

# EFFECT OF THYMOL BLUE, NIGHT BLUE AND METHYL VIOLET ON THE CAPACITY OF THE DROPPING MERCURY ELECTRODE

by S. L. GUPTA, *Physico-Chemical Laboratories, Birla College of Science, Pilani*

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## ABSTRACT

The effect of thymol blue, night blue and methyl violet has been investigated on the dropping mercury electrode capacity. At pH 5.6 and 1.0 thymol blue system is distinguished by the occurrence of a main peak and a satellite. The cause of the satellite has been discussed. It has been seen that although the night blue is showing sufficiently high depression of capacity due to adsorption, the desorption peaks are very small. The causes of this have been discussed. The nature of the peaks caused by thymol blue, night blue and methyl violet has also been discussed.

## 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 (1935). 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 (1946). The pulsating field technique as modified by Doss and Kalyanasundaram (1952) is found to be very convenient for the investigation of these phenomena. Breyer and Hacobian (1952) have also used a similar technique for such investigations. The earlier papers have shown how surface active substances influence the dropping mercury electrode capacity by getting adsorbed at the mercury-aqueous interface (Doss and Gupta, 1952, 1954, 1956; Gupta, 1953a, b, 1954a, b, 1955a, b). 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 thymol blue, night blue and methyl violet on the capacity of the dropping mercury electrode under different conditions of pH, concentration and frequency.

## 2. EXPERIMENTAL

2.1. Thymol blue, night blue and methyl violet used were Merck's quality.

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 (Doss and Kalyanasundaram, 1952; Doss and Gupta, 1952). This consists in applying to a dropping mercury electrode, 50 cycles a.c. ripple of  $\pm 45$  mv (r.m.s.) over the d.c. potential and observing the alternating component of the resulting pulsating current. As

the capacitative 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 (Doss and Gupta, 1954). The dropping mercury electrode was cathodic throughout the measurements.

For investigating the effect of frequency of the a.c. ripple on the behaviour of night blue at the dropping mercury electrode, the series circuit described in the previous paper (Gupta, 1954a) using B.S.R. oscillator (B.S.R. Ltd., Berks, England) as the source of alternating current was used. The results are represented in Figs. 1 to 6.

### 3. DISCUSSION

3.1. *Thymol Blue*.—At pH 12.3 there is only one main peak at about 1.0 volt which goes on progressively increasing with increase in concentration. Except for very dilute solutions there is no shift in the position of the peak. At pH 5.6 and 1.0 the system is distinguished by the occurrence of a main peak and a satellite at all the concentrations examined (*vide* Figs. 2 and 3). At pH 5.6 the main peak and the satellite occur at about 0.65 volt and 1.1 volts respectively, whereas at pH 1.0 the main peak and the satellite occur at about 0.4 volt and 1.5 volts respectively.

Satellites have been observed by Elving in his work on alcohols (Loveland and Elving, 1952), using oscillographic technique. In the opinion of the present author, these multiple peaks as well as those reported in the present paper are caused by changes of state of the adsorption film occurring as a result of the changes in the applied potential.

At pH 1.0 the peaks observed are relatively small in magnitude, due to the thymol blue becoming uncharged at low pH. The behaviour at higher cathodic voltages indicate that the peaks are getting less sharp and are being shifted to less cathodic potentials.

3.2. *Night Blue*.—It is to be seen that although the night blue is showing sufficiently high depression of capacity due to adsorption, the desorption peaks are small. This is in accordance with the theory proposed in the earlier paper (Gupta, 1954b). Owing to the high molecular weight, the night blue molecules are unable to adsorb and desorb sufficiently quickly in the pulsating field at the desorption potentials. The low peak might also be caused by the low charge per mole of night blue in the micellar state. The desorption peak is therefore small. It is also to be noted in the case of night blue that the desorption peaks although small tend to decrease in magnitude as the concentration of the night blue increases. This is presumably caused by the increase in the degree of polymerization at higher concentrations. Fig. 5 shows that the increase in frequency decreases the depression of the capacity due to adsorption. This behaviour indicates that the film does not appear to have any considerable deterrent action on the passage of

the high frequency current. The increase in frequency is also found to lower the desorption peaks. This feature shows that there are certain slow processes contributing towards passage of electric charge through the interface during sorption and desorption cycles. It may be that the sorption and desorption processes themselves may take time or it may be that the other attendant processes such as distribution of ions may be slow. This is a matter for further investigation.

3.3. *Methyl Violet*.—This system could not be tried at  $pH$  12.3 as it got precipitated at that  $pH$ . However, at  $pH$  5.8 and 1.75 the system shows very high peaks. There are two peaks at both the  $pH$  values; one being at about 1.3 volts and the other at about 0 volt. At  $pH$  5.8 there is again a halt and a slight tendency for the peak on the negative side at about 0.9 volt whereas at  $pH$  1.75 there is definitely a small peak at about 0.6 volt.

3.4. *The Nature of the Peaks*.—A comprehensive study (Gupta, *unpublished*) of the peaks has indicated that the peaks obtained with thymol blue at all the three  $pH$  values tried are desorption peaks.

The peaks with night blue also appear to be desorption peaks.

The peak with methyl violet at 0 volt ( $pH = 5.8$ ) appears to be due to desorption whereas the peak at 1.34 volts ( $pH = 5.8$ ) appears to be due to chemical reaction.

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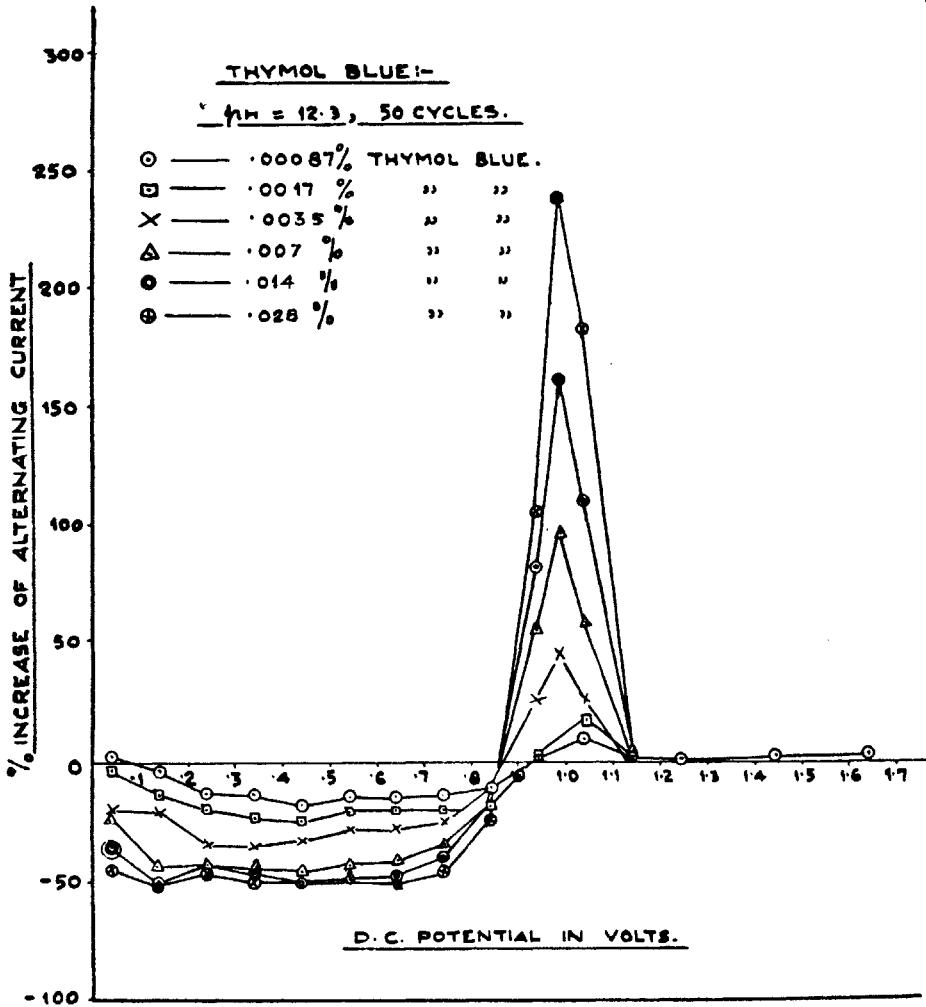


FIG. 1.

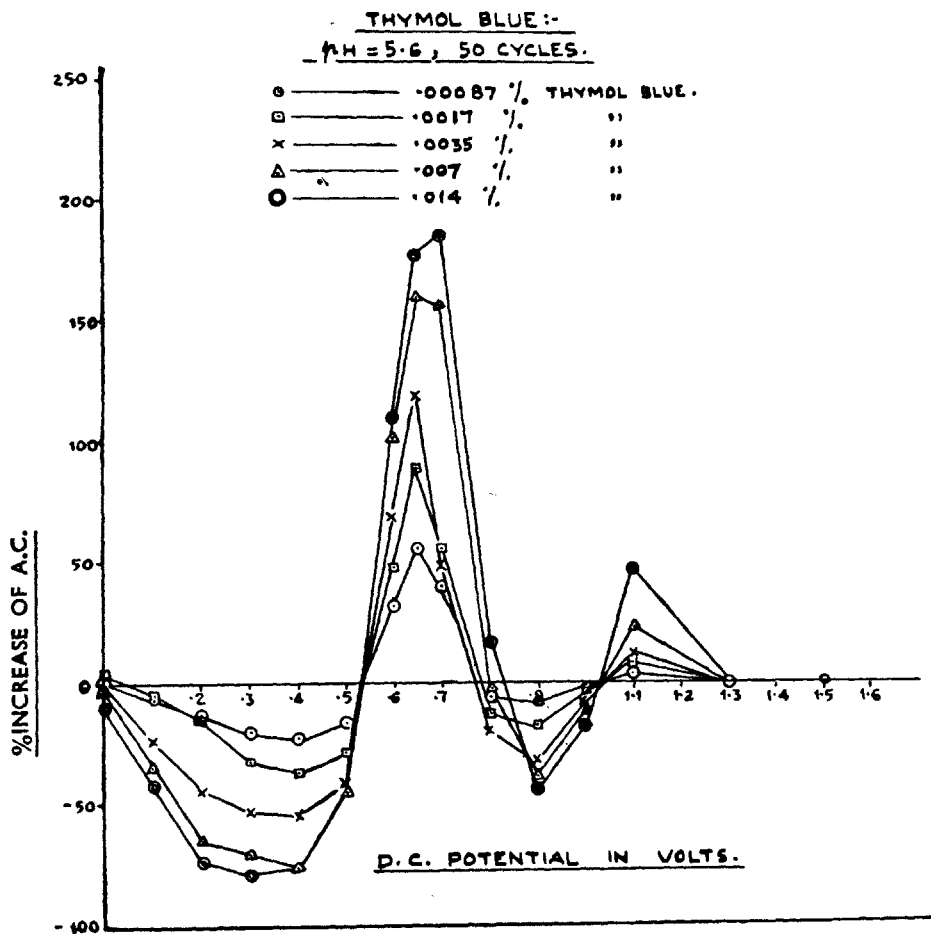


FIG. 2.

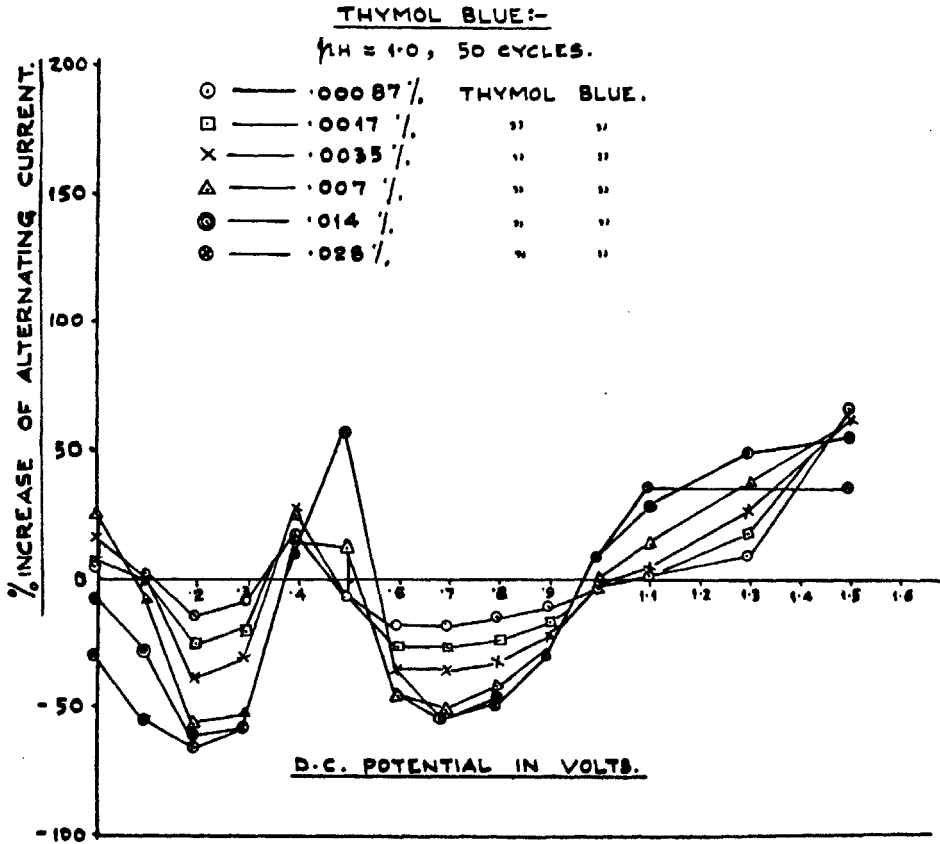


FIG. 3.

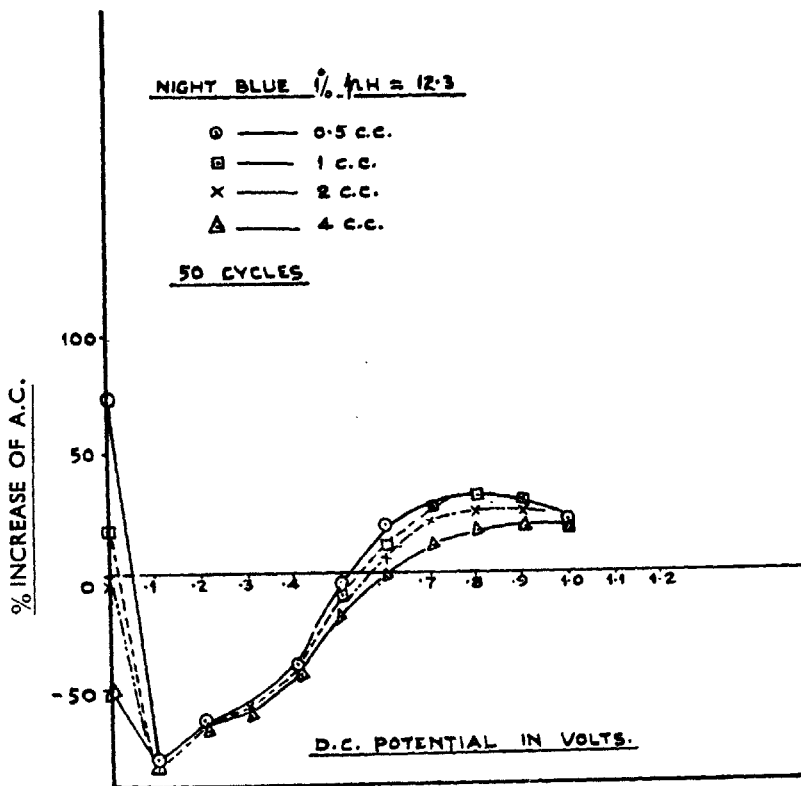


FIG. 4.

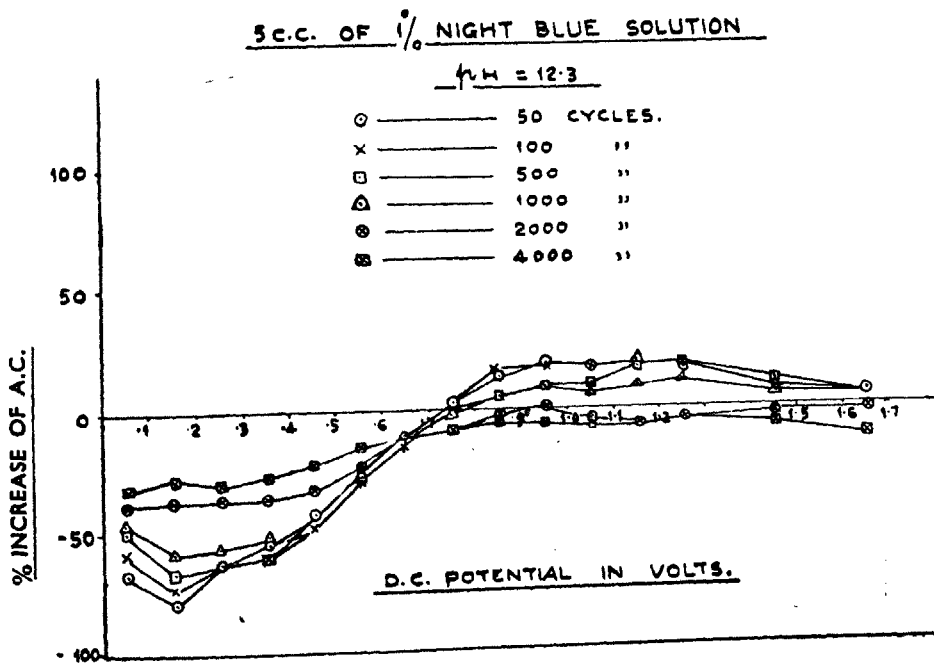


FIG. 5.

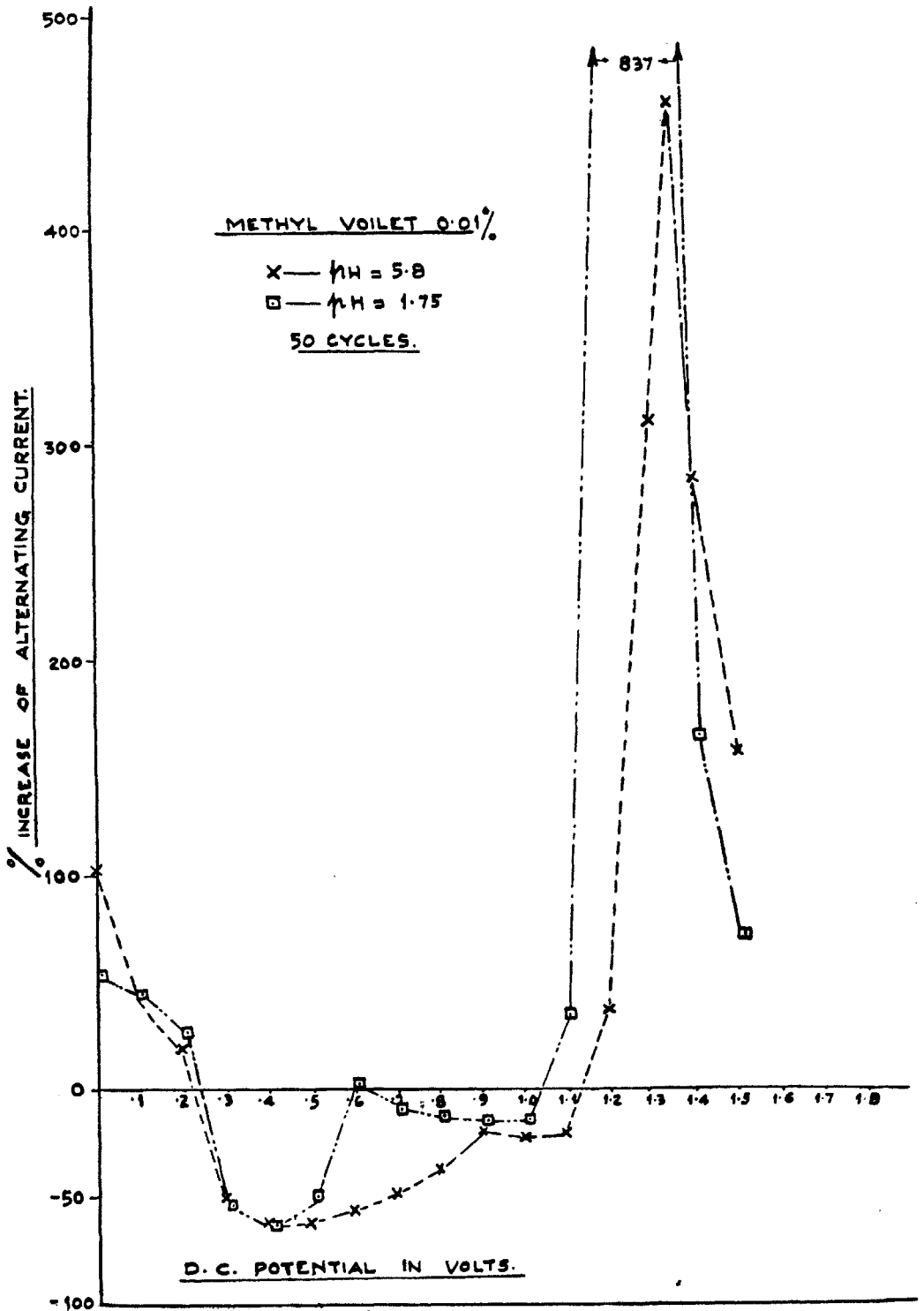


FIG. 6.



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