

ELECTROCAPILLARYPHORESIS, A POTENT CAUSE OF DESORPTION PEAKS AND POLAROGRAPHIC MAXIMA

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THE effect of surface active substances on the differential capacity of a dropping mercury electrode was first reported by Frumkin and Proskurnin.¹ They showed that the surface active substance depresses the capacity of the dropping mercury electrode at the electrocapillary zero. Furthermore, they observed that at certain potentials on either side of the electrocapillary zero, there is an abrupt increase in the differential capacity, which is referred to as the desorption peak.

The depression in the capacity has been established as due to the strong adsorption of the surface active substance. The adsorption is mainly caused by the tendency on the part of the hydrophobic group of surface active substances to get away from water.² This has been aptly referred to as squeezing type of forces by Grahame.³ The hydrophobic group finds itself in a relatively high potential energy state within the network of hydrogen bonds in the aqueous media. The hydrophobic group therefore tries to get out of the water and gets adsorbed on the dropping mercury electrode. This adsorption takes place unhindered at the electrocapillary zero. At potentials sufficiently removed from the electrocapillary zero, the intensely charged mercury surface would attract the water dipoles preferentially, which would lead to desorption of the surface active substance. The desorption is found to occur rather abruptly at well-defined potentials, characteristic of the system.

It has to be pointed out, however, that the occurrence of the peak at the desorption potential is yet to be explained. The desorption should have normally raised the capacity to that obtained with pure indifferent electrolyte; actually, however, the peak capacity at desorption potential attains a value which may be several hundred per cent. higher than the capacity with the pure indifferent electrolyte at that potential. The enormous peaks in the differential capacity observed have been explained as produced by the excursions of the potentials due to the superimposed A.C. ripple causing sorption and desorption processes, which are supposed to

cause a high dynamic capacitance. This explanation has been accepted by all the workers so far.

With a view to elucidate further this phenomenon, the effect of stirring on differential capacity of the dropping mercury electrode was studied. The experimental set-up was nearly the same as used by Doss and Gupta.⁴ The voltage drop resistor was kept constant at 200Ω . The Philips GM 6017 Vacuum Tube Voltmeter was used as an amplifier, and the amplified current was rectified and measured by a galvanometer with a suitable shunt. Since the resistive impedance of the rest of the circuit was low as compared with the impedance due to the capacity of the dropping mercury electrode, the galvanometer deflections were nearly proportional to the differential capacity. The other details of the experimental set-up are as follows:—

$m = 0.936$ mg. per sec.

$t = 5.8$ sec. per drop in 0.1 M KCl, open circuit.

$h = 63$ cm. of mercury.

A.C. ripple = 30 mV. (r.m.s.); 50 cycles.

D.C. potentials are with reference to saturated calomel electrode.

Indifferent electrolyte = 0.1 M — KCl.

$1 \mu\text{A}$ (r.m.s.) = 30 divisions of galvanometer deflection.

The galvanometer deflections give the electric double layer capacity in arbitrary units.

Surface active substance = sodium dioctylsulphosuccinate ("Manoxol-OT" of "100 per cent." quality kindly spared by the Imperial Chemical Industries).

It was observed that the capacity at desorption potential, on stirring, rose up and gave nearly the same value of the capacity, irrespective of the concentration of the surface active substance and nearly equal to that which was got with the pure indifferent electrolyte under stirred conditions. For example at a potential of -1.35 V. (*vide* Fig. 2), it is seen that the capacity increases from 95 to 203 units. Similarly at the same D.C. voltage in the case of the pure indifferent electrolyte (Fig. 1), it rises to about 210 units. This interesting feature indicated to us that the surface active substance may be bringing out a stirring effect at the desorption potential.

Accordingly this aspect was further investigated. In order to examine whether any movements occur at the mercury-aqueous interface, a narrow strong beam of light from an arc lamp was directed to the dropping mercury

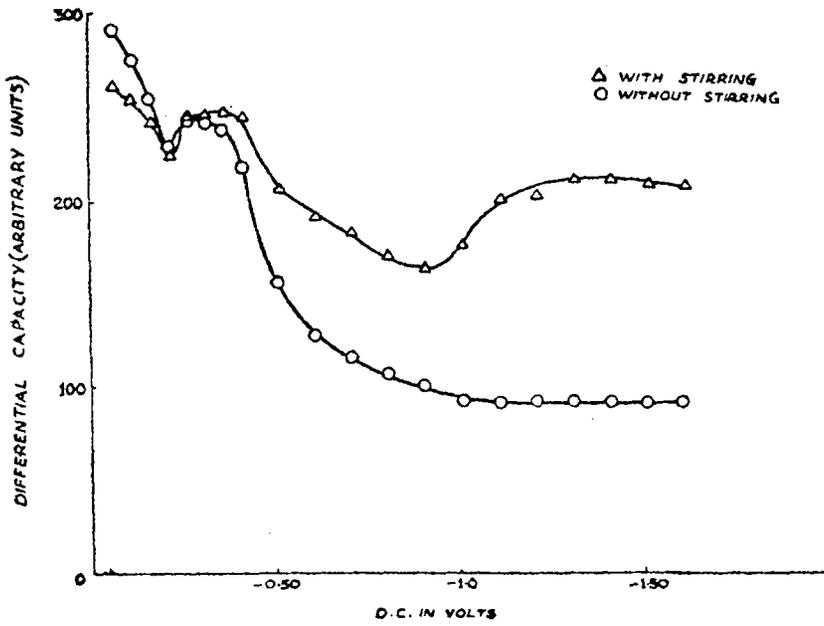


FIG. 1. 0.1 M KCl.

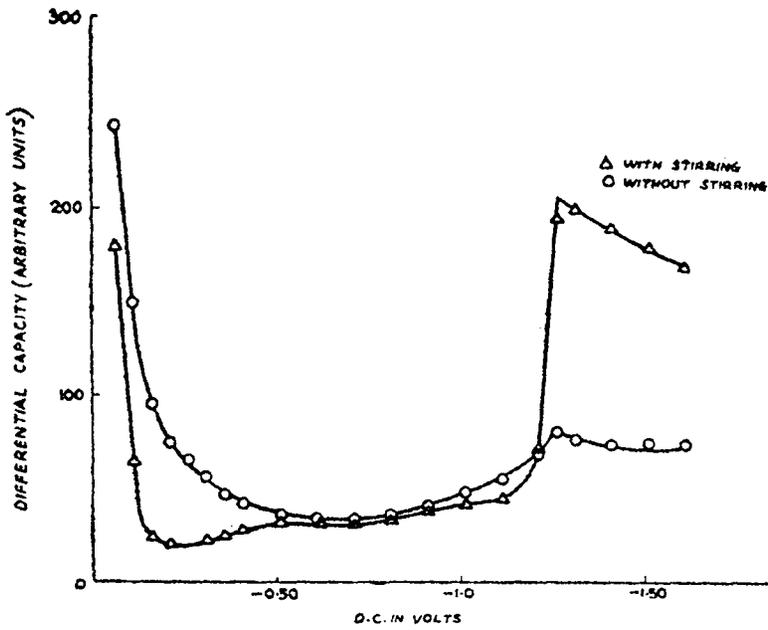


FIG. 2. 0.0025% Manoxol-OT in 0.1 M KCl.

electrode and observations were made at right angles to the beam through a microscope. A small amount of fine talc powder was added to render the liquid movements visible. A careful examination showed that vigorous directed movement of the liquid was occurring at the mercury drop in the neighbourhood of the desorption potential. It was also further observed that the directed movement was much less at other potentials corresponding to small capacities of the dropping mercury electrode.

The directed movement of liquid at the dropping mercury electrode known to occur at polarographic maxima, was first discovered by Antweiler⁵ by his carefully designed schlieren technique. It is now shown by us that similar vigorous directed movement occurs at the desorption peaks of the tensammetric curves. We have also observed that the movement is not dependent on the presence of the A.C. ripple. The results bring out clearly that this movement is a major, if not the sole, factor in producing the desorption peak and especially in enhancing its abruptness.

Antweiler⁵ and Stackelberg⁶ rightly attributed the polarographic maxima as having been caused by these directed movements. The directed movement at mercury drop was, however, interpreted by Antweiler⁵ as due to the electrokinetic effects. This is not probable, as the movements are extremely fast and the potential gradients involved are comparatively of a low order. Doss⁷ and Stackelberg⁸ rightly attributed the movement to the differences in the interfacial tension at the different portions of the mercury drop. To account for these differences in the interfacial tension, Stackelberg postulated that they are caused by the shielding effect of the capillary, leading to the establishment of different potentials at the different points on the aqueous side of the mercury-aqueous interface. He took the analogy from the observations that he made with his experiments on the mercury pool and the large stationary drops.^{6, 8} It has to be pointed out, however, that his experiments with large pool of mercury and stationary drops dealt with comparatively large currents and large voltage drops in the solution. In view of this, large differences can occur in the potential at the different points on the aqueous side of the mercury-aqueous interface of the extensive mercury surfaces dealt with. It appears to the present authors, however, that such large differences in potential cannot be caused by the current passing under conditions of polarography, due to the facts that (a) the mercury drops are extremely small in size, (b) the aqueous solutions are highly conducting and (c) the currents met with are small. This is especially true of tensammetric curves, wherein the currents involved are extremely small since only condenser currents exist. It is to be pointed out in this connection that in tensammetric experiments

the movements persist even in the absence of the A.C. ripple when the D.C. current passing is a small fraction of a micro-ampere. The potential differences caused by the shielding effect would, therefore, be negligible. This is further confirmed by the fact that the occurrence of the polarographic maxima as well as the desorption peaks is practically independent of the distance of the dropping mercury electrode from the pool electrode.

The present authors, on the other hand, consider that the explanation given by Doss and Kalyanasundaram² for the differences in the interfacial tension at the dropping mercury electrode, is more plausible. According to them the *fresh* mercury surface emerging out of the capillary which has its interfacial tension corresponding nearly to that of electrocapillary zero, takes finite time before it attains the proper value of the interfacial tension by interacting with the aqueous solution and the potential existing. The mercury drop, therefore, would have different interfacial tensions at different portions of the drop. These differences however can be large or small according to the circumstances. In the polarographic maximum exhibited by a reducible ion, it is the slowness of the electrode reaction at the half-wave potential that is mainly responsible for the differences in the interfacial tension at the different parts of the mercury drop. These differences therefore get eliminated once the reaction is made faster by raising the potential sufficiently to a more negative value. This explains how proper concentration polarisation occurs at higher negative potentials whereas near the half-wave potential peak-like maximum occurs. Furthermore, at the maximum of the electrocapillary curve, the differences in the interfacial tension would practically vanish; this explains why no polarographic maximum is observed near the electrocapillary zero. The presence of sufficiently high concentrations of adsorbable surface active substances would also help in reducing the differences in the interfacial tension at the different points on the mercury drop. This explains the action of the surface active substances as inhibitors of polarographic maxima.

The same explanation also holds good in the case of desorption peaks. At the desorption potential due to the differences in the state of adsorption of the surface active substance at the different portions of the drop (caused by the time taken for the electro-chemical and adsorption equilibria), large differences in the interfacial tension arise and give rise to the vigorous directed movements.

We would, therefore, emphasise that *the polarographic maxima as well as the desorption peaks in tensammetric curves are caused by electrocapillary-*

phoretic movements which are in their turn caused mainly by the effect of fresh surface emerging from the capillary tip.*

The observation of electrocapillaryphoretic movements, although to a lesser extent at other potentials, brings out clearly a neglected factor which is of importance in interpreting the data obtained in such systems. The dropping mercury electrode is normally preferred to a mercury pool or a stationary drop in view of the fact that in the former case one deals with a fresh surface of mercury and the interference by the surface active impurities would be negligible; but the observations made in this paper indicate that great caution should be exercised in interpreting the data obtained from the dropping mercury electrode. *These observations are therefore of profound significance and lead to the conclusion that one should make sure in every case that the electrocapillaryphoretic movements are negligible before any quantitative interpretation is given to the data obtained with the dropping mercury electrode.*

SUMMARY

The effect of sodium diocetylphosphosuccinate on the differential capacity of dropping mercury electrode in 0.1 M KCl solution is studied. It is observed that at the desorption potential, vigorous directed movement of liquid occurs at the mercury-aqueous interface. This movement is shown to be responsible for the desorption peak in the differential capacity-potential curve.

The cause of the directed movement is further examined. Arguments are given to support the ideas of Doss and Kalyanasundaram, that the movement is caused by the emerging surface of mercury having a different interfacial tension from that of the older surface, and that the shielding effect of the capillary postulated by Stackelberg does not appear to play an important part either in the production of the desorption peak or the polarographic maxima.

It is found that the directed movement of liquid occurs although to a less extent at potentials far removed from the desorption potential. This result is of great significance in that it points at the importance of looking for such movements before interpreting quantitatively the data obtained with a dropping mercury electrode.

* Doss⁷ observed similar movements at mercury pool when alternating current is incident and termed the phenomenon as *Electrocapillaryphoresis* since the movements are caused by electrocapillary effects.

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