

BEHAVIOUR OF SURFACE-ACTIVE SUBSTANCES AT THE DROPPING MERCURY ELECTRODE

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Received July 7, 1952

INTRODUCTION

SURFACE-ACTIVE substances are known to affect the capacity of mercury-aqueous solution interfaces. A quantitative study of the phenomenon has been started in this laboratory and a previous communication gives the effect of a number of organic substances like acetone, thymol blue, isobutyl alcohol and gelatin at different concentrations on the capacity of the dropping mercury electrode near the electro-capillary zero.¹ Further the effect of some sparingly soluble substances like benzene, toluene, xylene and amyl alcohol has also been reported. The present paper deals with the extension of the work to other cathodic potentials. A general theory has been formulated for accounting for the observed phenomenon.

EXPERIMENTAL

The apparatus employed in the present investigation is the same as what has been described before.² This consists in applying a constant a.c. pulse of ± 40 mv. r.m.s. over the d.c. potential and observing the a.c. component of the resulting pulsating current. The magnitude of the average a.c. current is nearly a measure of the average differential capacity of the dropping mercury electrode. The averaging is not only with reference to the area of the mercury drop which is changing all the time but also with reference to the applied cathodic potential which is oscillating all the time. One important improvement was that a regulated a.c. supply was employed thereby avoiding any fluctuations in current due to fluctuations in a.c. mains. This regulation was brought about by using a current regulator lamp (Barretter of G.E.C., England) so that the sine wave form of the original current supply was maintained in the regulated supply as well.

The constants of the dropping mercury electrode are as follows:—

$$m = 0.00306 \text{ gm./sec.}$$

' t ' is given in the tables.

The effect of bromo cresol purple, thymol blue, bromo thymol blue and cetyl pyridinium bromide on the capacity of the dropping mercury electrode was investigated at different cathodic potentials applied through the pool

electrode. The potentials of the capillary electrode have been expressed with reference to the saturated calomel electrode. The indifferent electrolyte was 0.1 N—KCl which was shaken with a little mercury and calomel to avoid any time effects while in contact with the pool. Further, 0.5% of sodium sulphite was added to avoid any influence of dissolved oxygen.

All the above substances investigated showed similar behaviour. The results obtained with bromo cresol purple are given in detail in Table I and Fig. 1. The a.c. current observed is roughly a measure of the capacity. The exact values can be calculated if needed from the data given.

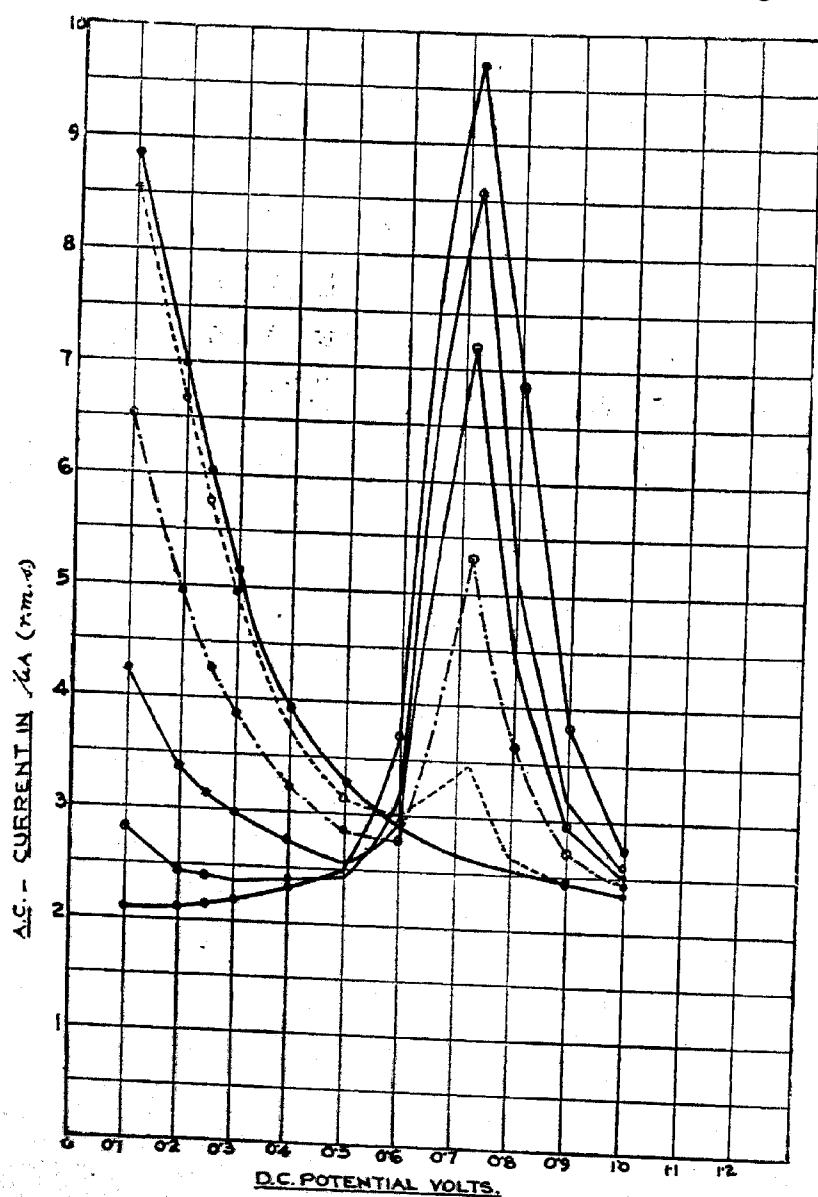


FIG. 1. Behaviour of Bromocresol Purple at the Dropping Mercury Electrode in Pulsating Fields.

TABLE I
Electrolyte: 0.1 N KCl + 0.5% Na₂SO₃

D.C. potential (volts)	Current μ A (r.m.s.)	Time for 25 drops
0	71.6	17.4"
0.1	8.84	17.8"
0.2	6.95	18.8"
0.25	6.02	18.8"
0.3	5.16	18.8"
0.4	3.90	18.2"
0.5	3.25	18.0"
0.6	2.89	17.8"
0.7	2.65	17.6"
0.8	2.54	17.0"
0.9	2.43	16.0"
1.0	2.36	15.2"

Electrolyte: 0.1 N KCl + 0.5% Na₂SO₃ + 0.0002% bromocresol purple

D.C. potential (volts)	Current μ A (r.m.s.)	Time for 25 drops
0	71.6	18.8"
0.1	8.55	19.4"
0.2	6.69	19.8"
0.25	5.77	19.8"
0.3	4.99	19.2"
0.4	3.70	18.4"
0.5	3.15	18.2"
0.6	3.00	18.0"
0.7	2.81	17.4"
0.72	3.46	17.2"
0.8	2.67	16.8"
0.9	2.45	16.0"
1.0	2.37	15.4"

Electrolyte: 0.1 N KCl + 0.5% Na₂SO₃ + 0.001% bromocresol purple

D.C. potential (volts)	Current μ A (r.m.s.)	Time for 25 drops
0	63.6	19.4"
0.1	6.46	19.8"
0.2	4.94	20.2"
0.25	4.27	20.2"
0.3	3.87	19.6"
0.4	3.20	18.8"
0.5	2.86	18.6"
0.6	2.74	18.2"
0.7	3.98	17.8"
0.72	5.30	17.5"
0.8	3.56	17.0"
0.9	2.68	16.4"
1.0	2.45	15.6"

Electrolyte: 0.1 N KCl + 0.5% Na₂SO₃ + 0.002% bromocresol purple

D.C. potential (volts)	Current μ A (r.m.s.)	Time for 25 drops
0	62.2	18.6"
0.1	4.25	19.4"
0.2	3.38	19.8"
0.25	3.14	20.0"
0.3	2.99	20.0"
0.4	2.74	19.4"
0.5	2.56	19.2"
0.6	2.84	18.8"
0.7	6.07	18.4"
0.72	7.22	18.0"
0.8	4.34	17.4"
0.9	2.92	16.6"
1.0	2.49	15.8"

Electrolyte: 0.1 N KCl + 0.5% Na₂SO₃ + 0.003% bromocresol purple

D.C. potential (volts)	Current μ A (r.m.s.)	Time for 25 drops
0	57.3	17.6"
0.1	2.82	18.0"
0.2	2.47	18.2"
0.25	2.41	18.2"
0.3	2.39	18.2"
0.4	2.38	18.2"
0.5	2.41	18.4"
0.6	3.18	18.4"
0.7	7.46	18.2"
0.72	8.61	17.6"
0.8	5.19	17.5"
0.9	3.14	17.0"
1.0	2.54	16.0"

Electrolyte: 0.1 N KCl + 0.5% Na₂SO₃ + 0.006% bromocresol purple

D.C. potential (volts)	Current μ A (r.m.s.)	Time for 25 drops
0	17.0	17.4"
0.1	2.12	17.8"
0.2	2.12	18.2"
0.25	2.14	18.2"
0.3	2.17	18.4"
0.4	2.32	18.4"
0.5	2.43	18.4"
0.6	3.78	18.4"
0.7	8.78	18.2"
0.72	9.70	18.2"
0.8	6.88	18.2"
0.9	3.82	17.4"
1.0	2.73	16.4"

DISCUSSION

1. *The Effect of Bromocresol Purple on the Form of Capacity, Voltage Curve.*—Curve 1, Fig. 1 gives the a.c. current voltage curve for the indifferent electrolyte (N/10 KCl in 1% aqueous Na_2SO_3) in absence of any surface-active substance. The capacity of the dropping mercury electrode is high at low cathodic voltages and falls quickly up to about 0.5 volts and then much more slowly up to 1 volt. In presence of bromocresol purple, the capacity values at lower cathodic potentials get lowered. Higher concentrations produce progressively greater lowering. The percentage lowering of the capacity is maximum at a cathodic potential of 0.25 volt which is nearly the electro-capillary zero of the system; at still higher cathodic potentials the capacity lowering effect diminishes and at potentials higher than 0.5 to 0.6 volt there is actually an increase in the capacity with increase in voltage. The a.c. current voltage curve exhibits a maximum at a cathodic potential of 0.72 volt and then sharply falls off. The curve becomes steeper at the maximum as the concentration of bromocresol purple increases and the maximum rises to very high magnitudes at the higher concentrations. It is also of interest to note that all the maxima occur at the same cathodic potential within the limits of experimental error irrespective of the concentration of bromocresol purple.

2. *The Theory of the Capacity Phenomena at Mercury Capillary Electrodes.*—Whereas the lowering of the capacity brought about by surface-active substances was observed by many earlier workers, the enormous rise in the capacity has not been quantitatively studied earlier. A qualitative detection of large increase in the capacity has been reported by Heyrovsky and co-workers³ who employed oscillographic potential-time curves. A theory has been put forth by these workers to explain the behaviour. Doss and Kalyanasundaram⁴ proposed a different formulation to explain the data on pyridine. We shall attempt to give a more generalised theory with a view to interpret all the data available.

The changes in the capacity are caused essentially by adsorption of the surface-active substances at the mercury solution interfaces. The surface-active substances adsorbed may act in two ways. (1) They may alter the distribution of ions in the double layer on the aqueous side of the interfaces and (2) they may interfere with the interactions necessary between the two phases for the transmission of electric charge across the interface. Though by definition a surface-active substance is one which lowers the surface tension of water and should therefore, be expected to get adsorbed at the air-aqueous interface, it is found that these very substances also get adsorbed at

oil-aqueous solution interfaces as well as at mercury-aqueous solution interface. This appears to be due to the hydrophobic portion (which is invariably present in surface-active substances) trying to get out of water irrespective of what it finds outside water, be it air, oil, or mercury. Such adsorption would take place relatively unhindered at the electrocapillary zero. At potentials on either side of the electrocapillary zero the mercury drop would get charged positively or negatively which would result in the water dipoles being attracted to the charged interface. Consequently the adsorption of surface-active substances would fall off on either side of the electrocapillary zero.

The maximum adsorption may not however exactly coincide with the electrocapillary zero as one has to take into account the possible effects of the surface-active substances being ionized and having dipolar groups within their molecules. At potentials sufficiently removed from the electrocapillary zero on either side there would be the desorption of the surface-active substance leading to a rise in the capacity of the electric double layer. If this desorption takes place more or less sharply, the dropping mercury electrode would exhibit a high differential capacity at that stage and would lead to a high a.c. current maximum in pulsating fields.

Let us derive an expression for the variation of adsorption with the potential of the dropping mercury electrode. It is assumed that adsorption equilibrium is nearly, if not completely, attained. Following Glasstone, Laidler and Eyring⁵ it is assumed that the heat of adsorption of the surface-active substance is lowered by k_2V at a potential of V volts with reference to electro-capillary zero. Further the heat of adsorption of bromo cresol purple which is negatively charged would get lowered due to mutual interaction of the molecules in the adsorbed layer by an amount equal to $K_3\theta$, where θ is the fraction of the total surface of the mercury drop covered by bromo-cresol purple. Thus the equation for adsorption becomes

$$\frac{\theta}{1-\theta} = k_1 \cdot c e^{\frac{e_0 - k_2V - k_3\theta}{kT}} \quad (1)$$

differentiating we get

$$\frac{d\theta}{dV} = - \frac{k_2}{\theta(1-\theta) + k_3} \quad (2)$$

In examination, equation (2) shows that $\frac{d\theta}{dV}$ becomes maximum when $\theta = 0.5$. This would also be nearly the stage at which there would be a maximum change of capacity with voltage.

Let V^* be the potential at which θ becomes 0.5, then, we get, from equation 1,

$$k_1c = e^{-\frac{\epsilon_0 - k_2V^* - 0.5k_3}{kT}} \quad (3)$$

or

$$\frac{dV^*}{d \ln c} = \frac{kT}{k_2} \quad (4)$$

From (4), it is clear that V^* should be a rectilinear function of $\ln C$.

3. *Application of the Above Theory to the Effect of Bromocresol Purple System.*—It is found (*vide* Fig. 1) that the bromocresol purple shows the maximum depressing effect upon the capacity at a cathodic potential of 0.25 volt. An examination of the time per drop (Table I) indicates that this potential is nearly the electrocapillary maximum, as required by the theory.

The steep maximum exhibited by the curves (Fig. 1) at a cathodic potential of 0.72 volt, is to be explained as due to a high value of $\frac{d\theta}{dV}$. The position of maximum should therefore, nearly correspond to V^* . Equation (4) shows that V^* should be a linear function of $\ln C$ which is found to hold as shown by Doss and Kalyanasundaram⁴ in the case of data on pyridine obtained by Heyrovsky and co-workers. This also holds in the present case; but the slope of the curve of V^* plotted against $\ln C$ is zero within the limits of experimental error. The low value of the slope is presumably due to a high value of k_2 . The value of the constant k_2 is determined by the extent to which the voltage (with reference to electrocapillary zero) applied effects the selective adsorption of water dipoles, and thereby brings about the desorption of the surface-active substance. The factors which affect K_2 need further investigation.

CONCLUSION

It is clear from the observations recorded in this paper that many of the surface-active substances not only lower the differential capacity of the dropping mercury electrode due to the adsorption in the neighbourhood of electrocapillary zero, but also they produce a steep sharp local rise in differential capacity at higher cathodic potentials where desorption of the substance occurs. There would also be a similar steep rise at high anodic potentials but other complications may come up at these high potentials. These results point to the possibility of variations in behaviour which can be taken advantage of to some extent, to characterise the surface-active substances. For the quantitative determination, one can take advantage

of as much the rise in capacity at high cathodic potentials as the lowering of the capacity at the electrocapillary zero. The question as to which of these would give better results is a matter for further investigation.

SUMMARY

It is found that the differential capacity of the dropping mercury electrode is affected mainly in two ways by added surface-active substances. At about the electrocapillary zero there is a strong lowering of the capacity due to adsorption of surface-active substances. At some higher cathodic potential there is enormous increase in differential capacity leading to a maximum and is followed by a sharp fall in the capacity; the latter is due to the desorption taking place more or less sharply at the higher cathodic potentials. The theory of the phenomenon has been formulated.

ACKNOWLEDGEMENT

The authors wish to thank Professor J. M. Saha, Director, Indian Institute of Sugar Technology, for his kind interest in the work.

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