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Direct Oxidation of Dimethylsulphoxide and Reduction of Maleic Acid in Methanesulphonic Acid Medium*

Vellasamy Devadoss, C Ahmed Basha, and Krishnamoorthy Jayaraman

Abstract

The direct electro oxidation of dimethylsulphoxide (DMSO) to dimethylsulphone ($DMSO_2$) at a Pb/PbO_2 anode and electro reduction of maleic acid (MA) to succinic acid (SA) at stainless steel cathode have been has been carried out in methane sulphonic acid (MSA) medium in a batch divided cell. It is to be noted that, as methane sulphonic acid medium (MAS) is biodegradable, it is a preferred medium for the electrochemical reactions.

The process parameters such as concentration of MSA, DMSO and current density have been critically examined and the comparative performances of Pb/PbO_2 with TSIA electrode as well as the reusing of electrolyte under optimum conditions have been investigated. The reaction parameters such as acid concentration, current density, the use of divided and undivided cells, etc. have been studied on electrochemical reduction of MA to SA.

In the case of direct electro oxidation of dimethylsulphoxide to dimethylsulphone, the current efficiency on TSIA anode has been around 60- 65% while that with Pb/PbO_2 has been more than 90%. The electro reduction of MA to SA has given current efficiency around 65 – 70%. Based on the result obtained on trials, the optimum parameters of the reaction found to be 1.0 M acid concentration and 5.0 A dm^{-2} current density. Divided cell has given good results when compared to undivided cell.

KEYWORDS: electro synthesis, direct oxidation and reduction, dimethylsulphone, succinic acid, methane sulphonic acid

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1. INTRODUCTION

A wide range of electro organic synthetic reactions have been studied in laboratories around the world (Tomilov et al., 2007). Virtually all organic reactions can be carried out electrochemically with suitable electrolyte, electrode, solvent etc. Recently, electrochemical reactions have been reported with the use of aprotic electrolyte media and also the use of less common acids and bases. Compared to aprotic electrolyte media the aqueous based electrosynthesis often results in less complex electrochemistry, better pH control, lesser problems in processing and hence the aqueous based electrosynthesis has a predominant role in industrial electroorganic synthesis.

A wide range of electroorganic synthetic reactions (both anodic and cathodic) have been carried out in acid media. Among cathodic reactions, some of the important synthetic reactions have been studied include reduction of carbon–carbon double bonds (Cerefice and Fields, 1974), reduction of carboxylic acids (Ochoa et al., 1993), reduction of nitro compounds (Udupa, 1979) etc. and anodic reactions such as oxidation of alcohol to acids (Degner, 1982), oxidation of aromatic hydrocarbons to quinones (Clarke et al., 1976), oxidation of phenol (Eastman, 1977) etc. Most of the reactions have been carried out in media such as aqueous sulphuric acid, hydrochloric acid, acetic acid etc. There have been very few reactions about the study of organic reactions using methane sulphonic acid (MSA) as electrolyte. Wawzonek et al. (1956) have studied the polorographic behaviour of aromatic nitro compounds and triaryl carbons in methane sulphonic acid. They have reported that MSA is a suitable solvent for the pologrаphic study in a range upto –0.9V–1.0V vs Hg pool. In the present study the electro oxidation of dimethylsulphoxide (DMSO) to dimethylsulphone ($DMSO_2$) and the electrochemical reduction of maleic acid (MA) to succinic acid (SA) have been taken up as typical reactions with the use of MSA as the electrolyte medium.

1.1 Oxidation of Dimethylsulphoxide to Dimethylsulphone

The direct electrochemical oxidation of dimethylsulphoxide to dimethylsulphone in methanesulphonic acid medium can be represented as

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{S}-CH_3 \xrightarrow[\text{Aq.}CH_3SO_3H]{(Pb/PbO_2)/TSIA} CH_3-\underset{\underset{\displaystyle O}{\|}}{\overset{\overset{\displaystyle O}{\|}}{S}}-CH_3 + 2e^- \qquad (1)$$

Dimethylsulphone find application as solvent in extractive distillation, electroplating baths, production of adhesives (Budavari, 1989) etc. Molten

$DMSO_2$ is a suitable electrolyte for lithium intercalation batteries (Pereira-Rames et al., 1986). It is normally prepared from dimethyl sulphide or DMSO. The oxidation of DMSO is carried out in hot nitric acid at 120 – 150°C giving 86% yield of $DMSO_2$ (Goheen and Bennett, 1961). Dimethylsulphone is also produced photo–chemically from DMSO using photosensitizers (Schenck and Krauch, 1963). Electrochemical oxidation of dimethyl sulfide in acetonitrile in the presence of 1% water yields $DMSO_2$ (Bard, 1978). The electrochemical oxidation as well as the reduction of DMSO and sulpholane in aqueous sulphuric acid medium on platinum electrode was reported (Velayutham and Noel, 1992).

Voltammetric responses of the anodic oxidation of DMSO in 1M H_2SO_4 on polypyrole–PbO_2 electrode was also reported (Vasudevan et al., 2000). And the electrosynthesis of $DMSO_2$ from DMSO on DSA in sulphuric acid medium have been reported (Swann et al., 1949). There are no reports about the use of MSA medium for voltammetric and preparative work relating to the synthesis of $DMSO_2$ from DMSO.

1.2 Reduction of Maleic Acid

The direct electrochemical reduction of maleic acid to succinic acid in methanesulphonic acid medium can be represented as

$$\begin{array}{l} CH\ COOH \\ \| \\ CH\ COOH \end{array} + 2H^{+} + 2e^{-} \xrightarrow[\text{Aq. } CH_3SO_3H]{\text{Stainless Steel}} \begin{array}{l} CH_2\ COOH \\ | \\ CH_2\ COOH \end{array} \qquad (2)$$

Maleic acid is reducible at both low over–voltage (Elving and Tectelbaum, 1949; Vassiliev et al., 1979) and high over–voltage (Kolthoff and Lingane, 1952) metals. On the high over–voltage Hg electrode, the 2e, $2H^{+}$ reaction is presumed to proceed via ECE mechanism over a wide pH range (Mairanovskii, 1962; Parsons and Reilly, 1970). Capacitance measurements on Hg electrode indicate MA adsorption (Kanakam et al., 1967) over a wide potential range. The commercial process for the electrochemical reduction of MA to SA was developed on lead electrode in sulphuric acid medium (Jayaraman et al. 1995). In recent studies, the lead electrode is replaced by electro catalytic anodes (Vijayabarathi et al., 1995) and Ti/ceramic TiO_2 anodes (Vasudevan, 1995).

The present literature survey indicates that MSA has not been employed as an electrolyte for direct oxidation of DMSO or reduction of MA or indeed any other organic compound. This is understandable since MSA is not relatively cheap when compared to other mineral acids commonly employed. However, in the present research work it was felt desirable to take up a simple system each for

the direct oxidation and reduction studies to evaluate the performance of this acid under these circumstances.

Cyclic voltammetry (CV) has been a widely adopted technique for the investigation of electrochemical processes over the entire potential window available for electroorganic synthesis.

Hence, both cyclic voltammetry and preparative work on the oxidation of DMSO and reduction of MA have been hence adopted for the present investigation.

2. MATERIALS AND METHODS

High purity dimethylsulfoxide (DMSO) (S.D Fine Chemicals Ltd, India) and Maleic acid (S.D. Fine Chemicals Ltd., India) used were of high purity. All other chemicals used in these investigations were of either AR or spectroscopic grade. All the solutions were prepared in doubly distilled water. The ion-selective membrane Nafion 423 (Dupont, USA), cation exchange membrane was used as a separator (diaphragm).

2.1 Cyclic Voltammetry

A single compartment cell with Glassy Carbon, Tokai GC-A type (Tokai Electrode Manufacturing Company Ltd., Japan) as working electrode, platinum as counter electrode and saturated calomel electrode as a reference electrode has been used for CV studies. A potentiostat /galvanostat Model IM6 has been used for obtaining voltammograms. The working electrode has been fixed in a glass tube using epoxy resins. The electrode area has been 0.0706 cm^2. The electrical contact of the glassy carbon electrode (GCE) has been made through a mercury pool. A standard procedure for pre-treatment of electrode has been adopted to get reproducible results. The GCE has been polished to mirror finish using fine emery paper and the surface has been cleaned by cotton to remove any powdery material on the electrode surface, and then degreased thoroughly using trichloroethylene. Then the electrode has been washed with triple distilled water. Then Mechanically pretreated electrode has been electrochemically activated by dipping in de-aerated 0.1 mol L^{-1} potassium chloride solution and has been activated by electrochemical cycling as described in the literature (Noel and Anantharaman, 1989).

The GCE has been potentio dynamically cycled between – 0.5 to +1.5V Vs SCE in 0.1 mol L^{-1} potassium chloride for about 20-30 minutes at sweep rate of 20 mVs^{-1}. After recording the background current, 2.0 mmol L^{-1} potassium ferrocyanide has been added and then potential has been scanned from –.5 to +0.6 V to get a reproducible voltammogram of ferrocyanide/ ferricyanide system with ΔE_p (peak potential separation) value around 60 mV. Such an activated-electrode

will be able to give reproducible results for a few hours. For removal of oxygen from electrolyte, nitrogen has been used (purified by passing it through a series of wash bottles containing alkaline pyrogallol, 1.0 mol L^{-1} sulphuric acid, conductivity water and molecular sieve respectively). All the experiments have been carried out at 25 ± 1 ^{o}C. In all experiments, the electrochemical cell has been washed with nitric acid, distilled water and finally triple distilled water before recording the cyclic voltammogram. Electrochemical activation procedure has been adopted whenever the electrode reproducibility was lost. For calculating experimental data, care has been taken to detect the background current at each cycle.

2. 2 Electrochemical Reactors

The electrochemical batch reactors have been used for direct reaction studies in divided (Figure 1a) and undivided (Figure 1b). The divided cell has been provided with two (anolyte and catholyte) compartments. The anolyte and catholyte compartments have been separated by Nafion 423 (cationic exchange membrane) which has a capacity of 100 mL and 500 mL respectively. The cell has been made up of PVC. The cell contents have been agitated by a glass stirrer connected to electrical motor provided with a speed control unit.

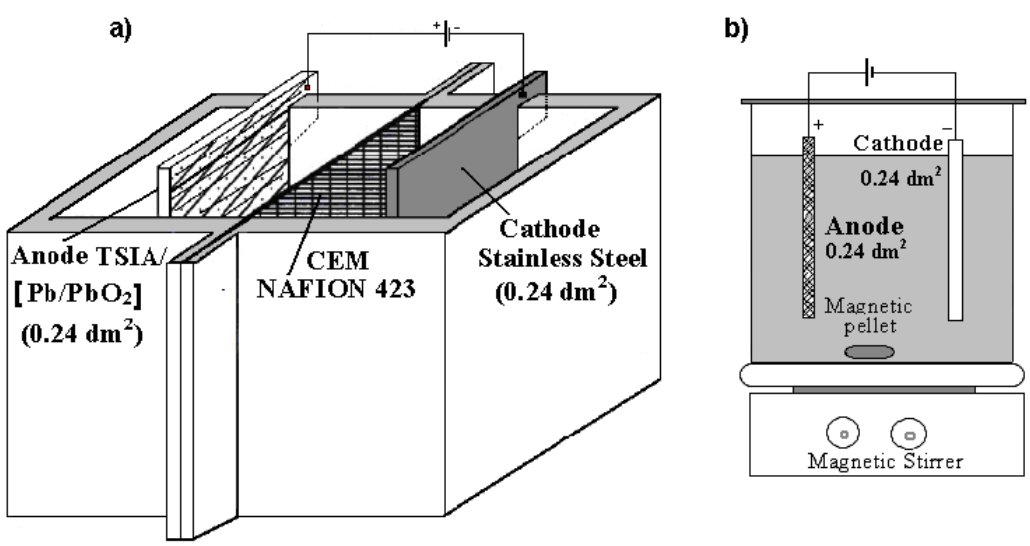

Figure 1. Schematic diagrams of electrochemical batch reactor: a) Divided Cell b) Undivided Cell

For preparative studies, Lead/Lead dioxide (0.24 dm^2) and titanium substrate insoluble anode, TSIA (0.24 dm^2) with TO_x-RuO_x-IrO_x coating (Subbiah, 1990), have been used as anodes and stainless steel (0.24 dm^2) was the cathode. Other instruments such as DC regulated power supply (APLAB DC Power Supply 0-20A 0-30V), stirring unit, heating source, cryostat (Julabo Make F10 model) have been employed for preparative electrolysis. The cell set up used for direct studies has been shown in Figure 1.

2.3 Electrochemical oxidation of DMSO to $DMSO_2$

The preparative studies of the oxidation of dimethylsulphoxide to dimethylsulphone have been carried out in a divided rectangular cell as per the experimental conditions listed in the Table 1.

For the oxidation of DMSO, aqueous MSA of concentration varying from 0.25 M – 2.0 M have been used as electrolyte. DMSO has been dissolved in MSA to get the desired concentration which has been used as anolyte and aqueous MSA has been used as catholyte.

Table 1. The Experimental Operating Conditions

Parameters	**Direct Electro oxidation of DMSO to $DMSO_2$**	**Direct Electro reduction of MA to SA**
Anode	Lead dioxide (0.24 dm^2)	TSIA (0.24 dm^2)
Cathode	Stainless Steel	Stainless Steel (0.24 dm^2)
Anolyte	DMSO in MSA(0.25 –2.0 M)	10% (w/v) MA in aq. MSA
Catholyte	Aqueous MSA (0.25 – 2.0M)	Aqueous MSA (0.25M – 2.0M)
Type of cell	Divided	Divided
Diaphragm	NAFION 423	NAFION 423
Charge passed	Theoretical	Theoretical
Current density	1.0 $A.dm^{-2}$	5.0 $A.dm^{-2}$
Reactor Hold up	100 mL	100 mL

Electrochemical oxidation studies were conducted to optimize various reaction parameters such as current density, acid concentration etc., to obtain maximum yields and current efficiency of the sulphone.

Constant current electrolysis has been carried out in the oxidation of DMSO to $DMSO_2$. Studies have been conducted to evaluate the reaction parameters such as acid concentration, current density, comparative performance of TSIA electrode with PbO_2 and the reusing of electrolyte under optimum conditions.

After the electrolysis was over, the acidic electrolyte has been neutralized and the solution has been evaporated using a rotary evaporator. The residue obtained has been thoroughly extracted by ethyl acetate solvent. A white crystal has been obtained after the distillation of the solvents. For reuse of electrolyte, experiments have been carried out till the products are separated by cooling to 10°C. The crystals have been thoroughly washed with chilled water and dried. The weight of sample has been noted after drying. The melting point of the crystals tallies with literature value 108°C. The product has been confirmed from FTIR spectra photometer using Perkin Elmer Model Paragon 500. Neat liquid was used for recording FTIR measurements in the range of 400 – 4000 cm^{-1}. Typical FTIR spectrum of isolated dimethylsulphone has been shown in Figure 2.

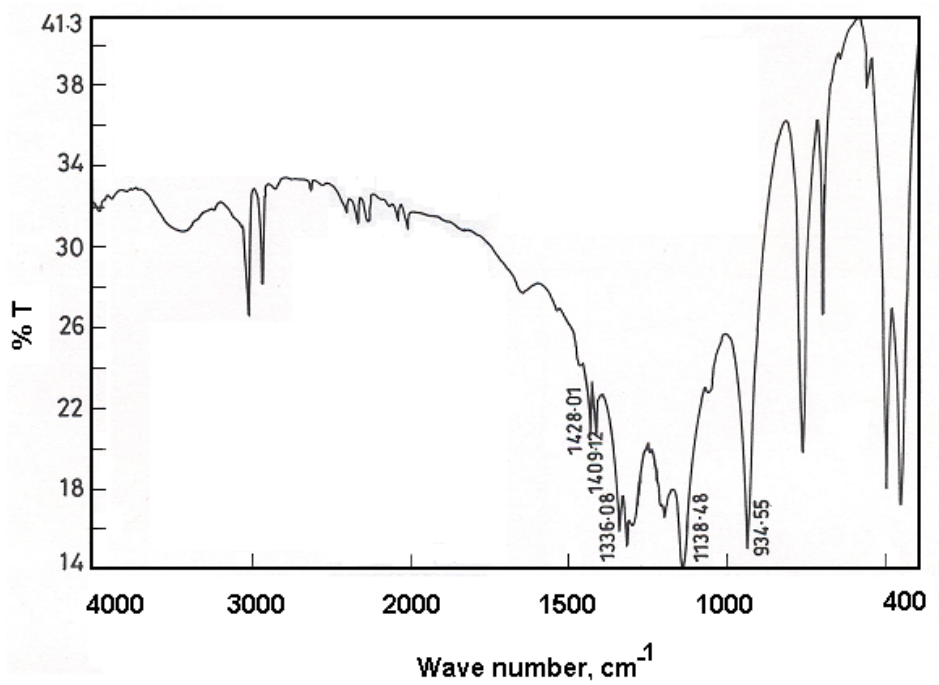

Figure 2. Typical FTIR spectrum of dimethylsulphone obtained by direct electrochemical oxidation of dimethylsulphoxide

The FTIR spectrum of the isolated DMSO exhibited strong absorption bands at 1138 cm^{-1} corresponding to symmetric >S = 0 stretch and at 1314 and 1336 cm^{-1} due to asymmetric >S = 0 stretch. The strong band at 1030 – 1080 cm^{-1} corresponding to >S = 0 stretch of DMSO has been absent in these spectra.

Analysis of the products has been also done by recording Proton NMR spectra using 350 MHz (Brucker eV 300 NMR spectrophotometer meter). $CDCl_3$ has been used as solvent and tetramethyl silane (TMS) as reference (δ = 0 ppm for

TMS). All the signals have been observed down field to TMS. Distinct major peaks have been identified and compared with reported values. NMR spectrum has been recorded up to 15 ppm down field from TMS. Absolutely no peaks have been observed from 10 to 15 ppm in all the cases. Typical proton-NMR spectrum of $DMSO_2$ has been shown in Figure 3. A single peak observed at 3.0 ppm shows the presence of $DMSO_2$.

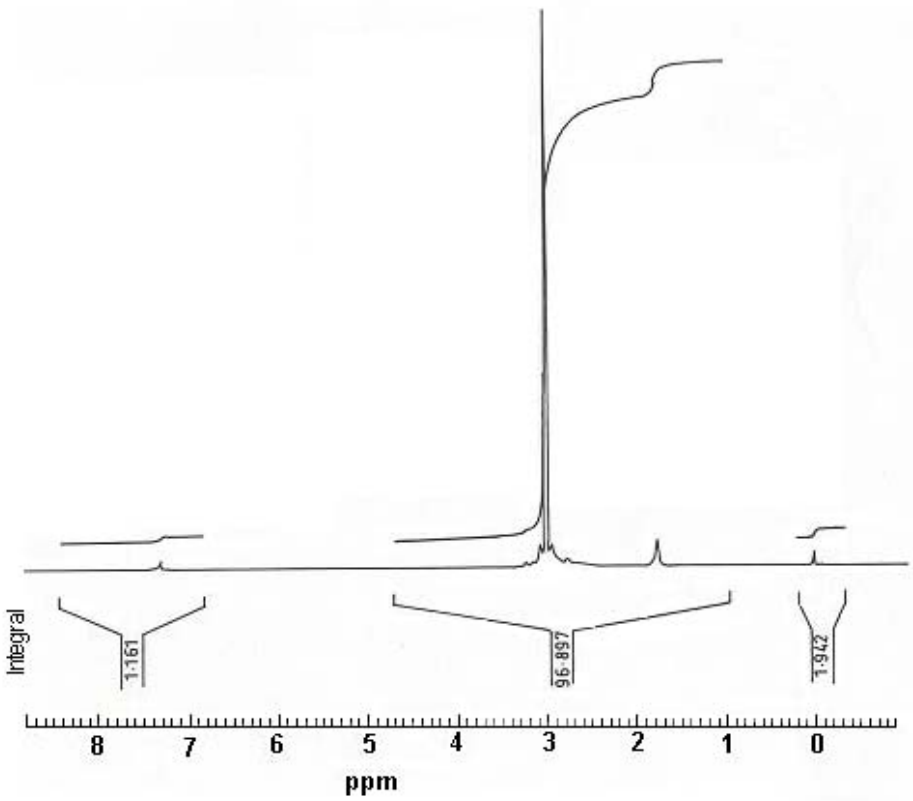

Figure 3. Typical proton-NMR of dimethylsulphone obtained by direct electrochemical oxidation of dimethylsulphoxide

2.4 Electrochemical reduction of MA to SA

For this reduction reaction studies, also a similar procedure has been adopted and MA has been dissolved in aqueous MSA to get the desired reactant concentration. The experimental operating conditions have been listed in the Table 1. The procedures adopted for the optimizations have been similar to those applied for the oxidation reactions. Solution of MA in methane sulphonic acid has been prepared by taking 10 g (0.86 M max. solubility) dissolved in the desired acid concentration. Studies have been conducted to evaluate the reaction parameters

such as acid concentration, current density, use of divided and undivided cells etc. After the electrolysis was over, the electrolyte has been kept for cooling below 10°C for an hour. White crystals settled at the bottom have been separated by filtration.

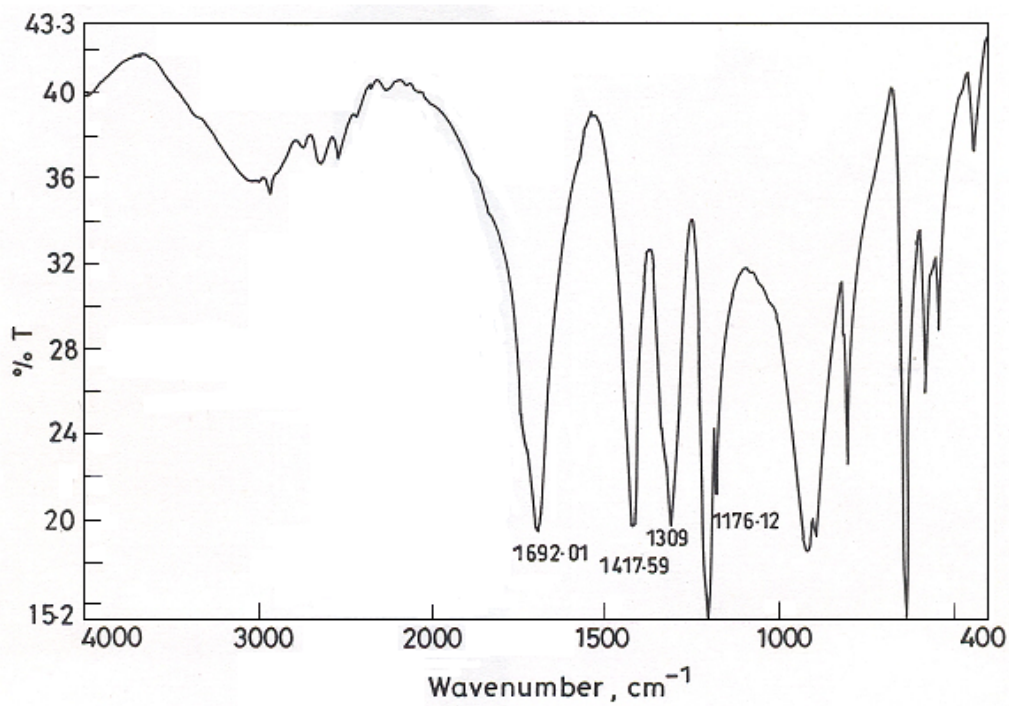

Figure 4. Typical FTIR spectrum of SA obtained by electrochemical reduction of MA

The crystals have been thoroughly washed with ice water and dried. The weight of sample has been noted after drying. The melting point of the sample was 187°C (literature value 185 – 187°C). The typical FTIR spectrum of sample has been shown in Figure 4. The FTIR spectra of the SA matched that for an authentic sample (Grasselli, 1973; Grassell, 1989) with carbonyl stretch at 1692 cm^{-1} apart from other absorptions. The strong absorption of >C = C< at 1640 cm^{-1} observed for MA was absent in the IR spectra of the product.

3. RESULTS AND DISCUSSION

3.1 Oxidation of DMSO to $DMSO_2$ in MSA Medium

3.1.1 Cyclic Voltammetry

The voltammetric behaviour of dimethylsulphoxide (DMSO) in methanesulphonic acid medium has been investigated at different DMSO concentration and different sweep rates (v). Typical cyclic voltammogram obtained at different DMSO concentrations in 1.0 M MSA at 40 mVs^{-1} have been shown in Figure 5(i). The peak current (i_p) and peak potential (E_p) responses for this system have been also summarized in Table 2.

Table 2. Cyclic Voltammetric Data for Oxidation of DMSO

Conc. of DMSO (mM)	[Sweep rate]$^{1/2}$ $\sqrt{(V/s)}$	i_p (mA)	E_p (V)	$i_p/Cv^{1/2}$
50	0.2	11.97	1.80	1.197
75	0.2	17.95	1.82	1.196
100	0.2	24.80	1.83	1.240
125	0.2	31.64	1.82	1.260
150	0.2	40.76	1.82	1.350
125	0.1000	21.95	1.80	1.175
125	0.1414	25.65	1.81	1.145
125	0.2000	31.50	1.82	1.260
125	0.2828	41.33	1.83	1.169
125	0.4000	57.00	1.84	1.140

A distinct oxidation peak is observed around 1.82 V vs SCE at higher concentration of DMSO. In Figure 5(i), at lower concentration the oxidation peak is not sharp. The peak current increases linearly with concentration of DMSO.

Table 3a. Effect of Acid Concentration. Conditions: anolyte: DMSO in MSA, catholyte aqueous MSA, current passed theoretical, current density 1.0 A dm^{-2}

No.	MSA conc. (M)	Cell Voltage (V)	$DMSO_2$ Formed (g)	Current Efficiency (%)
1	0.25	2.5 - 4.0	5.34	81.10
2	0.50	2.5 - 4.5	6.13	93.10
3	1.00	3.5 - 5.0	4.72	71.68
4	2.00	3.5 - 5.0	3.82	58.05

Typical cyclic voltammogram obtained at different sweep rates of 125 mM DMSO have been shown in Figure 5(ii). The peak current has also been increases linearly with sweep rates. The i_p is directly proportional to $v^{1/2}$ indicating that the oxidation has been a diffusion controlled process. These observations suggest that DMSO undergoes distinct oxidation on glassy carbon electrode in MSA medium. Other high oxygen over voltage anodes may also be employed for the oxidation of this compound as indicated by the preparative electrolysis experiments presented below.

Initially the electrochemical oxidation of DMSO to dimethylsulphone has been carried out in different acid concentrations (0.25 – 2.0M). Lead–dioxide has been used as anode. It has been observed from the cyclic voltammetry study that the oxidation potential of dimethylsulphoxide was very close to oxygen evolution region, hence the current density has been initially maintained at a low value (1.0 A dm^{-2}).

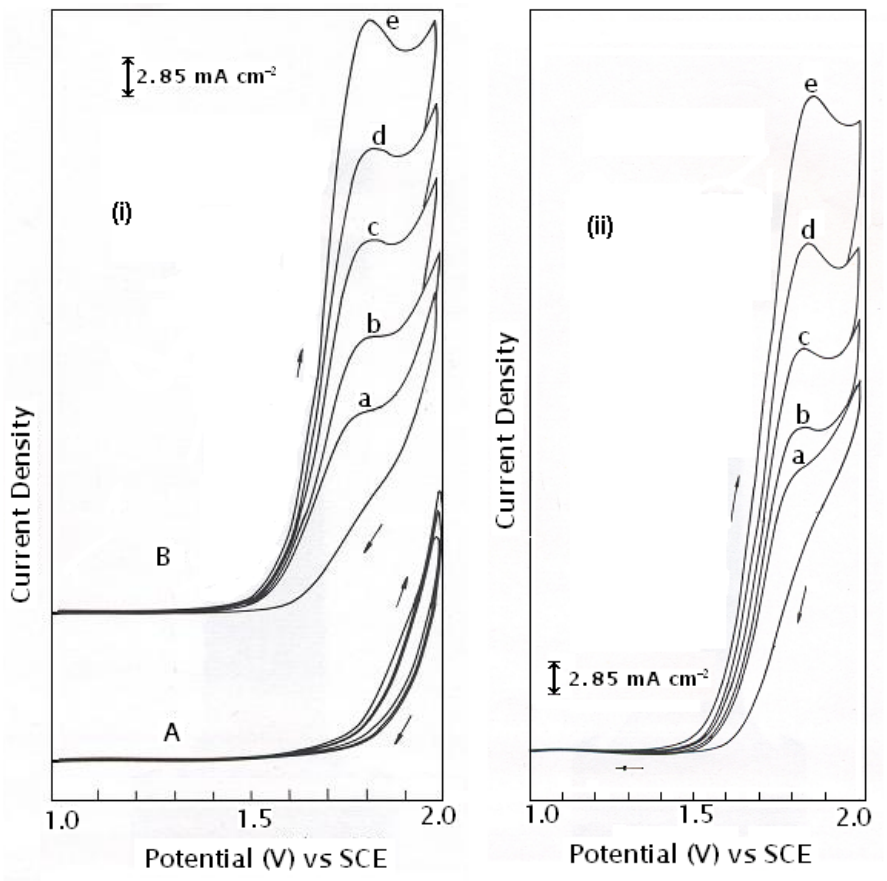

Figure 5. Typical cyclic voltammogram on GCE in 0.1 M MSA showing i) the effect of DMSO concentration at sweep rates of 40 mV s^{-1}. Conditions: B- Conc. of DMSO a) 50, b) 75, c) 100, d) 125 and e) 150 mM and A-Background
ii) The effect of sweep rates at 125 mM DMSO . Conditions: Sweep rates a) 10, b) 20, c) 40, d) 80 and e) 160 mV s^{-1}.

3.1.2 Preparative Studies

Table 3b. Effect of Current Density. Conditions: anolyte DMSO in 0.5 M MSA, catholyte aqueous 0.5 M MSA (Other conditions as in Table 3a)

No.	Current Density ($A.dm^{-2}$)	Cell Voltage (V)	$DMSO_2$ Formed (g)	Current Efficiency (%)
1.	0.25	2.0 – 2.5	6.37	96.78
2.	0.50	2.0 – 2.5	6.29	95.61
3.	1.00	2.5 – 3.0	6.33	95.56
4.	2.50	3.5 – 4.0	6.02	91.48
5.	3.50	3.5 – 5.0	5.14	78.21
6.	5.00	3.5 – 6.0	3.42	51.97
7.	7.50	3.5 – 7.0	2.11	32.11

The effects of acid concentration on current efficiency have been shown in Table 3a. The current efficiency has been around 90% for 0.5 M acid concentration. The current efficiency decreases with increasing acid concentration. It has been observed that 0.5 M acid concentration has given a good current efficiency.

The effect of anodic current density on current efficiency has been reported in Table 3b.

Table 3c. Effect of DMSO Concentration. Conditions: anolyte DMSO in 0.5 M MSA, catholyte aqueous 0.5 M MSA, current density 2.5 A dm^{-2} (Other conditions as in Table 3a)

No.	Amount of DMSO taken (g)	Charge Passed (Ah)	$DMSO_2$ formed (g)	Current Efficiency (%)
1.	2.50	1.72	2.41	79.82
2.	5.45	3.75	6.02	91.48
3.	7.50	5.15	7.37	81.60
4.	10.0	6.87	7.50	62.25

The current density has been varied from 0.25 $A.dm^{-2}$ to 7.5 $A.dm^{-2}$. It has been observed from the table that low current density (upto 2.5 $A.dm^{-2}$) favours good current efficiency and yield efficiency. The current efficiency has been around 90% at low current density when compared to high current densities (around 50%). The cell voltage has also been increases at high current densities. The effect of reactant concentration on current efficiency has been tabulated in Table

3c. It is seen from the table that the current efficiency has been maximum in the range 5.45 – 7.5% of DMSO concentration. The reuse of supporting electrolyte is very important in view of industrial application. For this purpose an attempt has been made to reuse the MSA solution after product recovery.

Table 3d. Reuse of Electrolyte under Optimum Conditions Conditions: anolyte DMSO in MSA, catholyte aqueous 0.5 M MSA (Other conditions as in Table 3a)

No.	Amount of DMSO taken	Cell Voltage	$DMSO_2$ Formed	Current Efficiency
	(g)	(V)	(g)	(%)
1.	7.60	3.0 - 3.5	--	--
2.	5.45	3.0 - 3.5	--	--
3.	5.45	3.0 - 3.5	--	--
4.	5.45	3.0 - 4.0	4.30	62.77
5.	5.45	3.0 - 4.5	6.13	93.02
6.	5.45	3.0 - 5.0	5.96	90.57
7.	5.45	3.0 - 6.0	6.02	91.48
8.	5.45	3.0 - 6.0	5.98	90.82
9.	5.45	3.0 - 6.0	5.87	89.15

Table 3e. Electrochemical Oxidation of DMSO to $DMSO_2$ in MSA medium on TSIA electrode(Other conditions as in Table 3a)

No.	Amount of DMSO taken	Cell voltage	$DMSO_2$ Formed	Current Efficiency
	(g)	(V)	(g)	(%)
1.	5.48	2.5 - 3.0	--	--
2.	7.67	3.0 - 3.5	--	--
3.	5.45	3.5 - 4.0	--	--
4.	5.45	3.5 - 4.0	7.30	45.01
5.	5.45	3.5 - 4.0	3.14	47.72
6.	5.45	3.5 - 4.0	4.25	64.58
7.	5.45	3.5 - 4.0	4.40	67.11
8.	5.45	3.5 - 5.0	3.66	55.65
9.	5.45	3.5 - 5.5	3.92	59.58

The results are shown in Table 3d. After the product was saturated in the electrolyte it was separated by cooling the electrolyte to $10^{o}C$. The current

efficiency was around 60% when the products were separated out after saturation. In the subsequent addition, the current efficiency has been around 90%.

A comparative performance of TSIA with lead dioxide has also been studied in view of the alternate anode material for the oxidation of DMSO to $DMSO_2$. The results are tabulated in Table 3e. The current efficiency with TSIA anode has been around 60 – 65% while PbO_2 has given 90% current yield.

3.2 Reduction of MA to SA in MSA Medium

3.2.1 *Cyclic Voltammetry*.

The voltammetric behaviour of MA in MSA medium has been investigated using glassy carbon electrode. Typical cyclic voltammograms obtained for different concentrations of maleic acid at sweep rate of 80 mVs^{-1} in 1.0 M MSA has been shown in Figure 6(i). It has been observed from the figure that the reduction of MA takes place very close to hydrogen evolution region. A reduction wave has been observed around –0.9V vs SCE. The cathodic wave and peak current (i_p) increase linearly with MA concentration. Similar trends have also been noticed in the voltammogram recorded at different sweep rates. The voltammograms have been shown in Figure 6(ii). At lower sweep rate (80 mVs^{-1}) the reduction wave is distinctly noticed.

At higher sweep rates the reduction wave merged with hydrogen evolution because of the closeness of the reduction wave with background current region. Quantitative tabulation of peak current and peak potential values has been quite difficult.

Table 4. Cyclic Voltammetric Data for the reduction of MA in MAS medium

Conc. of DMSO (mM)	$[\text{Sweep rate}]^{1/2}$ $\sqrt{(V/s)}$	i_p (mA)	E_p (V)	$i_p/Cv^{1/2}$
50	0.2828	13.68	0.90	0.9674
50	0.4	18.24	0.92	0.9120
50	0.5656	24.51	0.92	0.8666
50	0.8	35.34	0.94	0.8835
75	0.2828	20.80	0.93	0.9806
100	0.2828	27.07	0.95	0.9572
125	0.2828	34.28	0.97	0.9696

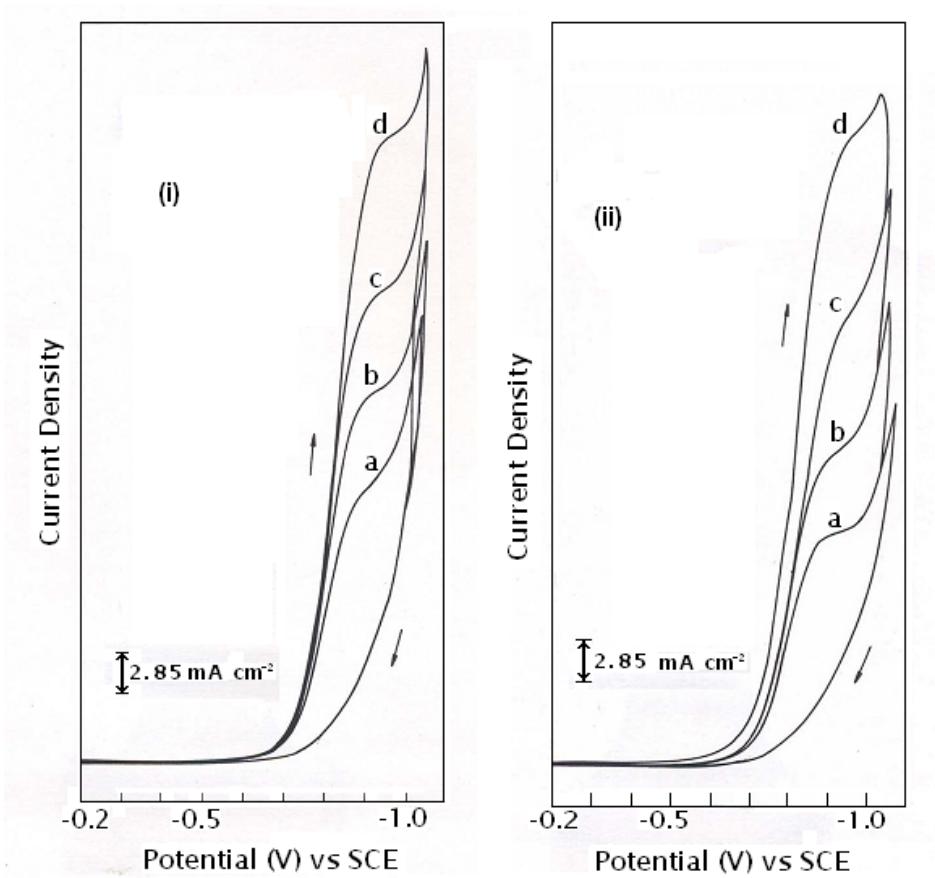

Figure 6. Typical cyclic voltammogram on GCE in 0.1 M MSA showing:
i) effect of MA concentration at sweep rates of 80 mV s^{-1}. Conditions: Conc. of MA a) 50, b) 75, c) 100 and d) 125 mM
ii) The effect of sweep rates at 50 mM MA. Conditions: Sweep rates a) 80, b) 160, c) 320 and d) 640 mV s^{-1}.

However, the tabulated data with appropriate background correction (Table 4) still suggest reasonable linear relationship between cathodic peak current and concentration of MA as well as square root of sweep rates. $i_p/C\nu^{1/2}$ for example has been found to be reasonably constant. The closeness of voltammetric reduction wave with background reduction processes suggest that overall current efficiency would be low especially when electrodes with high hydrogen over voltage are not employed.

3.2.2 Electrochemical Reduction of MA to SA in MSA medium

The electrochemical reduction of MA to SA in MSA medium has been carried out in different acid concentrations from 0.25 to 2.0 M using stainless steel as cathode at constant current density of 5.0 $A.dm^{-2}$ and the result have been tabulated in Table 5a**.** It is seen from the table that the current efficiency has been around 80% on 1.0 M MSA concentration.

Table 5a. Eletrochemical Reduction of MA to SA in MSA medium. Effect of Acid Concentration

No.	Acid Concentration (M)	Cell Voltage (V)	SA Formed (g)	Current Efficiency (%)
1.	0.25	2.5 – 3.0	6.86	67.45
	0.25	2.5 – 3.0	6.55	64.44
2.	0.50	2.5 – 3.5	7.23	71.09
	0.50	2.5 – 5.5	7.32	71.97
3.	1.00	2.5 – 4.0	8.35	82.14
	1.00	2.5 – 4.0	8.40	82.59
4.	2.00	3.0 – 5.0	5.28	51.91
	2.00	3.0 – 5.	5.21	51.23

The current efficiency decreases with increasing acid concentration. The effect of current density on current efficiency has been studied at 1.0 M acid. The results have been reported in Table 5b. It is seen that at lower current density range of 1.0 – 5.0 $A.dm^{-2}$ the current efficiency has been around 80-90%. At high current density the current efficiency decreased to around 50%.

Table 5b. Electrochemical Reduction of MA to SA in MSA medium. Effect of Current Density

No.	Current Density (Adm^{-2})	Cell Voltage (V)	SA Formed (g)	Current Efficiency (%)
1.	1.0	2.5 – 3.0	9.10	89.47
2.	1.5	2.5 – 3.0	8.67	85.25
3.	2.5	2.5 – 3.0	8.92	87.70
4.	5.0	2.5 – 3.5	7.88	78.80
5.	7.5	4.0 – 5.0	5.71	56.14
6.	10.0	4.0 – 8.5	4.02	39.52

Table 6 reports the results of the reduction of MA in an undivided cell. In undivided cells, the studies have been carried out with the optimized conditions of 1.0 M acid and 5.0 $A.dm^{-2}$. It is seen from Table 6 that the current efficiency has been around 50%. Table 7 reports the results of reusing the electrolyte under optimum conditions in a divided cell.

Table 6. Electrochemical Reduction of MA in undivided cell.

No.	Cell Voltage (V)	SA Formed (g)	Current Efficiency (%)
1.	2.0 – 2.5	5.30	52.21
2.	2.0 – 2.5	5.61	55.26
3.	2.0 – 3.0	5.42	53.29
4.	2.0 – 3.5	4.88	47.93
5.	2.0 – 4.0	4.93	48.47
6.	2.0 – 4.0	5.21	51.22
7.	2.0 – 4.0	5.11	50.24
8.	2.0 – 4.5	5.45	53.58
9.	2.0 – 4.5	5.88	52.90
10	2.0 – 5.0	5.42	53.29

Studies have been conducted in 1.0 M MSA at a current density of in 5.0 $A.dm^{-2}$ of concentration. The MA concentration has been maintained around 10% (w/v) throughout the experiments. The current efficiency has been nearly constant around 65-70%.

Table 7. Reuse of Electrolyte Under Optimum Conditions

No.	Amount of MA taken (g)	Cell Voltage (V)	Charge Passed (Ah)	SA Formed (g)	Current Efficiency (%)
1.	40.0	2.5 – 3.5	17.25	24.81	65.62
2	25.0	3.0 – 3.5	14.25	20.83	66.42
3.	20.0	3.0 – 3.5	12.75	19.57	69.79
4.	20.0	3.0 – 4.5	15.20	23.23	69.22
5.	25.0	3.0 – 5.0	15.20	24.30	72.38
6.	25.0	3.0 – 5.0	14.20	23.10	73.87
7.	20.0	3.0 – 5.5	12.75	19.79	70.52

4. CONCLUSIONS

The elelctrochemical oxidation of dimethylsulphoxide to dimethyl-sulphone using methane sulphonic acid medium on glassy carbon electrode has been investigated. The oxidation potential of DMSO was 1.82 V vs SCE. Diffusion controlled,

oxidation peak around 1.82 V vs SCE was observed by cyclic voltammetric technique. In the preparative electrolysis, Lead dioxide electrode has given good current efficiency (90-95%) under the conditions of current density range 1.0 – 2.5 $A.dm^{-2}$ and electrolyte concentration 0.5 M MSA. TSIA electrode gave marginally low current efficiency compared to lead dioxide electrodes.

The electrochemical reduction of MA to SA in MSA medium on glassy carbon electrode gave a reduction wave around –0.9V vs SCE. The reduction of MA involves a diffusion controlled process. In the preparative studies stainless steel cathode yields current efficiency around 65 – 70%. Based on the result obtained on trials, it is arrived that the optimum parameters of the reaction are 1.0 M acid concentration, and 5.0 A dm^{-2} current density. Divided cells give good results when compared to undivided cells.

It is to be noted that, as methane sulphonic acid medium (MAS) is biodegradable, it is a preferred medium for the electrochemical reactions.

ABBREVIATIONS AND SYMBOLS USED

DMSO	Dimethylsulphoxide
$DMSO_2$	Dimethylsulphone
MA	Maleic Acid
SA	Succinic Acid
MSA	Methane Sulphonic Acid
TMS	tetramethyl silane
DSA	Dimensionally Stable Anode
TSIA	Titanium Substrate Insoluble Anode
GCE	Glassy Carbon Electrode
CV	Cyclic Voltammetry
i_p	peak current, mA
E_p	peak potential, V
v	sweep rates, mV s^{-1}

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