undergo a one step, two-electron reduction at Pt electrode [14].

Coulometric experiments carried out at glassy carbon electrode at 25°C in ternary melt at a potential of -1.1 V give a value of two for n (1.9 $\pm$ 0.04). Reduction product shows no anodic step in the reverse sweep. So the $SO_2^{\cdot-}$ produced in the first step must have been completely consumed in the second step. As the first step corresponds to a one electron reduction [13] and the total n for the two steps together is found to be 2, the second step should correspond to a further one electron process. This step could be due to one of the following reductions:

$$SO_2^{\cdot-} + e \longrightarrow SO_2^{2-} \quad ...(1)$$

or

$$2SO_2^{\cdot-} \xrightarrow{\text{dimerise}} \underset{\text{(dithionite)}}{S_2O_4^{2-}} \quad ...(2a)$$

followed by

$$S_2O_4^{2-} + 2H^+ + 2e \longrightarrow S_2O_3^{2-} + H_2O \quad ...(2b)$$

Dimerisation - reduction reaction (2) is ruled out for the following reasons:

(i) Dithionite gives an anodic oxidation step in the reverse scan [13]. This is absent in the present case.

(ii) Dithionite reduction (reaction 2b) is a two-electron, two-proton reaction. Addition of p-toluene sulphonic acid or monochloroacetic acid should shift this reduction potential. Experiments carried out with the addition of p-toluene sulphonic acid or monochloroacetic acid in the present case does not show any shift of E_{pc2}.

It is thus concluded that the second step is due to the reduction reaction (1). In such a case, i_{pc2} is expected to be equal to i_{pc1}. The current in second step is however very small at 25°C. But this current increased with rise in temperature. The ratio i_{pc2}/i_{pc1} increases continuously with temperature (Table 2).

The observed low value of i_{pc2} may be due to the much greater irreversibility of the second step compared to the first electron transfer. The increase in current ratio with temperature is due to the increase in the reversibility (αn_a) of the reduction process. It is worth noting that the second step is not observed at higher sweep rates (Table 1) due to negative shift of the second reduction potential. The ratio of currents become nearly one at slow sweep rates (Table 2) and at higher temperature. Since more time is available for the reduction under constant potential coulometric experimental conditions, all SO_2 could be reduced giving a value of n = 2.

The scheme 1 for second step is confirmed from independent experiments with pure dithionite in the melt. The cyclic voltammogram (CV) of dithionite with slow sweep rates is given in Fig. 2. The reduction is found to occur at the same potential as observed with SO_2 alone in the melt. The second reduction peak is observed only with slow sweep rates as in the case of SO_2 reduction. But dithionite is known to undergo thermal decomposition according to equilibrium:

$$S_2O_4^- \rightleftharpoons SO_2 + SO_2^- \qquad ...(3)$$

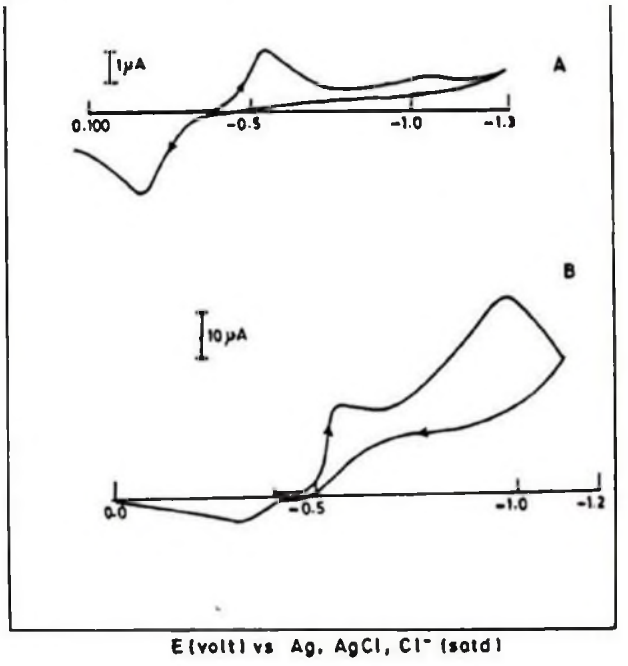


Fig2 Cyclic Voltammograms of Dithionite
Electrode GCE; Medium Amide Melt; Dithionite conc. 5 x 10^{-3} M/l;
(A) Scan rate 0.002 V/Sec (25°C);
(B) Scan rate 0.01 V/Sec (85° C)

Table 2

I_{pc2}/I_{pc1} ratio for Sulphur Dioxide Reduction

SO_2 content 2 mM

Temp t/°C	i_{pc2}/I_{pc1} at Sweep rate V/Sec 0.003	0.005	0.007	0.01	0.02
Ternary Melt					
25	0.017	-	-	-	-
45	0.56	0.45	-	-	-
75	-*	0.9	0.8	0.72	-
85	-*	0.92	0.9	0.8	0.54
Molten Acetamide					
85	-*	0.92	0.90	0.82	0.55

* Peaks are not well separated.

Decomposition occurs upto 7 - 10 % at 25°C [13]. Further, dithionite dissociates (the reverse of dimerization) according to

$$S_2O_4^{=} \rightleftharpoons 2SO_2^{\cdot-} \quad ...(4)$$

Both equilibria shift to the right with increasing temperatures. The SO_2 formed in (3) is reduced in the first cathodic step to $SO_2^{\cdot-}$. This along with $SO_2^{\cdot-}$ from dissociation (4) will be reduced in the second step. This accounts for rapid increase of i_{pc2} with temperature. However, the ratio of i_{pc2}/i_{pc1} is found to be always higher than those observed with only SO_2 in the melt (Table 3). At higher temperatures, the ratio becomes even greater than 1. This is not observed with SO_2 alone in the melt.

Influence of Light on the Reduction Process

Illumination of the electrode - electrolyte interface increases the reduction currents of both steps (Fig.1). The increase in the reduction current of first step is already described [15,16] and is due to the photo-assisted catalytic production of SO_2 at the interface. The mechanism suggested was:

$$SO_2 + e \longrightarrow SO_2^{\cdot-}$$
$$SO_2^{\cdot-} + h\nu \longrightarrow SO_2^{\cdot-} \text{ (excited)}$$
$$SO_2^{\cdot-} \text{ (excited)} + X \longrightarrow SO_2 + X^{-}$$

X is an electron acceptor in solution ; it may be the solvent molecule. The regenerated SO_2 undergoes further reduction resulting in increase of i_{pc1}. The increase in concentration of $SO_2^{\cdot-}$ produced under illumination conditions may be responsible for the increase in the current i_{pc2} also. Both electrochemical and spectroscopic evidence were provided to support the mechanism.

It is also observed that with the illuminated interface, the E_{pc2} shifts in the positive direction (by about + 0.2 V) and the reduction can be observed at even higher sweep rates compared to those under dark conditions. The shift of peak potentials in the presence of light can be explained in terms of the energy levels of SO_2 and $SO_2^{\cdot-}$ as follows:

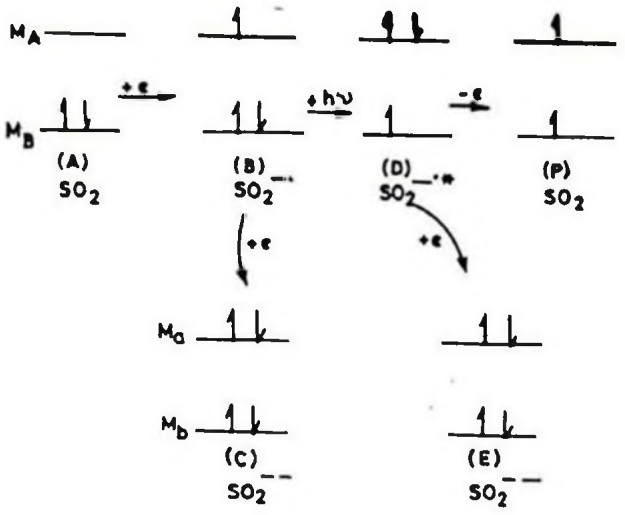
Table 3

I_{pc2}/I_{pc1} Ratio in the Dithionite containing Melt

Dithionite 4 mM

Temp t/°C	I_{pc2}/I_{pc1} at Sweep rate V/Sec 0.003	0.005	0.007	0.01	0.02
Ternary Melt					
25	0.23	0.25	-	-	-
45	0.74	0.61	0.5	-	-
75	- •	1.15	1.00	0.9	-
85	- •	1.6	1.5	1.4	1.00
Molten Acetamide					
85	- •	1.7	1.52	1.5	1.02

• Peaks are not well separated



When an electron is to be transferred to the species $SO_2^{\cdot-}$ in dark, it has to go to the upper level in B; Result is C. On the other hand, when the interface is illuminated, photo-excitation can occur and one electron from the MB level may be transferred to MA level (D). Now in the second reduction step, the electron from the electrode can go to the vacant lower level of D. The energy requirements are now smaller and reduction can occur at more positive potentials. Similarly when the excited $SO_2^{\cdot-}$ looses an electron to the solution, the energy levels of the resulting SO_2 may be depicted as in figure F. The reduction of this SO_2 will be easier than that of A. A small shift in E_{pc} is observed on illumination.

Mercury electrode

When sweep rate exceeds 0.05 V/sec, the CV of low SO_2 concentration melt shows only one cathodic peak and one anodic peak with a fresh mercury surface. This reduction peak was shown to be due to the one electron reduction of SO_2 to $SO_2^{\cdot-}$ and the anodic peak due to the oxidation of dimerised $SO_2^{\cdot-}$ ($S_2O_4^{--}$) to SO_2 was seen. Illumination is found to double this peak current.

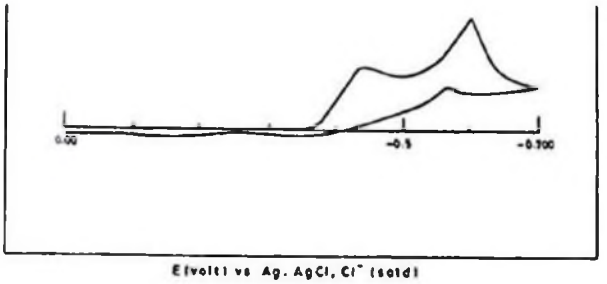


Fig3 Cyclic Voltammograms for SO_2 Reduction
Electrode Mercury (0.025 cm^2);
Medium LN Melt; T = 25°C;
Scan rate 0.005 V/Sec

When slow sweep rates are employed, a second reduction peak is observed (Fig.3). The second cathodic maximum is more peaked than for a diffusion controlled process. The second reduction is observed even at higher sweep rates with higher concentrations of SO_2. I_{pc2} is comparable to I_{pc1} but $I_{pc2} - v^{1/2}$ plots are not linear. On the other hand I_{pc2} - v plot is a straight line with an intercept on the Y - axis (Fig.4). Whenever the second reduction step is observed, the anodic peak current on the reverse scan is considerably reduced. If the potential is held at the first reduction step for some time and then the cathodic sweep applied, an increase in I_{pc2} is observed. The increase is larger with increased times of holding.

The reduction processes are similar to that at GCE under similar conditions. Similarity of reduction processes at GCE and HMDE suggests that, the second reduction step at the mercury also involves $SO_2^{\cdot-}$. But the I_{pc2} - v linearity and the

shape of the peak indicates that a surface process is in operation.

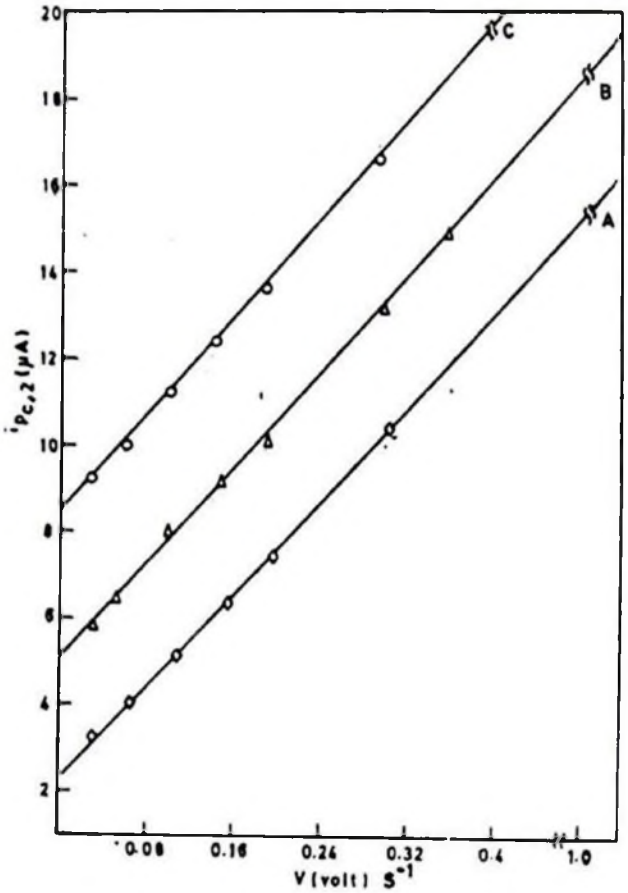


Fig4 i_{pc2} *vs* v **plots for** SO_2 **Reduction**
Electrode Mercury (0.025 cm^2);
Medium AN Melt;
SO_2 conc. (A) 2.6 mM (B) 3.9 mM and (C) 5 mM

Reduction of a surface species in the case of SO_2 reduction at mercury surface was also reported in aqueous medium [1]. From the chronopotentiometric study of SO_2 reduction, Jacobson and Sawyer [1] reported a second reduction step when low currents (leading to long transition times) were employed. This was attributed to an inhibited electrode reaction, the inhibition being the result of adsorption of the first reduction product of SO_2. A second reduction step was also reported in the polarographic studies in the reduction of SO_2 by Reynolds and Yuan [2]. This was attributed to a one-electron reduction of $SO_2^{\cdot-}$ to SO_2^{2-} or HSO_2 to H_2SO_2.

The first reduction step on mercury electrode is reversible even at 25°C [13] but it is reversible on GCE only above 65°C. The second reduction process is also probably much faster when a mercury electrode is used, particularly since a surface reduction is involved. The shift of E_{pc2} with scan rate is smaller and hence second step is observed even at higher scan rates.

In contrast to the behaviour on GCE, a current due to the anodic oxidation of dithionite is observed with mercury electrode even when the sweep is reversed beyond the second reduction potential. Only with very slow sweep rates or with a halt at the second reduction potential the anodic oxidation is negligible. Hence it is concluded that not all $SO_2^{\cdot-}$ is consumed in the second reduction within the time corresponding to higher sweep rates; some dimerisation can still occur.

The second reduction step is also observed with higher sweep rates even with a smaller concentration of SO_2, provided a mercury drop, aged in solution is used. The C-E variation are then distorted.

It is therefore suggested that an adsorbed $SO_2^{\cdot-}$ species is involved in the second reduction. $SO_2^{\cdot-}$ perhaps interacts with a SO_2 species and chemisorbed or interacts with a chemisorbed SO_2 species to form an electroactive species (A). If the process of interaction is slow, the second reduction may be observed only with slow sweep rates. The extent and rate of formation of (A) will be higher with a higher

concentration of SO_2 in solution and the second reduction observed at higher sweep rates.

The surface complex may be SO_2-$SO_2^{\cdot-}$ and this complex has been reported in the coulometric reduction of SO_2 [5].

The effects of illumination on this second reduction are not studied because of the distorted peaks. Some increase in current is however observed.

CONCLUSIONS

1. $SO_2^{\cdot-}$ undergoes a one electron reduction to SO_2^{2-} in amide melts at glassy carbon electrodes and can be observed only at very slow sweep rates.

2. The reduction process is more facile under illuminated conditions.

3. At mercury electrodes, surface processes are involved.

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