The oxidation of the biologically very important dimethyl sulfoxide system has been the subject of investigations. In the present study Dimethyl sulfoxide (DMSO) has been oxidized to dimethyl sulfone by anodic electrolysis at a rotating platinum electrode. The polarographic method has been used to study qualitatively the effect of maxima suppressor gelatin, fuchsin, methyl red, thymol blue and supporting electrolyte HCl, CH3COOH on oxidation wave of DMSO. Polarographic oxidation of DMSO in 0.1 M HCl, 0.1 M CH3COOH solution using optimum concentration of fuchsin, methyl red, thymol blue as surface active substances is followed to determine the DMSO present in synthetic sample by calibration method. Wave analysis indicate the irreversible nature of the oxidation process which involves oxidation of dimethyl sulfoxide to dimethyl sulfone thereby increasing the oxidation state of sulphur from +2 to +4 state.

**Abstract**

The oxidation of the biologically very important dimethyl sulfoxide system has been the subject of investigations. In the present study Dimethyl sulfoxide (DMSO) can be oxidized to dimethyl sulfone by anodic electrolysis at a rotating platinum electrode. The polarographic method has been used to study qualitatively the effect of maxima suppressor gelatin, fuchsin, methyl red, thymol blue and supporting electrolyte HCl, CH3COOH on oxidation wave of DMSO. Polarographic oxidation of DMSO in 0.1 M HCl, 0.1 M CH3COOH solution using optimum concentration of fuchsin, methyl red, thymol blue as surface active substances is followed to determine the DMSO present in synthetic sample by calibration method.

**Methodology**

All chemicals were of A.R. grade. Solvent were purified before use. Sulfoxide samples were synthesized from A.R. grade chemicals. D.C. Recording polarograph along with OmniScribe recorder were, used to record the polargram using Rotating Platinum Electrode (R.P.E.) and Saturated Calomel Electrode (S.C.E.) as an anode and cathode respectively. 50 ml total volume was maintained for each measurement.

**Effect of maxima suppressor and supporting electrolyte on polarographic wave of dimethyl sulfoxide**

The maxima suppressor capacity of gelatin, fuchsin, methyl red and thymol blue on anodic wave of Dimethyl sulfoxide in presence of...
A calibration curve for \( i_d \) as a function of concentration of dimethyl sulfoxide was prepared under different experimental conditions given in Table 1. The \( i_d \) for the unknown was measured under corresponding experimental conditions and concentration was read out from the graph.

### Observation

**Effect of maxima suppressor and supporting electrolyte on polarographic wave of dimethyl sulfoxide**

Maxima suppressor capacity of fuchsin, methyl red and thymol blue on the anodic wave of dimethyl sulfoxide in 0.1 M HCl medium are shown in Figures 1-3. Dimethyl sulfoxide produces good sigmoid anodic waves in presence of 0.1 M HCl as supporting electrolyte and suitable concentration of fuchsin, methyl red, thymol blue as maxima suppressors. The wave height increases with pH (Figure 4).

### Results and Discussion

**Effect of maxima suppressors on polarographic waves of dimethyl sulfoxide**

Surfactant mainly gelatin, fuchsin, methyl red and thymol blue are added to obtain smooth, easily measurable limiting currents in 0.1 M HCl/CH\(_3\)COOH as supporting electrolyte. The use of gelatin (in 0.1 M HCl/CH\(_3\)COOH), fuchsin, methyl red and thymol blue (in 0.1 M CH\(_3\)COOH) are found to give unsatisfactory results in which cases a definite amount of maxima suppressors (1.25 \times 10^{-3} g to 1.625 \times 10^{-3} g) and diluted to 50 ml with water. Polarogram of each system was recorded on D.C. Recording polarograph between 600 to 1600 mV using R.P.E.-S.C.E. system. Further experiments were carried out under similar conditions. Supporting electrolyte - maxima suppressor combinations as shown in Table 1 gave good results and was used for further determination of dimethyl sulfoxide.

### Polarographic determination of dimethyl sulfoxide (calibration method)

A calibration curve for \( i_d \) as a function of concentration of dimethyl sulfoxide was prepared under different experimental conditions as given in Table 1. The \( i_d \) for the unknown was measured under corresponding experimental conditions and the concentration was read out from the graph.

### Effect of supporting electrolyte on polarographic waves of dimethyl sulfoxide

Effect of various concentrations of hydrochloric acid on the anodic wave of dimethyl sulfoxide in presence of 2.5 \times 10^{-5} % fuchsin/2.5 \times 10^{-5} % methyl red/1.25 \times 10^{-4} % thymol blue is found to produce similar results as shown in Figure 4. At former concentrations of hydrochloric acid, the apparent diffusion current found to increase as HCl concentration changes from 0.01 to 1 M, at the same time decomposition potential shifts to more negative potential. In 0.01, 0.1 and 1 M HCl medium, the decomposition potential of dimethyl sulfoxide is found to be 844, 812 and 800 mV respectively as may be seen from Figure 4. At higher concentrations (>1 M) of HCl, the wave height decreases considerably due to decrease in the apparent diffusion coefficient; decomposition potential remains unaffected. The blank species predominates at limiting current region of dimethyl sulfoxide wave at higher concentrations of HCl.

### Polarographic determination of dimethyl sulfoxide (calibration method)

Table 1: The optimum concentration of supporting electrolyte - maxima suppressor for determination of dimethyl sulfoxide by polarographic calibration method.

| Supporting electrolyte | Maxima suppressor |
|------------------------|-------------------|
| 0.1 M HCl              | 2.5 \times 10^{-5} % Fuchsin |
| 0.1 M HCl              | 2.5 \times 10^{-5} % Methyl red |
| 0.1 M HCl              | 2.5 \times 10^{-5} % Thymol blue |
| 0.1 M HCl              | - |
| 0.1 M CH\(_3\)COOH    | - |

**Figure 1: Effect of Fuchsin concentration on the anodic wave of 0.1 M Dimethyl sulfoxide in 0.1 M HCl.**
Effect of Methyl red concentration on the anodic wave of 0.1 M Dimethyl sulfoxide in 0.1 M HCl.

Effect of Thymol blue concentration on the anodic wave of 0.1 M Dimethyl sulfoxide in 0.1 M HCl.

Effect of HCl concentration on the anodic wave of 0.1 M Dimethyl sulfoxide in presence of 1.25 x 10^{-3} % Thymol blue.

Figure 2: Effect of Methyl red concentration on the anodic wave of 0.1 M Dimethyl sulfoxide in 0.1 M HCl.

Figure 3: Effect of Thymol blue concentration on the anodic wave of 0.1 M Dimethyl sulfoxide in 0.1 M HCl.

Figure 4: Effect of HCl concentration on the anodic wave of 0.1 M Dimethyl sulfoxide in presence of 1.25 x 10^{-3} % Thymol blue.

Figure 5 (A): Calibration polarogram for Dimethyl sulfoxide determination in 0.1 M HCl with 2.5 x 10^{-5} % Fuchsin. (B): Calibration curve for Dimethyl sulfoxide.

Figure 6 (A): Calibration polarogram for Dimethyl sulfoxide determination in 0.1 M HCl with 2.5 x 10^{-4} % Methyl red. (B): Calibration curve for Dimethyl sulfoxide.

Figure 7 (A): Calibration polarogram for Dimethyl sulfoxide determination in 0.1 M HCl with 2.5 x 10^{-4} % Thymol blue. (B): Calibration curve for Dimethyl sulfoxide.

Figure 8 (A): Calibration polarogram for Dimethyl sulfoxide determination in 0.1 M HCl. (B): Calibration curve for Dimethyl sulfoxide.
favourable conditions is given by the data in Table 2. The DMSO produces an abnormally small limiting current in 0.1 M HCl or 0.1 CH₃COOH, and the ratio i/C decreases markedly with increasing concentration of DMSO. Hence in an unknown case it is always necessary to verify the relation between i and C. This indicates that the limiting current is not diffusion controlled but is governed by the actual rate of the electrode reaction; hence the limiting current is not strictly as linear function of concentration even when correction is applied for the residual current.

The polarographic method has been used to follow the decomposition of DMSO in a 0.1 M hydrochloric acid. A somewhat more steeply rising curves are obtained with a rotating platinum electrode as indicated in Figures 5-9. There is no strict proportionality between the diffusion current and the concentration of DMSO even when the proper correction is applied for the residual current. Plot of E against log (i - i)/i yields a straight line (Figure 10). However, the slope of the log plot differs from the theoretical value 0.030 V for the oxidation process involving 2 number of electrons hence the value of n calculated from the slope has no significance (Table 3) E₁/₂ is not constant and depend on the concentration of the dimethyl sulfoxide. All these points indicate the irreversible nature of the oxidation process:

\[ \text{H}_3\text{C} \backslash \text{S} \text{O} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{C} \backslash \text{S} \text{O} \text{O} + 2\text{H}^+ + 2\text{e}^- \]

Which involves oxidation of dimethyl sulfoxide to dimethyl sulfone thereby increasing the oxidation state of sulfur from +2 to +4 state.

**Conclusion**

2.5 × 10⁻⁵% funchsin/2.5 × 10⁻⁴% methyl red/1.25 × 10⁻³% thymol blue is found to produce optimum result. Decomposition potential remains constant at ~ 800 mV with varying concentrations of surface active substances.

| DMSO, M | i₀ Observed | i/C |
|---------|-------------|-----|
| 0.1 M HCl – 2.5 × 10⁻⁵% Fuchsin At 1088 mV | 0.7 | – |
| 0.107 | 2.6 | 1.9 | 17.8 |
| 0.161 | 2.8 | 2.1 | 13 |
| 0.214 | 3 | 2.3 | 10.7 |
| 0.268 | 3.35 | 2.65 | 9.9 |
| 0.401 | 3.65 | 2.95 | 7.4 |

| DMSO, M | i₀ Observed | i/C |
|---------|-------------|-----|
| 0.1 M HCl – 2.5 × 10⁻⁴% Methyl red At 1050 mV | 0.85 | – |
| 0.11 | 1.8 | 1.15 | 10.5 |
| 0.54 | 2 | 1.35 | 2.5 |
| 1.07 | 2.15 | 1.5 | 1.4 |
| 1.61 | 2.6 | 1.95 | 1.2 |

Table 2: Calibration Data for Dimethyl Sulfoxide.

| DMSO, M | i₀ at 1150 mV | i/C | E₁/₂, mV | Slope of log (i₀ - i)/i vs E Plots, V value of n |
|---------|---------------|-----|----------|-----------------------------------------------|
| 0.005   | 3.4           | 680 | 1023     | 0.03 | 0.107 | Theo |
| 0.027   | 3.8           | 141 | 1023     | 0.03 | 0.101 | Exptl |
| 0.107   | 4.3           | 40  | 1010     | 0.03 | 0.11  | Theo |
| 0.161   | 4.9           | 31  | 999      | 0.03 | 0.122 | Exptl |
| 0.268   | 5.5           | 21  | 1015     | 0.03 | 0.107 | Theo |

Table 3: Comparison of Theoretical and Experimental values of slope of log plots and n of Dimethyl sulfoxides at various concentrations in 0.1 M HCl.

DMSO gives a well-defined wave in hydrochloric acid and to some extent in acetic acid. The waves are suitable for quantitative estimation.

Wave analysis indicate the irreversible nature of the oxidation process which involves oxidation of dimethyl sulfide to dimethyl sulfoxide thereby increasing the oxidation state of sulphur from +2 to +4 state.

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