

EFFECT OF METHYL ORANGE ON THE CAPACITY OF THE DROPPING MERCURY ELECTRODE

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1. INTRODUCTION

THE first detailed investigation of the effect of surface-active substances on the capacity of the dropping mercury electrode was made by Proskurnin and Frumkin.¹ Their experiments showed the existence of two maxima with a strong depression in the middle part in the capacity-potential curve of sodium sulphate saturated with octyl alcohol. These features were confirmed by the more precise measurements of Grahame.² The pulsating field technique as modified by Doss and Kalyanasundaram is found to be very convenient for the investigation of these phenomena.³ Breyer and Hacobian have also used a similar technique for such investigations.⁴ The earlier papers have shown how surface-active substances influence the dropping mercury electrode capacity by getting adsorbed at the mercury-aqueous interface.⁵ At some of the applied D.C. potentials the capacity is also affected due to a dynamic contribution from the sorption and desorption processes which occur due to the pulsating field applied for measuring the capacity.

The present work relates to the effect of methyl orange on the capacity of the dropping mercury electrode under different conditions of pH and concentration. One distinguishing feature of this work is that the surface-active substance is a chemical compound of known structure and can be purified easily by crystallisation from its aqueous solution.

2. EXPERIMENTAL

2.1. Methyl Orange used was Merck's quality and recrystallised twice before use.

2.2. The mercury used for pool-electrode and dropping electrode was passed through Meyer's column, washed several times with distilled water, dried and passed through a sintered glass filter.

2.3. The other chemicals used were of 'Analar' quality of B.D.H.

2.4. *Technique of Measurement.*—The apparatus employed in the present investigation is the same as what has been described before.^{3, 3a} This consists in applying to a dropping mercury electrode, 50 cycles A.C. ripple of ± 45 mv. (r.m.s.) over the D.C. potential and observing the alternating component of the resulting pulsating current. As the capacitive impedance of the dropping mercury electrode is much higher than the rest of the impedance of the system, the magnitude of the alternating current gives a measure of the dropping mercury electrode capacity. The D.C. potentials have been expressed with reference to the saturated calomel electrode. The constants of the dropping mercury electrode are as follows:—

$$m = 0.0037 \text{ g./sec.}$$

$$t = 0.7 \text{ sec. per drop in } 0.1 \text{ M KCL (open circuit).}$$

0.1 Molar potassium chloride solution was used as the supporting electrolyte and was invariably shaken and kept in contact with mercury and mercurous chloride. In each case, the measurements were taken with the indifferent electrolyte and the effect of the surface-active substances has been expressed in terms of the percentage increase (with sign) of the alternating current, which gives practically the percentage increase in the average differential capacity. It has been shown by experiments that the percentage increase in the current brought about by surface-active substances of low molecular weight is independent of the size of the drop or even the time of the dropping within certain limits.^{5d} The dropping mercury electrode was cathodic throughout the measurements.

The results are represented in Figs. 1-4.

3. DISCUSSION

3.1. *Behaviour of Methyl Orange at pH 12.3.*—This system is distinguished by the occurrence of a main peak and a satellite at all concentrations examined from 0.0025% to 0.04% of methyl orange (*vide* Fig. 1). The satellite peak occurs at about 1.15 volts at all the concentrations studied. The main peak, however, changes its position and magnitude. As the concentration increases the peak tends to shift to more cathodic potentials. Furthermore, as the concentration increases, the magnitude of the peak diminishes at first and then increases to a high value.

In order to examine whether it is caused by any impurities present in the system, the methyl orange used was purified by repeated crystallisation. An examination of Fig. 4 shows that once recrystallised as well as twice recrystallised methyl orange behave in an identical manner. This shows

that the occurrence of the main and satellite peaks is a real phenomenon and not due to the effect of any impurity.

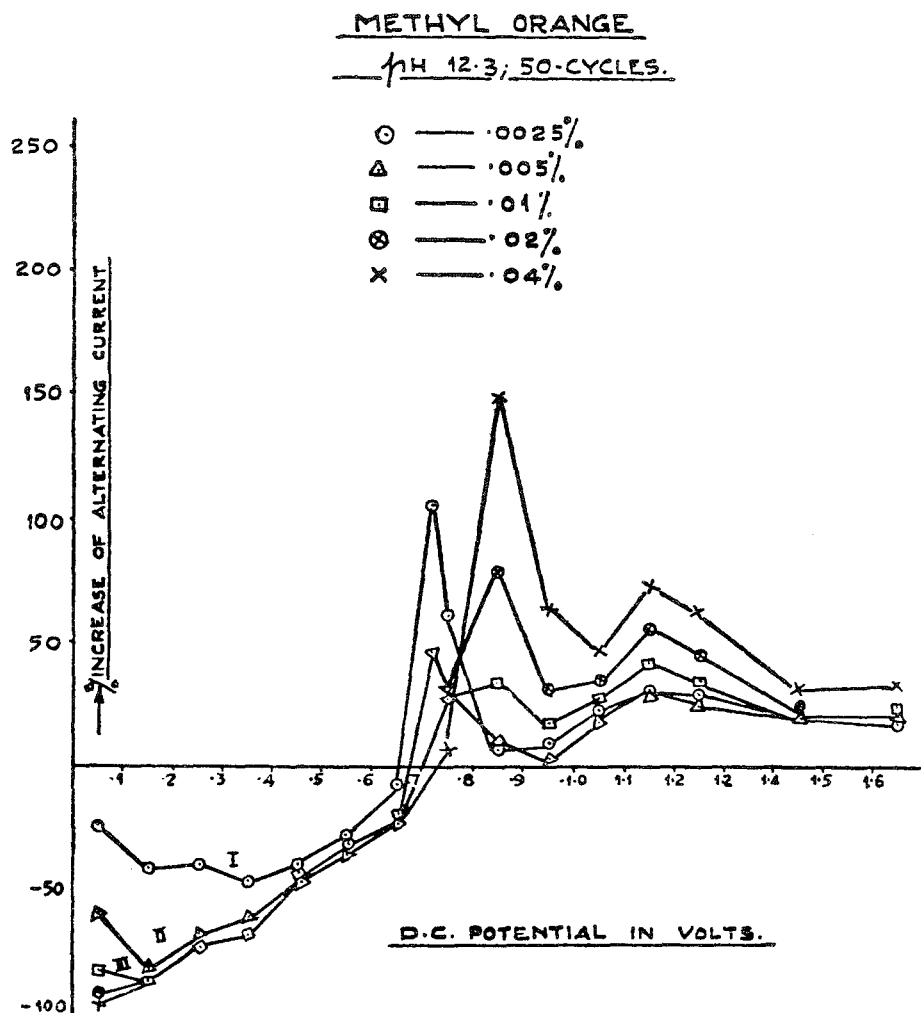


FIG. 1

The above results of extraordinary interest can be interpreted on the following hypothesis:—

The main peak is caused by the charge on the mercury surface converting the condensed film of adsorbed methyl orange into a vapour film, by a two-dimensional phase transition occurring more or less suddenly. The resulting vapour film is having a sufficiently high vapour pressure. The

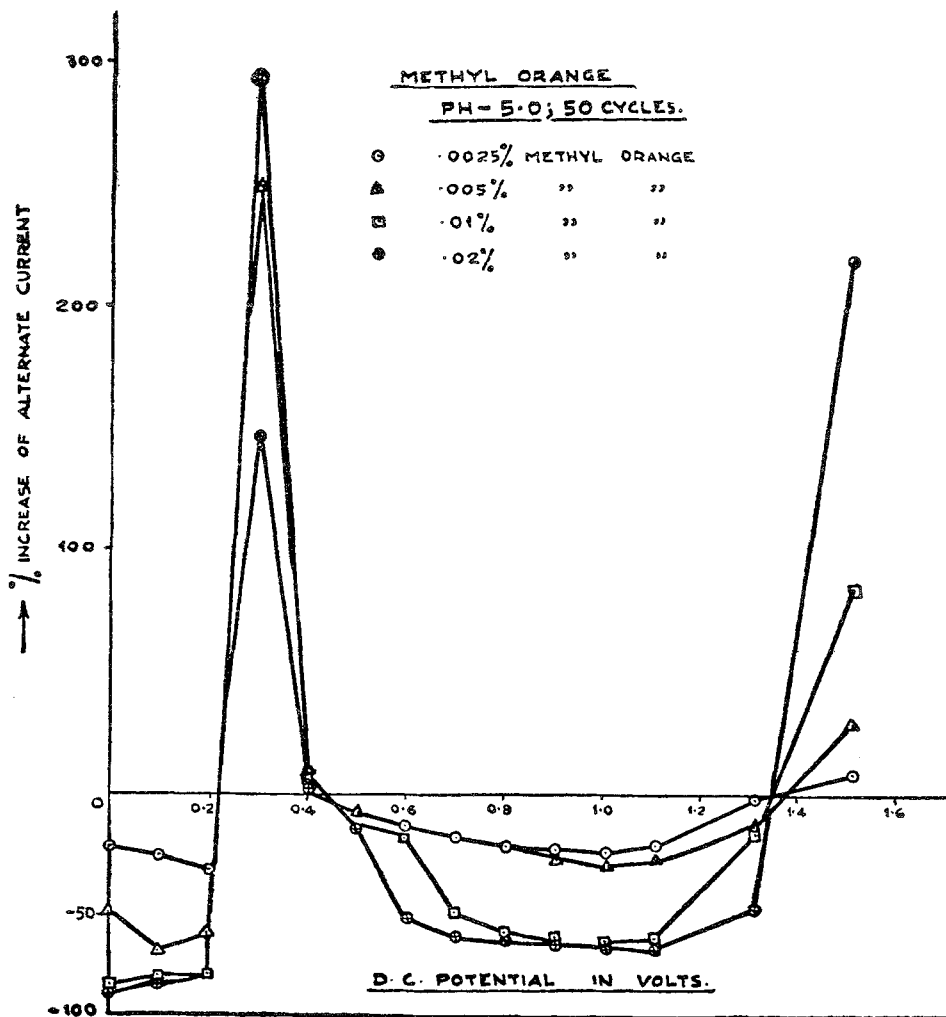


FIG. 2

satellite peak is caused by the complete desorption of the gaseous film at the higher voltage. The behaviour of the magnitude of the peak with changes of concentration of methyl orange is presumably connected with micelle formation. In very dilute solutions one is dealing with single molecule of methyl orange which can easily diffuse and have their full effect at the mercury solution interface. At intermediate concentrations, micelle formation sets in and brings down the rate of diffusion which lowers the magnitude of the peak. This goes up to 0.01% of methyl orange. At still higher concentrations the concentration of the micelle increases and hence the magnitude

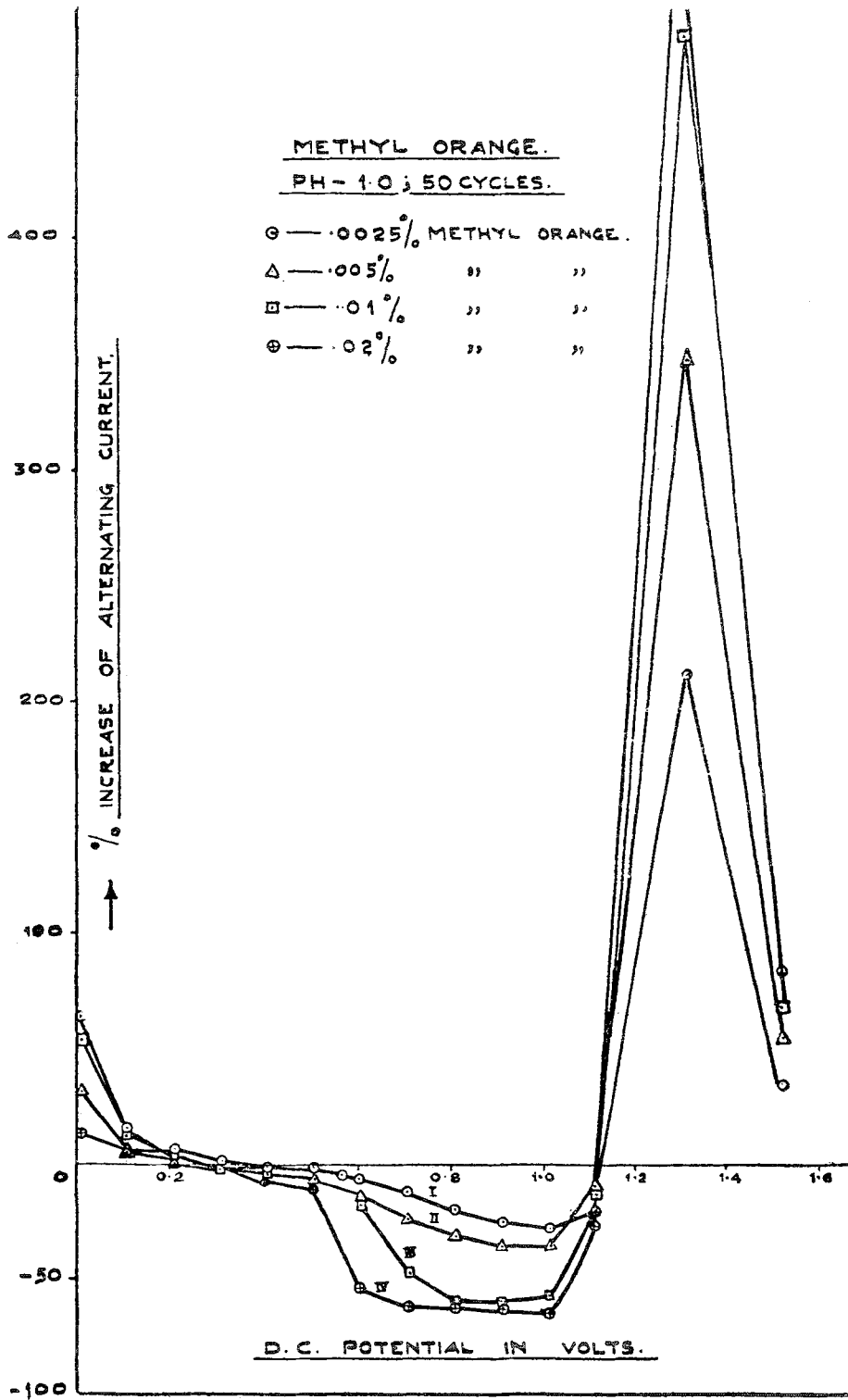


FIG. 3

of the peak also increases. The effect of concentration of methyl orange and other surface-active substances on peak potential will be considered in a separate paper.

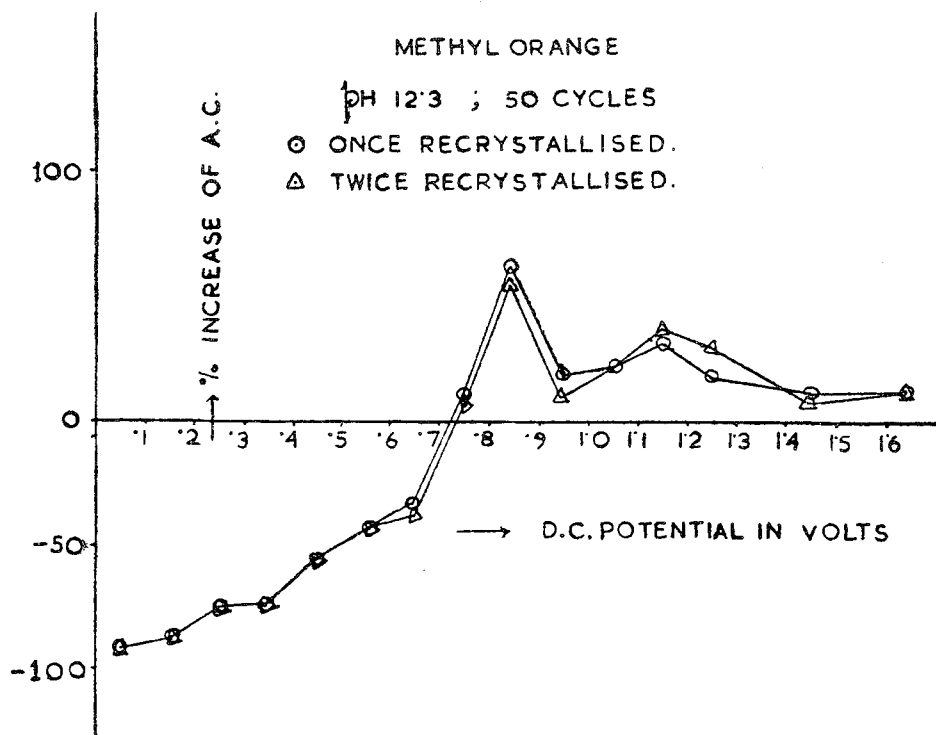


FIG. 4

3.2. *Behaviour of Methyl Orange at pH 5.0.*—The first important distinguishing feature at this pH value is the absence of the satellite peak. This is presumably due to the adsorptive forces being strong in the vapour film even after the phase transition, and a vapour film having a high concentration of the adsorbed molecules. This strongly adsorbed film appears not to get desorbed right up to a potential of 1.5 volts at which there is a peak due to the cathodic reduction of the substance.

In a separate paper⁶ a method has been described which can be adopted for finding out generally whether the peak is due to desorption or reduction. In the present case it appears that the peaks observed at lower voltages are due to desorption whereas those at a cathodic potential of 1.3 volts or higher are chemical peaks due to reduction.

3.3. *Behaviour of Methyl Orange at pH 1.0.*—The desorption peak is now at zero volt or even at the anodic side. The satellite peak is absent,

TABLE I

Effect of pH on Peak Potential

Substance used	Nature of peak	Peak potential at pH 1.0	Peak potential at pH 5.0	Peak potential at pH 12.3
<i>Class A</i>				
1. Methyl orange	.. Main peak ..	1.3 0	1.7 .3	>1.7 .85
	Subsidiary peak	1.15
2. Thymol blue	.. Main peak ..	<0	.65	.98
	Subsidiary peak	.5	1.1	..
3. Bromocresol purple	Main peak55	.95
4. Methyl blue	.. Main peak ..	.01	.2	.45
<i>Class B</i>				
5. Cetyl-pyridinium-bromide	Main peak	1.6 0	1.25 <0
<i>Class C</i>				
6. Isopropyl alcohol	Main peak ..	1.25 .15	1.35 .15	1.3 .15
7. Isobutyl alcohol	Main peak ..	1.25 .1	1.35 .1	1.3 .15
8. Benzene	.. Main peak9	.8
9. Toluene	.. Main peak95	.9
10. Amyl alcohol	.. Main peak	1.2	1.0
11. Ether	.. Main peak	1.1	1.2
12. Camphor	.. Main peak	1.2	1.3
13. Lisapol	.. Main peak	1.7 0	1.65 <0
	Negative peak9	.95
14. Cerfak	.. Main peak	1.37	1.4
	Negative peak85	0.9
		..	.1	0
15. Aerosol O.T.	.. Main peak	1.37 .1	1.4 0
	Negative peak85	.9
16. Lauryl- <i>p</i> -toluidine 2-sodium sulpho-nate	Main peak	1.35	1.4
	Negative peak85	.7
17. Methyl violet	.. Main peak ..	1.31	1.34	..
18. Methylene blue	.. Main peak ..	1.21	1.4	1.37

The absence of the satellite peak and other features can be interpreted as has been done in the case of pH 5.0. The peak at 1.3 volts is definitely a chemical peak caused by the cathodic reduction.

3.4.—*Effect of pH on a Peak Potential.*—The peak potentials whether it is of main peaks or subsidiary peaks get displaced by the change in pH. It is of interest in this connection to examine the behaviour of all the substances so far tried. Table I shows the summary of the results. The substances tried may be classified into three groups. Class A, comprising of methyl orange, thymol blue, bromocresol purple and methylene blue, shows a considerable shift towards more cathodic potentials with increase in pH. Class B, represented by cetylpyridinium bromide, shows a shift to less cathodic potentials at high pH. Class C, comprising of large number of substances, shows only a small shift in pH. No simple characteristic of these substances can be correlated with the present facts, but wherever the shift takes place, the whole curve appears to shift to the left or to the right. This indicates that the shift is due to the shift of the electro-capillary zero caused by these surface-active substances to different extents in different media.

There appears to be no interference by micelle formation at pH 1 or at pH 5.0. It may be that the micelle formation starts at much lower concentration at these pH values owing to high lateral adhesion.

4. SUMMARY

The study of the behaviour of methyl orange at the dropping mercury electrode has revealed many new and interesting features. The most important feature is the presence of the main as well as satellite desorption peaks at pH 12.3 and absence of the satellite peaks at pH 5.0 and 1.0. The causes of this have been discussed in this paper. It has also been observed that at pH 12.3, the main peak changes its magnitude which indicates micelle formation.

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