

BEHAVIOUR OF SURFACE ACTIVE SUBSTANCES AT THE DROPPING MERCURY ELECTRODE AT DIFFERENT FREQUENCIES OF THE APPLIED FIELD

BY S. L. GUPTA

(Indian Institute of Sugar Technology, Kanpur)

Received November 16, 1953

(Communicated by Prof. K. S. G. Doss, F.A.Sc.)

INTRODUCTION

WHILE studying the effect of surface active substances on the kinetics of discharge of metallic ions at the dropping mercury electrode in pulsating fields¹ it was observed that the velocity of discharge was greatly brought down by the presence of such substances as gelatine. An elegant technique based on measurement of phase difference has been used by Randles² who has reported that addition of gelatine brought down the rate of discharge of cadmium ion by a thousand times. Keilin has also made a similar observation in polarographic measurements.³ This has been attributed to the surface active substance getting adsorbed at the mercury surface and hindering the electrode processes in the covered areas. The adsorption of surface active substances is also known to lower the capacity of the electric double layer and is often responsible for low values of capacity reported in literature.⁴ From the point of view of studying the adsorbability of surface active substances at mercury-aqueous interfaces, it would be better to investigate the latter phenomenon as the number of complicating factors is smaller and the results would be easier to interpret.

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.⁵ 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.⁶ The pulsating field technique⁵ as modified in this laboratory is found to be very convenient for the investigation of these phenomena.⁷ Breyer and Hacobian have also used a similar technique for such investigations.⁸ Interesting results have been obtained with regard to the behaviour of bromocresol purple at the mercury-aqueous interfaces.^{9, 10} The present work relates to the effect of

the frequency of the a.c. ripple on the behaviour of the surface active substances at the dropping mercury electrode.

EXPERIMENTAL

Materials used.—1. Isobutyl alcohol was Merck's purest quality, redistilled twice in an all-glass apparatus collecting the fraction boiling from 106°–108° C.

2. Lauryl-*p*-toluidine-2-sodium sulphonate was a purified sample kindly prepared and supplied by Dr. K. Venkatraman, Director, Department of Chemical Technology, Bombay University.

3. The mercury used for the dropping and the pool electrodes was purified by passing several times through Meyer's column, washed with distilled water, dried and passed through a sintered glass filter.

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

Technique of measurement.—The technique (Fig. 2) consists in applying to the dropping mercury electrode a 45 mv. (r.m.s.) a.c. ripple of the required frequency over the d.c. potential and observing the alternating component of the resulting pulsating current. The B.S.R. oscillator of (B.S.R. Ltd., Berks, England) was used as the source of the alternating current. The frequency could be adjusted to any desired value. It was found, however, that the output voltage of the oscillator was fluctuating rather too much. To avoid this, the output of the oscillator was fed into a multipurpose amplifier fabricated as per our specifications by the Central India Radio, Kanpur, the line diagram of which is given in Fig. 1. The amplifier gain was adjusted to get an output of 220 volts. This was passed through a mains resistance and a current regulator lamp. The potential drop across the mains resistance was thus maintained constant within one per cent. and had a good wave form. The a.c. ripple was obtained from this by a suitable potentiometric arrangement.

Normally the experiments were done employing the series circuit as shown in Fig. 2. With a view to see if the reduction of the resistance of the system has any effect on the behaviour, an experiment was conducted with the a.c. ripple applied to the dropping mercury electrode by a parallel arrangement as shown in Fig. 3. The required d.c. voltage obtained from the potentiometer A was applied between the dropping mercury electrode D and the pool electrode P. The heavy inductance I helped to prevent the a.c. passing through the d.c. potentiometer. The a.c. ripple obtained by the arrangement described earlier was applied between D and P. The condenser C helped to prevent the draw of the d.c. current from the system

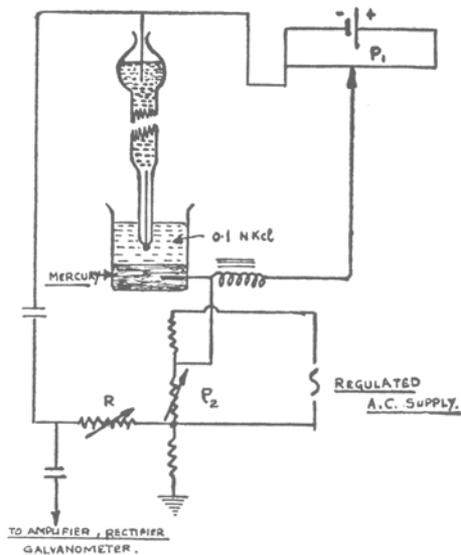


FIG. 3. Parallel Circuit

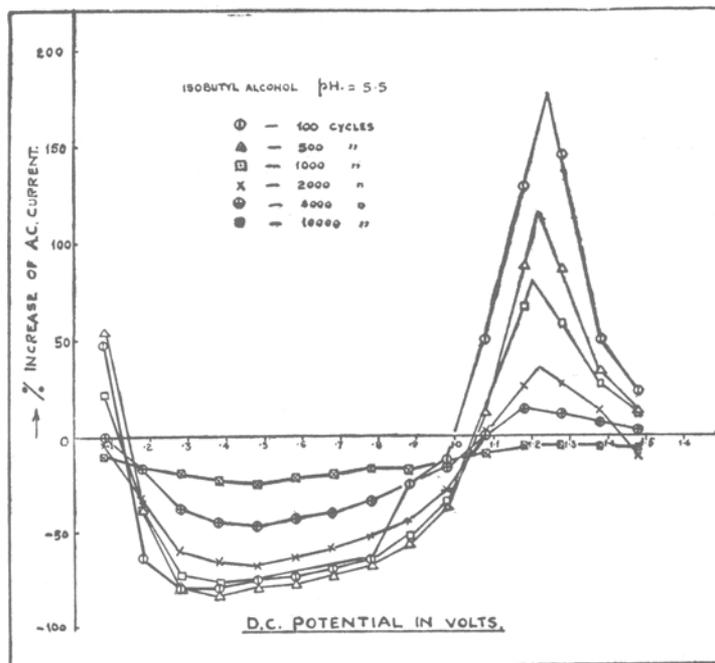


FIG. 4.

through the a.c. circuit. The d.c. potential between the dropping mercury electrode and the pool electrode were measured in every case directly

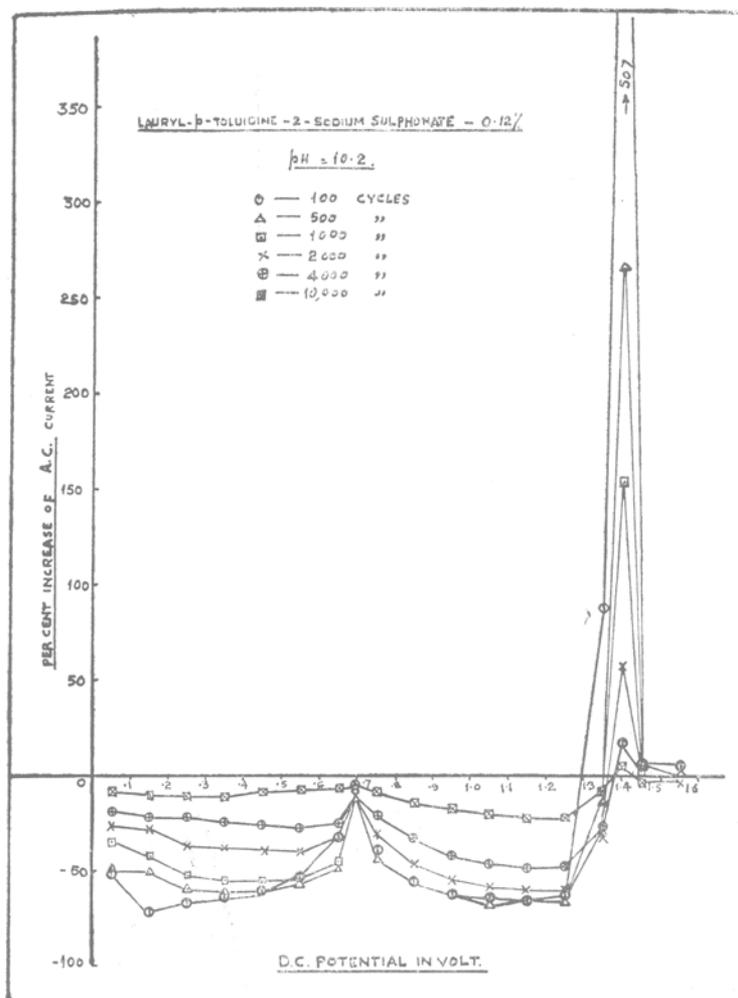


FIG. 5.

by means of a d.c. potentiometer. The potential of the pool electrode was also measured with reference to the saturated calomel electrode. The d.c. potentials of the dropping mercury electrode were then calculated as referred to the saturated calomel electrode and these values have been used for plotting in the graph. Decinormal potassium chloride solution was used as the indifferent electrolyte.

The behaviour of isobutyl alcohol is shown in Fig. 4. The behaviour of lauryl-*p*-toluidine-2-sodium sulphonate is shown in Figs. 5 and 6, the former gives the results obtained by the usual series circuit arrangement

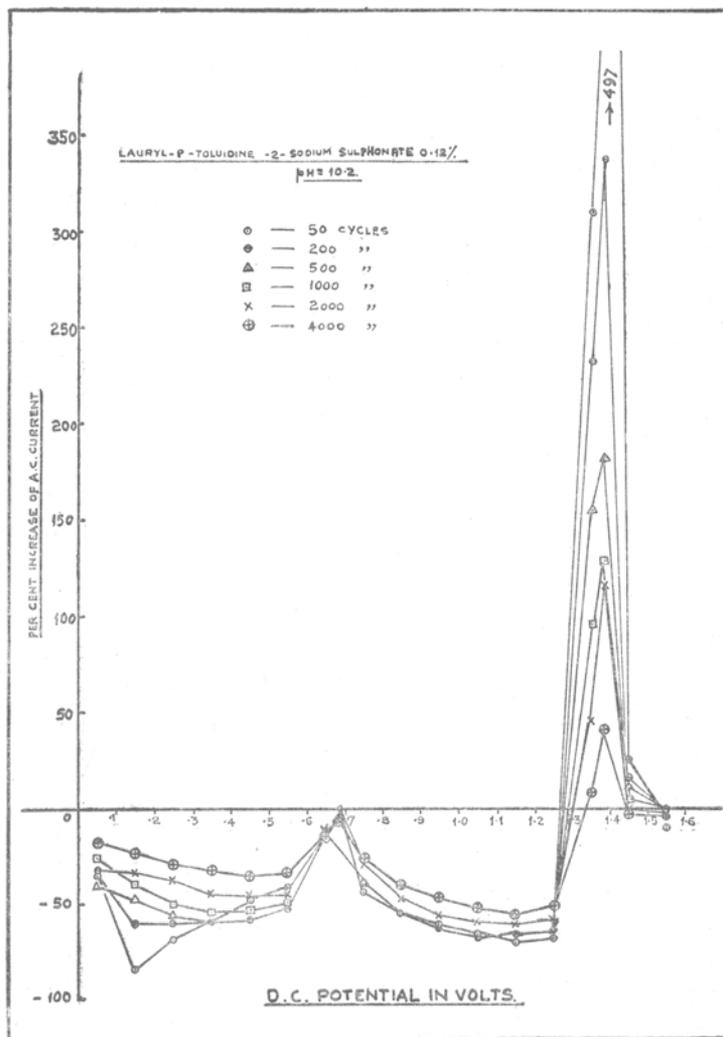


FIG. 6.

and the latter by the parallel circuit arrangement, described in this paper (Fig. 4).

DISCUSSION

A. *General features.*—An examination of Fig. 4 shows that isobutyl alcohol shows as usual a maximum depression of the dropping mercury electrode capacity in the neighbourhood of the electrocapillary zero. At a potential of about 1.2 volts the desorption peak develops. There is a clear indication of the development of another desorption peak on the anodic side of the electrocapillary zero as well,

Lauryl-*p*-toluidine-2-sodium sulphonate shows a similar depressing effect on capacity near the electrocapillary zero. At more cathodic potentials there are two desorption peaks exhibited. The first of them occurs at potentials at which the depression of the capacity is yet very effective and even at potentials very close to the peak the per cent. Δ_i is negative. This novel behaviour indicates a considerable change in amount of adsorption with potential; but the change is attended by relatively small transfer of electric charge across the interface. The second desorption peak occurring at still higher cathodic potentials (1.35 V) is a peak of unusually high magnitude reminding one of a reduction peak corresponding to a polarographic wave. This is not a reduction peak as this compound has no easily reducible group responding polarographically at this potential. The peak is not caused by any delayed reduction of oxygen, as the de-aerated solution shows nearly the same magnitude of the peak. The unusually high magnitude of this desorption peak is therefore presumably caused amongst other factors by the ionised end group bringing about large changes in the distribution of ions during sorption and desorption.

B. *Effect of frequency.*—One interesting feature is that the depression of the capacity due to adsorption at 0.5 volts d.c. is nearly independent of frequency from 50 to 1,000 cycles in both the systems studied. Any further increase in frequency decreases the depression of capacity due to adsorption. This behaviour indicates that *whereas the adsorption film effectively hinders electrode processes that give rise to the condenser current at low frequencies, the film does not appear to have any considerable deterrent action on the passage of the high frequency current.* This new fact is of profound significance and extension of these studies to other systems is likely to reveal the mechanism of the condenser current.

The increase of frequency is found to lower the main desorption peaks in both the systems examined (Figs. 4 and 5). It is to be noted that the per cent. increase of a.c. has been plotted and hence is of great significance. It may be recalled that the technique of measurement is such that the change of frequency does not introduce any error in the measurement.¹¹ It is, however, possible that at very high capacities and frequencies the resistive impedance of the system may become an important of the total impedance and influence the results. This was confirmed by the experiments using a parallel circuit (Fig. 4), involving very low resistive impedance, which gave higher peaks at the high frequencies (Fig. 6). The general behaviour however was reproduced by the parallel circuit as well, showing a decrease of the magnitude of the main desorption peaks with increase in frequency.

This amazing feature is revealing and 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.

SUMMARY

Increase in frequency is found to lower the depressing effect of the adsorption films of surface active substances on the dropping mercury electrode capacity. This fact appears to be of great interest from the point of view of elucidating the factors controlling the condenser current. Increase in frequency decreases the desorption peaks which points at the existence of some slow processes controlling the passage of electric charges during the sorption and desorption cycles.

ACKNOWLEDGMENT

The author wishes to thank Professor K. S. G. Doss, D.Sc., F.R.I.C., F.Inst.P., for his guidance and Professor J. M. Saha, Director, Indian Institute of Sugar Technology, Kanpur, for his kind interest in the work and the Uttar Pradesh Scientific Research Committee for a grant in aid.

REFERENCES

1. Kalyanasundaram and Tandon .. Unpublished.
2. Randles .. *Faraday Soc. Discussion*, 1947, 1, 11.
3. Keilfin .. *J. Am. Chem. Soc.*, 1948, 70, 1984.
4. (a) Breyer and Gutman .. *Faraday Soc. Discussion*, 1947, 1, 25.
(b) cf. Ershler .. *Ibid.*, 1947; 1, 48.
(c) cf. Bowden and Grew .. *Ibid.*, 1947, 1, 49.
5. Proskurnin and Frumkin .. *Trans. Far. Soc.*, 1935, 31, 110.
6. Grahame .. *Am. Chem. Soc.*, 1946, 68, 301.
7. Doss and Kalyanasundaram .. *Proc. Ind. Acad. Sci.*, 1952, 35, 27.
8. Breyer and Hacobion .. *Australian J. of Scientific Research*, Series A, 1952, 5, 500.
9. Doss and Gupta .. *Proc. Ind. Acad. Sci.*, 1952, 36, 493.
10. Gupta .. *J. Sci. and Ind. Res.*, 1953, 12B, 84.
11. Doss and Kalyanasundaram .. *Proc. Ind. Acad. Sci.*, 1951, 33, 298.