

# EFFECT OF SODIUM DIOCTYLSULPHOSUCCINATE ON THE DROPPING MERCURY ELECTRODE CAPACITY

by

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## ABSTRACT

Sodium dioctylsulphosuccinate (Manoxol OT) is shown to exhibit in the tensammetric curve, a hump from  $-0.7$  to  $-1.0$  V and a desorption peak at  $-1.35$  V. It has been shown that the hump is caused by dissolved oxygen. Effect of (a) concentration of Manoxol OT and (b) the magnitude of the a.c. ripple on the tensammetric curves has been studied and the results discussed. The d.c. polarograms indicate two waves, the first being caused by oxygen and second mainly by desorption, although the latter is also enhanced by the presence of oxygen.

## Introduction

The substance Manoxol OT (sodium salt of dioctyl ester of sulphosuccinic acid) is a powerful wetting agent. It has been shown recently that it can be used for the inhibition of corrosion of metals since it forms a protective adsorption film over the metal surface<sup>1</sup>. In view of this it is of interest to examine the adsorbability of Manoxol OT at different potentials using the dropping mercury electrode, so that the correlation between the adsorbability and corrosion inhibition power can be examined in detail. Doss and Gupta<sup>2</sup> studied the effect of Aerosol OT (a product manufactured by the American Cyanamide Co., U.S.A., having an identical composition) on the D.M.E. using 0.12 per cent solution at  $pH$  10.2 and 5.6. With a view to know the nature of adsorption of Manoxol OT on mercury surface under different conditions, a systematic study has been made and the results reported herein.

## Experimental

The apparatus employed in the present investigation was essentially the same as that used by Doss and Gupta<sup>3</sup>. The current passing through the dropping mercury electrode however passed through a voltage drop resistor of  $200\ \Omega$ . The voltage drop across the resistor was amplified by an a.c. amplifier (Philips GM 6017), rectified and fed on to a galvanometer with a suitable shunt. The galvanometer had a period of about 23 seconds. This arrangement had a sensitiveness corresponding to  $1\ \mu A = 30$  divisions of galvanometer deflection. The other details of the set up are:

$$m = 1.17\ \text{mg/sec}$$

$$t = 4.8\ \text{seconds in } 0.1\ \text{M KCl};$$

open circuit

$$h = 63\ \text{cm of mercury}$$

The studies were made with pure 0.1 M KCl solution, shaken up with mercury so as to avoid any further effect of the contact of mercury pool with the solution. All the D.C. potentials were measured using the mercury pool as the

reference electrode and with the necessary correction expressed as with reference to saturated calomel electrode.

The Manoxol OT, used was kindly supplied by the I.C.I. and was of "100 per cent" quality. The substance was dried by keeping it evacuated at  $60^{\circ}\text{C}$  for about 2 to  $2\frac{1}{2}$  hours and stored in a desiccator. A stock solution of 1 per cent concentration was made with water from which the required amount was pipetted out to get any desired concentration.

Sodium sulphite used was of "Merck Guaranteed Reagent" quality.

Since the resistance included in the circuit was usually very small compared to the capacitance impedance of the electrical double layer, the resulting alternating current component was a measure of the capacity of the electrical double layer in most cases. The percentage increase with sign of the alternating current component due to the presence of the surface active agent of the various corresponding D.C. potentials were calculated and the results have been plotted in graphs 1—5. The percentage increase (with sign) of the alternating current practically gives the percentage increase in the average differential capacity.

### Discussion

#### *Effect of magnitude of the a.c. ripple*

Figures 1 and 2 show the plots of percentage increase of alternating current component which directly gives the current (with sign) against the applied d.c.

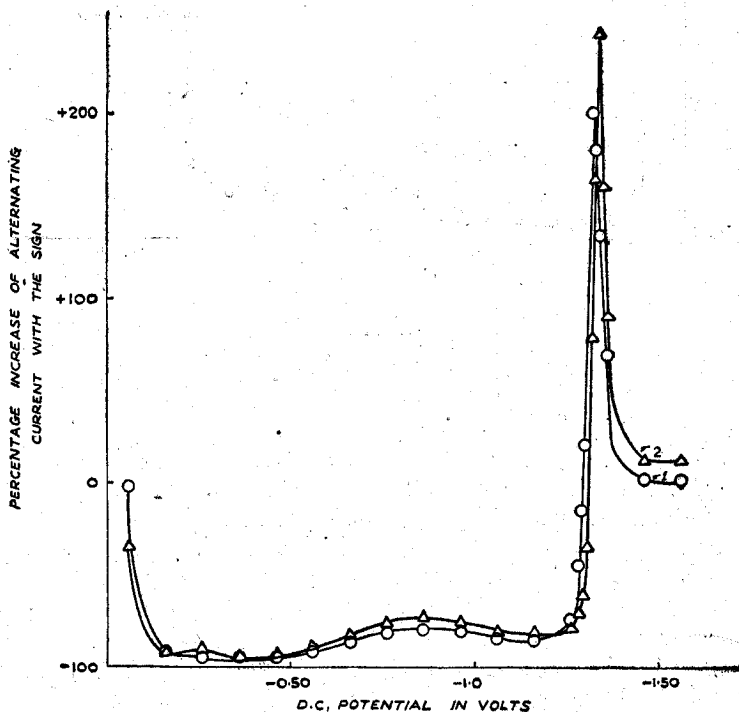


FIG. 1

0.01 % Manoxol OT in 0.1 MKCl

1. 40 mv (y.m.s.)

2. 30 mv (r.m.s.)

potential, of 0.01 per cent Manoxol OT for 10, 20, 30 and 40 mV (r.m.s.) of the superimposed alternating current ripple.

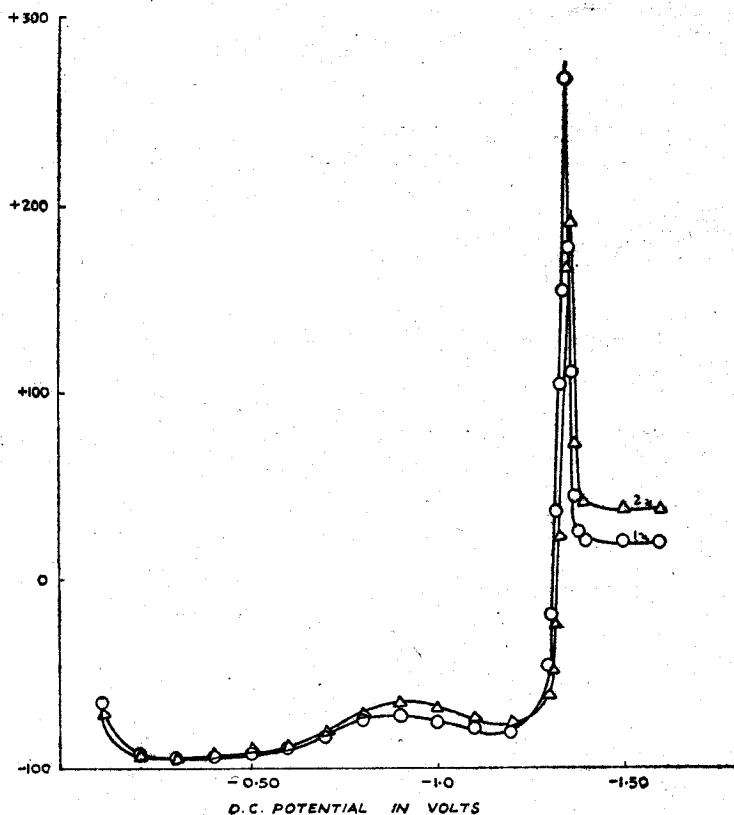


FIG. 2

0.01% Manoxol OT in 0.1MKCl  
 1. 20 mv (r.m.s.)  
 2. 10 mv (r.m.s.)

The adsorption region extends over a wide range of the d.c. potential *i.e.*, from  $-0.11$  V to about  $-1.31$  V. The maximum amount of adsorption corresponds the decrease in capacity by about 98 per cent. Almost the whole surface of the mercury appears to be covered with Manoxol OT. Change in the amplitude has only a small effect on the minimum of the double layer capacity.

All the curves show desorption peak in the neighbourhood of  $-1.35$  volts. In addition to this there is a small rounded hump in the region of  $-0.7$  V to  $-1.0$  V: at which the depression of the capacity is yet very effective and even at the summit of the hump the percent  $\Delta i$  is negative. This hump appears to be caused by dissolved oxygen since it is removed by the addition of sodium sulphite to the solution as will be seen later.

It has been shown by previous workers that with increasing amplitude of the a.c. voltage the desorption peak potentials are shifted towards less negative potentials. This has been verified in the present case by taking measurements

for one concentration (0.01%) using different amplitudes of the ripple voltage successively. The following table shows the variation of desorption peak potential with the amplitude.

Amplitude m.v. (r.m.s.)	Desorption peak potentials (vs.S.C.E.)
10 .. .. .	-1.35V
20 .. .. .	-1.35V
30 .. .. .	-1.34V
40 .. .. .	-1.33V

### The d.c. polarograms

To know whether Manoxol OT gives any reduction wave its D.C. polarogram has been recorded. Figure 3 shows the potential-current curves of 0.1 MKCl at two concentrations viz., 0.01% and 0.05% of a Manoxol OT. There is a small wave in the case of 0.01% and 0.05% Manoxol solutions at about 0.71V with respect to pool electrode which will be shown to be due to dissolved oxygen. Another slightly bigger wave is observed in both the concentrations at about

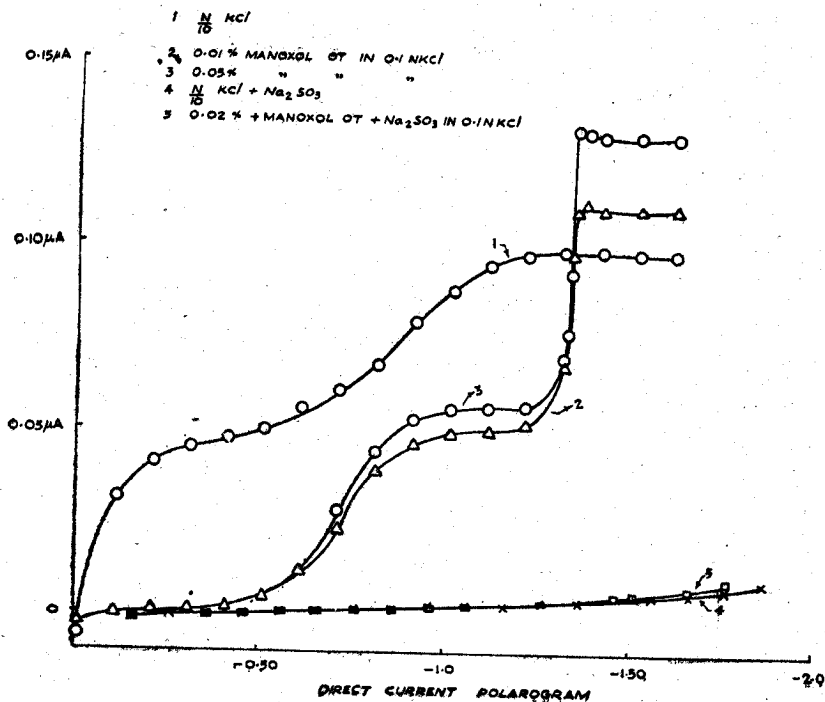


FIG 3.

—1.33 V. Since the limiting current is very small it cannot be due to any reduction of the substance. Assuming Ilkovic equation taking  $n=1$ ,  $D$  calculates to be  $5.76 \times 10^{-8}$  cm<sup>2</sup>/sec., which is far too small. Moreover, the limiting current does not increase proportionately with concentration. It may therefore be concluded that the wave is not due to reduction of Manoxol OT.

It can therefore be inferred that the D.C. waves and the A.C. peaks obtained with Manoxol OT at —1.35 v are not caused by reduction but by desorption. The higher residual current in the d.c. polarogram obtained at —1.35 v in presence of Manoxol is presumably caused by interfacial stirring due to differences in mercury-aqueous interfacial tension at the different regions of the mercury drop, under the particular circumstances.

That the D.C. wave at —0.7 V is due to oxygen is confirmed by the following observations. Figure 3 gives the D.C. polarogram of 0.02% Manoxol OT to which a weighed amount (0.04 g per 100 cc) of sodium sulphite has been added. The pH of the solution is found to be 7.7. The magnitude of the total current has been brought down very much by the addition of sodium sulphite. A plot on a larger scale (Figure 3a), however, reveals that the wave at —0.7V has disappeared, showing that it is caused directly or indirectly by dissolved oxygen. The wave at —1.35V however persists and appears to be caused by desorptions although oxygen also appears to be playing a part.

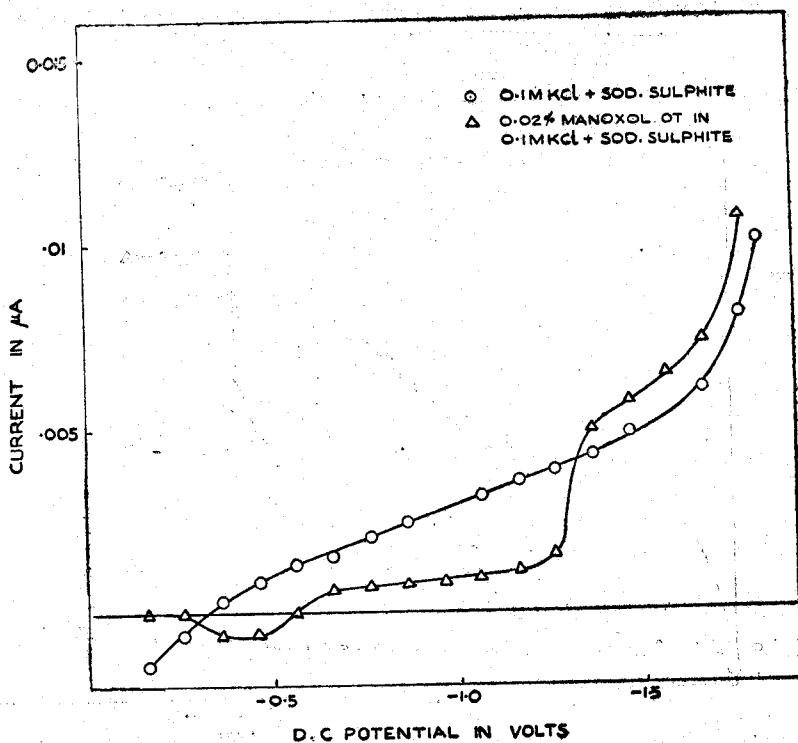


FIG 3a.

### Effect of Concentration of Manoxol OT

Curves 1, 2 and 3 of Figure 4 depict the percentage increase with sign of the alternating current component versus d.c. potentials for the concentration of 0.0025, 0.005, and 0.02% Manoxol OT. The amplitude of the superposed a.c. voltage is kept constant at 30 mV (r.m.s.). Here also it is found that the adsorption region extends over a wide range of potential i.e., from  $-0.1$  to  $-1.2$  V. Concentration does not affect much the current minimum. In all the three curves the desorption peak and the rounded hump are observed. The hump, as before, occurs in the adsorption region while the peak occurs at higher cathodic potentials. The peak value of the percentage increase of the alternating current component which is a measure of the desorption peak current (or tensammetric current) varies nonlinearly with the concentration. Figure 4(a) shows the plots of peak value of the percentage increase of the alternating current component versus concentration (in percent). As the concentration increases the desorption peak current first increases and then reaches a limiting value at about 0.016%. With increasing concentration the desorption peak potential is shifted to values away from the electrocapillary zero indicating that the desorption from more concentrated solution can be effective only at higher negative potentials.

Figure 5 shows the plots of percentage increase of the alternating current component (with the sign) against applied d.c. potentials for different concentrations of Manoxol OT to which sodium sulphite is added (0.04g per 100 cc which is the theoretically calculated amount required to remove the oxygen present assuming the solution being saturated with oxygen.) The *pH* of the solution is 7.7. The amplitude of the a.c. voltage is 30 mV. The hump found in figures 1, 2 and 5 has disappeared on the addition of sodium sulphite thus establishing that the hump is due to oxygen. This has been confirmed by repeating the measurements after passing a current of nitrogen. The desorption peak current is very much enhanced by the addition of the sodium sulphite.

The addition of sulphite does not affect the adsorbability of the Manoxol OT as judged from the current minimum. The addition of sulphite appears to shift the desorption peak potential slightly towards less negative potentials.

### DESORPTION PEAK POTENTIALS

Concentration of Manoxol OT in %	Indifferent electrolyte	
	0.1 MKCl only	0.1 MKCl + sulphite
0.0025 .. ..	$-1.26$ V	$-1.22$ V
0.005 .. ..	$-1.31$ V	$-1.24$ V
0.01 .. ..	$-1.33$ V	$-1.28$ V
0.02 .. ..	$-1.33$ V	$-1.31$ V

The correlation of the tensammetric measurements and corrosion inhibition will be dealt with in a later paper.

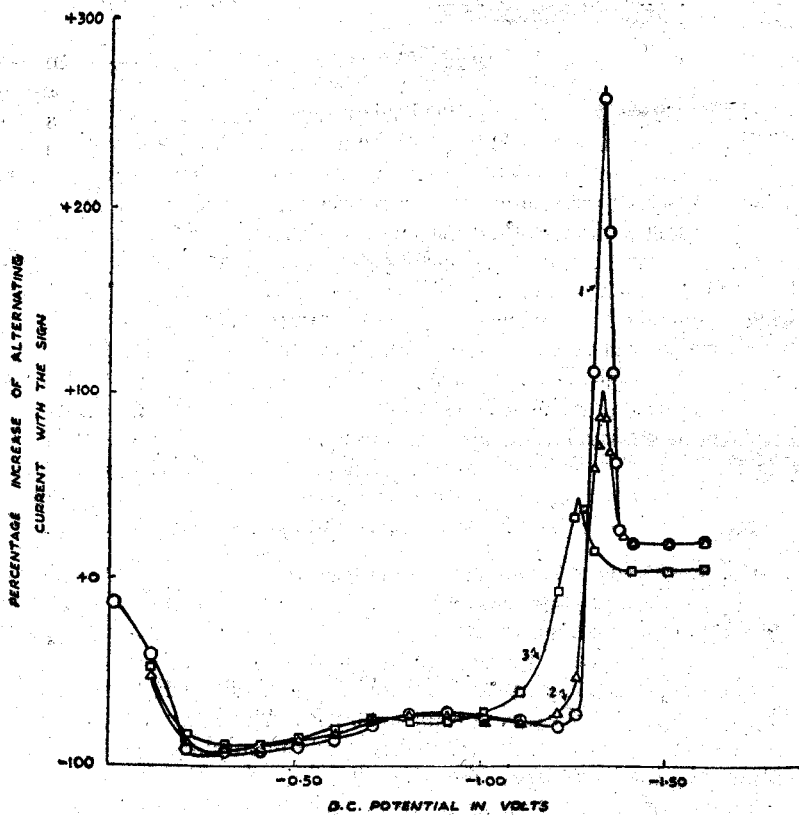


FIG. 4

A.C. Ripple 30 mv (r.m.s.)

1. 0.02% in 0.1 MKCl

2. 0.005 " "

3. 0.0025 " "

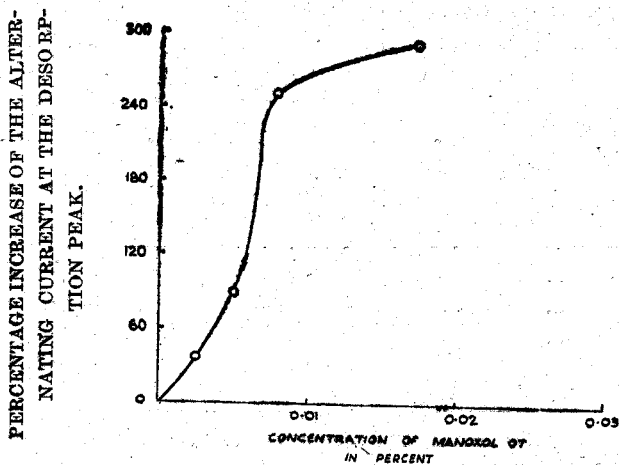


FIG 4 a.

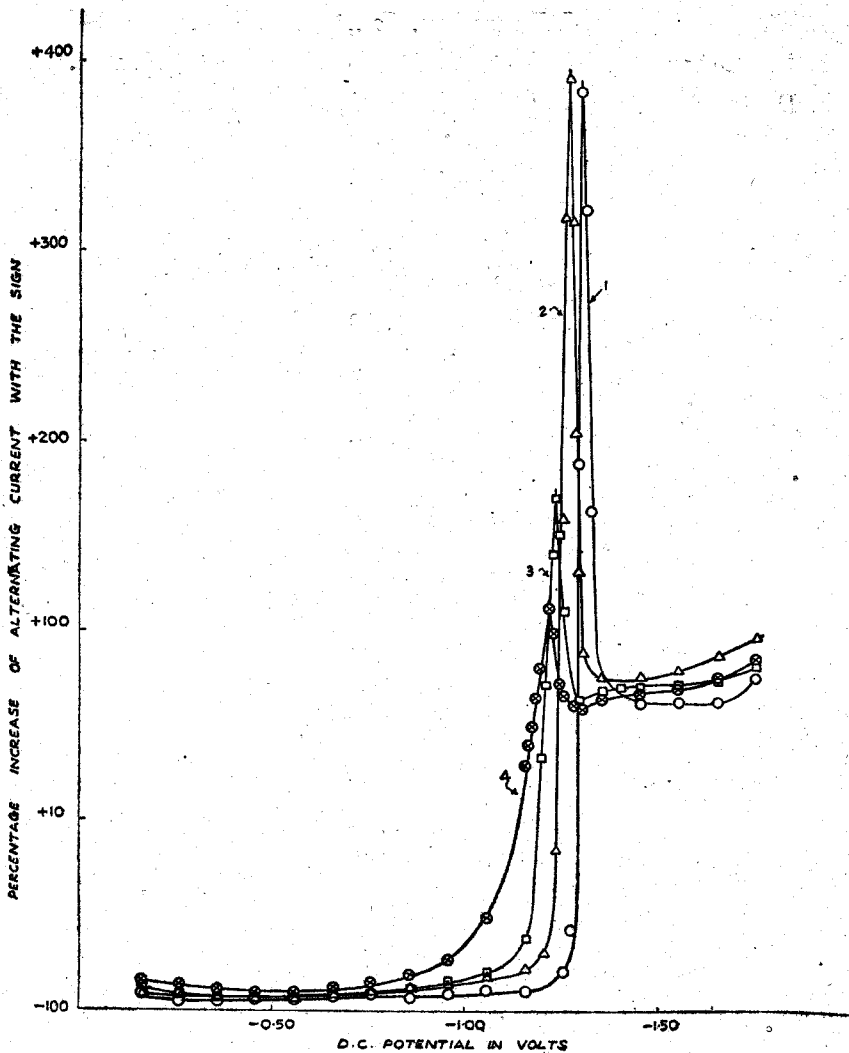


FIG 5.

A.C. Ripple 30 mv (r.m.s.)

1. 0.02% of manoxol OT in 0.1 MKCl
2. 0.01%       "       "       "       "
3. 0.005%     "       "       "       "
4. 0.0025%   "       "       "       "

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