

EFFECT OF SURFACE ACTIVE SUBSTANCES ON THE CAPACITY OF THE ELECTRIC DOUBLE LAYER

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INTRODUCTION

WHILE studying the effect of surface active substances on the kinetics of discharge of cadmium ion 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 gelatin. Randles² has used an elegant technique based on measurement of phase difference and has reported that the rate of discharge of cadmium ions is brought down a thousand-fold by the addition of gelatine. Similar results have been reported by Keilin³ who has found that the limiting current in polarography is lowered markedly by the presence of surface active substances; this has been attributed to the surface active substance getting adsorbed at the mercury surface and preventing electrode processes in the covered areas. The adsorption of surface active substances is known to lower the capacity of the electric double layer and is often responsible for low values of the capacity reported in literature.⁴ The present work relates to a detailed study of the effect of adsorption of a few surface active substances on the capacity of the electric double layer at the dropping mercury electrode.

EXPERIMENTAL

A simple technique for getting an idea of the capacity² of the electric double layer is afforded by the Breyer-Gutman technique⁵ based on the measurement of A.C. current produced by subjecting the dropping mercury electrode to pulsating fields. The technique consists in applying simultaneously a D.C. potential by the potentiometer P_1 (Fig. 1) and an A.C. ripple by the potentiometer P_2 and measure the A.C. component of the pulsating current produced, by measuring the A.C. potential drop across the resistance R . The details have been described previously.^{6,7}

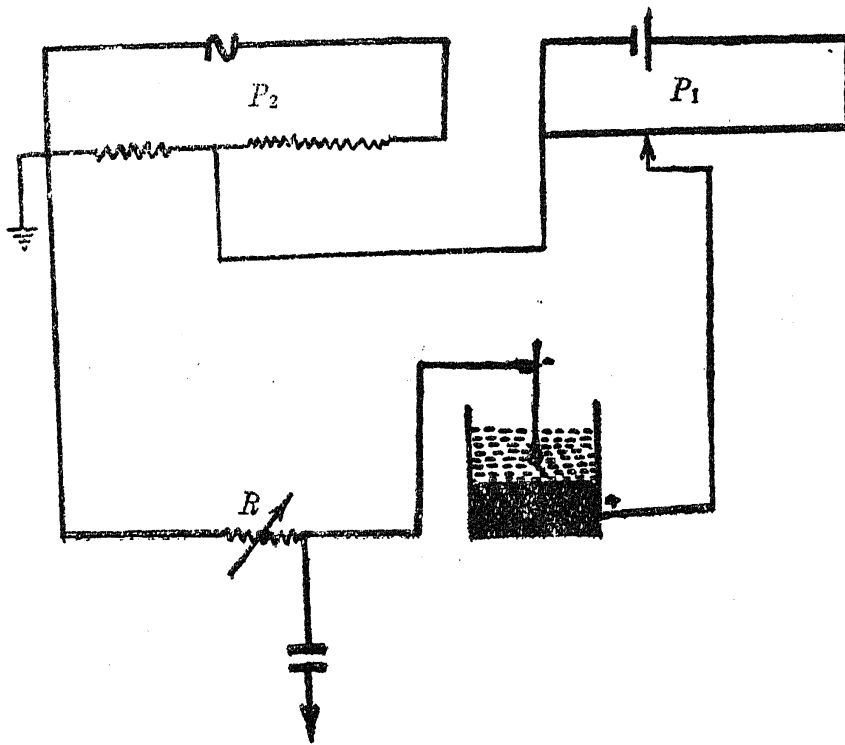


FIG. 1

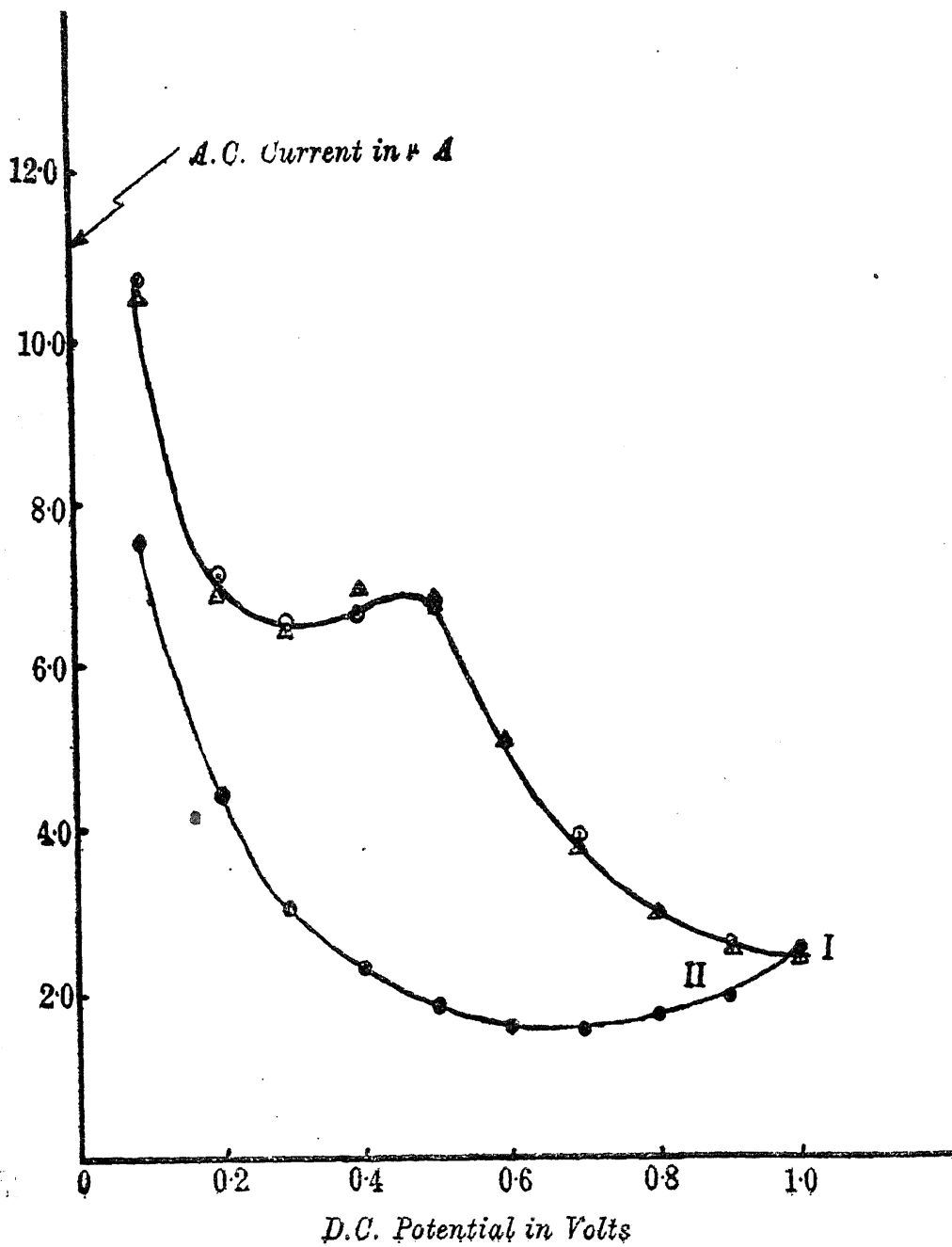


FIG. 2

The magnitude of the alternating current is directly a measure of the capacity of the electric double layer. Curve 1 in Fig. 2 gives the A.C. current-D.C. potential curve for one molar potassium chloride which is freed from air by bubbling hydrogen. Measurements are also taken with molar potassium chloride solution containing dissolved air; but the A.C. current values are found to be identical whether oxygen is present or not, as can be seen from Fig. 2. Hence the rest of the experiments are carried out without removal of air. Curve 2 represents the effect of surface active substances present in sugarcane juice at different D.C. potentials. An examination of the curve shows that the effect of surface active substances on the capacity of the electric double layer is maximum in the neighbourhood of an applied potential of 0.5 V which is near the electrocapillary zero. Similar observations have been made by Frumkin⁸ in his study of the effect of picein on the double layer capacity. Adsorption of pyridine also shows a similar feature. Later measurements are therefore limited to the effect produced at a D.C. potential of 0.5 V applied through the mercury pool. The effect of different concentrations of acetone, thymol blue, isobutyl alcohol and gelatin on the A.C. current developed, is given in Tables I to V. Table V gives the effect of addition of sparingly soluble organic substances on the double layer capacity.

TABLE I
Acetone

Volume in c.c. added to 30 c.c. of molar KCl	A.C. Current in μ A	Drop-time in sec.
0	6.97	5.1
0.2	6.65	5.08
0.4	6.22	.
0.8	5.27	..
1.0	4.89	..
1.2	4.42	5.06
1.4	3.99	..
1.6	3.66	5.02
1.8	3.40	..
2.0	3.20	4.98
3.0	2.42	4.9
4.0	2.15	4.86
5.0	2.00	..
6.0	1.89	4.80
7.0	1.80	4.80
8.0	1.76	..
10.0	1.68	4.74

TABLE II
Thymol Blue 0.04%

Volume in c.c. added to 30 c.c. of molar KCl	A.C. Current in μ A	Drop-time in sec.
0	7.06	5.32
0.5	5.50	5.42
1.0	3.99	5.42
1.5	2.83	5.42
2.0	2.09	5.34
2.5	1.72	5.18
3.0	1.56	5.1
3.5	1.45	5.1
4.0	1.38	5.0
4.5	1.35	5.0
5.0	1.31	5.0
5.5	1.31	4.98

TABLE III
Isobutyl Alcohol

Volume in c.c. added to 30 c.c. of molar KCl	A.C. Current in μ A	Drop-time in sec.
0	7.06	5.28
0.1	5.61	5.28
0.2	1.58	5.26
0.3	1.24	5.22
0.4	1.04	5.14
0.5	0.99	5.16
0.6	0.96	..
0.8	0.94	5.10
0.9	0.91	5.04
1.0	0.91	5.04
1.2	0.88	5.02

TABLE IV
Gelatin 2%

Volume in c.c. added to 30 c.c. molar KCl	D.C. Current in μ A.
0	7.19
0.05	6.08
0.1	5.41
0.15	4.51
0.2	4.05
0.25	3.77
0.4	3.44
0.8	2.89
1.6	2.88
2.6	2.86

TABLE V
Effect on Sparingly Soluble Organic Substances

Substance	% reduction in A. C. current
Benzene ..	95.1
Toluene ..	89.0
Amyl alcohol ..	86.9
Xylene ..	73.1

DISCUSSION

(1) *The effect of soluble surface active substances on the double layer capacity.*—The alternating current passing through the system depends upon (a) the capacity of the double layer and (b) the size of the drops. As seen from the tables, however, the drop time which is a measure of the size of the drop is not appreciably changing. From this it is clear that the A.C. current values are practically a measure of capacities of the electric double layer. That the A.C. current is mostly capacitative can be further confirmed from the fact that the magnitude of the current is practically directly proportional to the frequency of the A.C. current.⁷

It is found that as the concentration of the surface active substance increases, the double layer capacity diminishes in the first instance and finally attains a more or less constant value. The final low value obtained at high concentrations is different in different cases. The effect on the double layer capacity increases in the order: gelatine, acetone, thymol blue and isobutyl alcohol. These differences are partly due to the surface being covered to different extents at saturation and partly due to the differences in the double layer capacity of covered parts in the different cases. A quantitative formulation of these should await further accumulation of experimental data.

2. *Effect of sparingly soluble organic substances.*—The sparingly soluble substances have a profound effect in decreasing the double layer capacity. The effect in the decreasing order is with benzene, toluene, amyl alcohol and xylene. The large effect of benzene was at first feared to be due to the traces of thiophene. Accordingly the benzene was purified so as to get a sample not answering the test for thiophene. But the decrease in capacity remained nearly the same.

3. *Possible application.*—The observations made herein appear to be capable of application for the estimation of surface active substances. Amongst the other methods that are available are (a) determination of surface and interfacial tensions and (b) depression of polarographic maxima. The determination of surface tension or interfacial tension is attended by many difficulties and the correlation of the surface tension with the concentration of the surface active substance is often complicated. We may further point out that the interfacial tension between the mercury and the aqueous solution is only affected to a minor extent by the surface active substances examined herein and therefore would give no precise idea of the concentration. The method based on the polarographic maximum is open to criticism as the maximum is caused by the dynamic effects due to electrocapillaryphoresis⁹ at the dropping mercury electrode. (The electrocapillaryphoresis is perhaps brought about due to the fresh mercury surface just formed near the capillary tip having a different interfacial tension from that of the old surface at the apex of the drop due to the deposition of the ion getting discharged. At higher potentials the discharge of the ion is very quick and takes place even at the fresh surface sufficiently quickly to render differences in interfacial tension negligible; hence the electrocapillary phoresis ceases; the current falls). Such maxima can hardly be expected to be reproducible sufficiently to give precise measure of the surface active substances. From these points of view, measurement of double layer capacity affords an advantage. The double layer capacity itself can be measured by a number of methods. The methods based on D.C. current are definitely disadvantageous as the capacity is greatly influenced by the presence of oxygen. The Breyer and Gutman technique, on the other hand, has a unique advantage in this regard, since the presence of air has practically no influence on the magnitude of the alternating current observed. This is due to the fact that the electrode process involving oxygen is slow and does not follow the pulsating fields even when the pulsation are as low as 50 cycles per second. Further since the mercury drop is freshly being formed, there is no complication due to external contamination. An alternative to this technique would be the method described by Grahame¹⁰ using the bridge suitably modified, if necessary. The present method appears to be invaluable for control purposes wherever the elimination of surface active substances is to be followed up.

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