The Capacity of the Double Layer at a Mercury Anode.

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The development of the procedure for studying the anodic oxidation of metals at very low current density enables the capacity of the double layer at a mercury anode to be readily determined by the direct method and use of a special cell and constant current unit. No previous work on mercury from the present standpoint has been published. By using a mercury electrode of large surface area and very small currents (of the order of 10^{-7} A/sq. cm.) a considerable time is required for the charging of the electrode–solution interface so that it can conveniently be followed with a valve voltmeter. The results have been confirmed oscillographically and are shown to accord with theory.

IN a series of papers (El Wakkad and Emara, *J.*, 1952, 461, 1953, 3504, 3508; El Wakkad and Shams El Din, *J.*, 1954, 3094, 3098; El Wakkad, Shams El Din, and El Sayed, *J.*, 1954, 3103) on the anodic oxidation of metals at very low current density, the true surface areas of the anodes were determined from the value of the capacity of the anodic double layer before oxide formation. The value of the capacity of the anodic double layer was always taken to be 100 μF per true sq. cm. as estimated from correlation between the work of Hickling and of El Wakkad and Emara. No previous verification for this value has been published. The development of this procedure then used enables the capacity of the double

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layer at a mercury anode to be readily determined by the direction method and use of a special cell and constant current unit.   By using a mercury electrode of large surface area and a very small current, the time required for the charging of the electrode–solution interface is such that it can be followed with a valve voltmeter.   The results have also been confirmed oscillographically.   This value has also been deduced theoretically and the result agrees satisfactorily with the experimental results.

<div align="center">EXPERIMENTAL</div>

The Direct Potentiometric Method.—The circuit used in obtaining the variation of the potential of the mercury anode with the quantity of electricity passed employed a pentode valve as a constant-current device, so the current passing was largely independent of changes in the back e.m.f. of the electrode system.   The current was supplied from a 120-v dry battery.

The electrolytic cell used was of Pyrex glass without any rubber connections.   There were no greased ground joints on taps in contact with the solution.   The joints were water-sealed, a thin film of conductivity water being between the two parts of the joint.   The anodic compartment was a mercury pool, with a surface area of 22·9 sq. cm., connected to the electrical circuit through platinum contact.   The mercury used was prepared as described by El Wakkad and Salem (*J. Phys. Chem.*, 1950, **54**, 1371).   The mercury obtained during the last distillation was introduced directly into the cell.   The cathode compartment was fitted with a tight ground joint into the anode compartment and was placed in such position with regard to the anode as to ensure uniform distribution of the polarising current at the anode surface.   The cathode was a platinum spiral wire.   Two side tubes were for gas inlet and exit, the latter being fitted with a Bunsen valve.   Measurements were carried out in 0·1M-sodium hydroxide prepared from conductivity water and " AnalaR " solid.   The solution in the cell was boiled before use and cooled in an atmosphere of pure nitrogen.   The currents used were 2 and 4 microamp. per electrode (*i.e.*, the current densities were $8\cdot7 \times 10^{-8}$ and $1\cdot74 \times 10^{-7}$ A/sq. cm.).   In each measurement the mercury was first made cathodic to ensure the reduction of any oxide already present on the surface of the electrode (*idem, ibid.*).   The current was then reversed and the potential of the anode was recorded with the help of a valve voltmeter (Electronic Instruments, England).

During the first minute from the moment of reversing the current to start the anodic pulse, the potential of the mercury electrode changed very rapidly from the very negative value (hydrogen evolution) towards the positive anodic value.   The changes in potential during this minute, which are largely due to the decay of the hydrogen over-voltage, were neglected, and the potentials were recorded only during the build-up of the anodic double layer before oxide formation (El Wakkad, *et al.*, *locc. cit.*).

The reference half-cell was a saturated calomel electrode prepared according to Harned and Owen ("The Physical Chemistry of Electrolytic Solutions," 1943, p. 32).   All experiments were carried out at room temperature, 25° ±1°.

The Cathode-ray Oscillographic Method.—The circuit used was on the same principle as that used by Hickling (*Trans. Faraday Soc.*, 1945, **41**, 333; 1946, **42**, 518; see also Hickling and Spice, *ibid.*, 1947, **43**, 762; Hickling and Taylor, *Discuss. Faraday Soc.*, 1947, **1**, 277; *Trans. Faraday Soc.*, 1948, **44**, 762; El Wakkad and Hickling, *ibid.*, 1950, **46**, 820; El Wakkad and Salem, *J. Phys. Chem.*, 1952, **56**, 621; El Wakkad and Hickling, *ibid.*, 1953, **57**, 203); it records the variation of potential with the quantity of electricity passed.   A slight modification was necessary to make the circuit suitable for the present study : the cathode follower circuit was employed to transfer the voltage across the series of condensers to the X deflection plates of the cathode-ray tube without taking any current from the condenser.   The grid anodic voltage was decreased from 360 to 240 v, and thus the sensitivity was increased.   The single-sweep technique was adopted to get the necessary charging curves.   The electrolytic cell used was similar to that employed in the direct potentiometric method, but the mercury anode was of 0·60 sq. cm. area.   The cathode was a platinum spiral of approximately 0·5 sq. cm. in area.   Observations were made in an atmosphere of pure nitrogen in 0·1M-sodium hydroxide.   In each experiment the mercury electrode was first polarised cathodically for ∼20 sec., the current was then switched off for ∼30 sec., and the anodic polarisation was started.   Two polarising currents were used, *viz.*, 15 and 45 μA per electrode.   The capacity of the condenser in the circuit was 2 μF.   All experiments were carried out at room temperature, 25° ±1°.

A specimen from the results obtained is shown as an oscillogram (Fig. 1, reproduced from a photograph) in which the ordinate represents potentials and the abscissæ are proportional to

the quantity of electricity passed. Suitable horizontal reference lines at intervals of 0·25 v were photographed immediately after the polarisation track so that significant potential can be read directly from the oscillograms. The quantity of electricity passed at any stage in the polaris-ation is obtained from the known capacity of the condenser used (which was 2 μF) in the circuit and the horizontal displacement, which is governed by the voltage to which the condenser is charged. Suitable vertical lines at intervals of 10-volt are shown to enable the quantity of electricity passed during the polarisation process to be calculated.
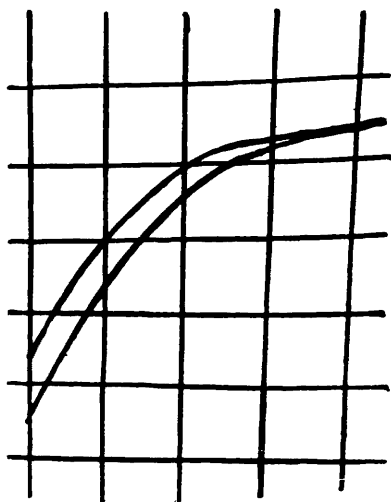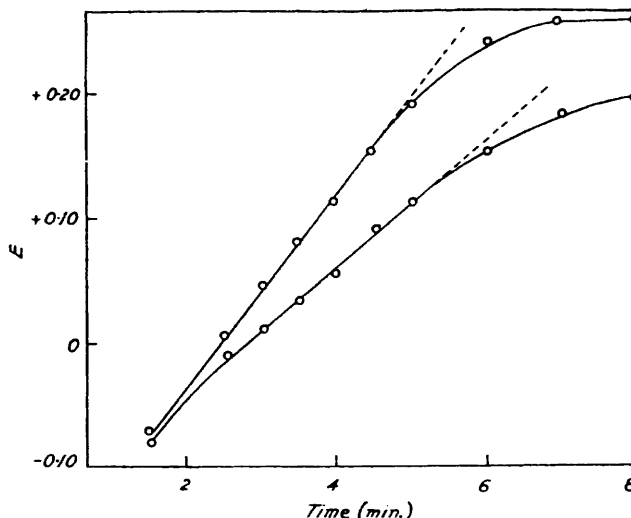

FIG. 1.

FIG 2.

RESULTS AND DISCUSSION

In Fig. 2, the lower curve is the characteristic charging curve (obtained by the direct potentiometric method) of the mercury anode with a polarising current density of $8·7 \times 10^{-8}$ A/sq. cm. in 0·1M-sodium hydroxide. The upper curve is obtained with a polarising current density of $1·74 \times 10^{-7}$ A/sq. cm. in the same solution. From the slopes of the two curves showing the change in potential as a function of the quantity of electricity passed, the capacity is found to be $c = 105$ and 127 μF per sq. cm. with polarising currents of $8·7 \times 10^{-8}$ and $1·74 \times 10^{-7}$ A per sq. cm., respectively.

Fig. 1 gives the characteristic charging curves obtained with the cathode-ray oscillo-graphy in 0·1M-sodium hydroxide with polarising currents of 15 and 45 μA/sq. cm. and a con-denser of 2 μF. From the known capacity of the condenser in the circuit, *viz.*, 2 μF, and the horizontal displacement which is governed by the voltage to which the condenser is charged as shown by the vertical lines at intervals of 10 v, the quantity of electricity passed in the linear part of the curve of Fig. 1 for 0·25 v change in the potential of our mercury anode was found to be 14·7 μ coulomb with a polarising current of 45 μA. This gives a capacity of 98 μF/sq. cm. For a polarising current of 15 μA the results also give a capacity of 98 μF/sq. cm. In the Table are shown the results obtained for the capacity of the double layer on the mercury anode as obtained by the direct potentiometric method and with the cathode-ray oscillograph.

Method	Polarising c.d., A	Capacity of double layer, μF/sq. cm.
Direct	$8·7 \times 10^{-8}$	105
,,	$1·74 \times 10^{-7}$	127
Cathode-ray oscillograph	$2·5 \times 10^{-5}$	98
,, ,,	$7·5 \times 10^{-5}$	98
		Mean 107

From these results it is clear that the value taken by El Wakked *et al.* (*locc. cit.*), *viz.*, 100 μF, for the capacity of the anodic double layer from the correlation between their work and that of Hickling is reasonable.

The value of the capacity of the anodic double layer can also be obtained theoretically as follows : We can regard the double layer formed during the polarisation of an anode to be simply of Helmholtz type. The capacity per unit area is given by

$$c = D/4\pi d \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where D is the dielectric constant of the medium between the layers and d is the distance between them. According to such a picture the anodic double layer will consist of a layer of hydrated OH^- ions on one side, the other side of the condenser being the layer of the metal ions at the surface of the anode; then if we know the radii of the hydrated OH^- and the metal ions and the dielectric constant of the medium, the capacity of the double layer can be obtained.

The volume of the hydrated OH^- ion was given by Bernal and Fowler (*J. Chem. Physics,* 1933, **1**, 515; *Trans. Faraday Soc.,* 1933, **29**, 1049) as 30 Å³. If such an ion is supposed to be a sphere, its radius will be about 3×10^{-8} cm. The radius of the metal ions can be taken to be between 1×10^{-8} and 2×10^{-8} cm. with a mean value of 1.5×10^{-8} cm. Now, Agar and Liopis (*Anales Fis. Quím.,* 1947, **43**, 1087), utilizing Stern's theory, assumed that the value of the dielectric constant of the medium which appears in the Debye term could be taken as that of water in the bulk. Webb (*J. Amer. Chem. Soc.,* 1926, **48**, 2589) has shown, by applying the Langevin–Debye theory (*J. Physique,* 1905, **4**, 648; Marx, " Handbuch der Radiologie," Leipzig, 1925, **6**, 618, 680), that owing to the orientation and inductive polarisation effects, the effective dielectric constant of water in an electric field of high intensity is lower than its macroscopic value. Similar effects are operative in the double layer at a charged interface, and accordingly use of the macroscopic dielectric constant in Stern's theory is invalid. Conway, Bockris, and Ammar (*Trans. Faraday Soc.,* 1951, **47**, 756) calculated the dielectric constant in the diffuse and Helmholtz double layers at a charged interface in aqueous solutions. They assumed that the aqueous medium could be treated as a continuous dielectric. For the purpose of the calculation for aqueous acid solutions, they considered that the thickness of the Helmholtz layer would approximate to the radius of the hydroxonium ion, *i.e.*, about 1.55 Å.

According to Grahame (*Chem. Rev.,* 1947, **41**, 441), hydration in the Helmholtz layer is unlikely to be greater than the primary solvating water molecule in the case of the proton; since, moreover, the dielectric constant at the outer plane of the Helmholtz double layer was found to vary between 8.15 and 23 for the cathodic double layer, where one side of the double layer was mainly formed by hydroxonium ions, one is bound to consider the Helmholtz anodic layer as formed of OH^- ions hydrated with one hydration sheath.

The radius of the hydrated OH^- ion was shown before to be 3×10^{-8} cm. The value of the dielectric constant at the outer plane of the Helmholtz double layer as obtained from the calculations of Conway, Bockris, and Ammar (*loc. cit.*) lies between 34 and 38. Substituting these values in equation (1), we obtain for the capacity of the anodic double layer values lying between 100.2 and 111.9 µF per sq. cm., in good agreement with the value found experimentally.

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