REDUCTION PROCESSES AT THE DROPPING MERCURY ELECTRODE IN PULSATING FIELDS : THE NICKEL ION

BY K. S. G. DOSS, F.A.SC. AND A. KALYANASUNDARAM

(*Indian Institute of Sugar Technology, Kanpur*)

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INTRODUCTION

BREYER AND GUTMAN[1] have evolved a new and interesting technique for studying the electrode kinetics of the reversible depolarising processes taking place at a dropping mercury electrode by superimposing an alternating field. Systems involving the discharge of cadmium, thallium and zinc ions have been studied by them with an alternating field of 50 cycles per second. The discharge of lead ions has been studied by a similar technique by Doss and Agarwal[2] using the oscillograph for measuring the alternating current. They have extended the study to different frequencies of the field ranging from 12·5 to 600 cycles per second. The present paper reports the work on the discharge of nickel ions studied by a modified technique.

EXPERIMENTAL

The circuit diagram is given in Fig. 1. The source of alternating current is a B.S.R. oscillator capable of giving frequencies ranging from 0–16,000 cycles per second. 10 Volts from the oscillator is fed on to a potentiometric arrangement ACDB consisting of the resistances R_1, R_2 and R_3. This arrangement serves to give 45 mv. across R_2 which is superimposed on the dropping electrode along with a D.C. voltage obtained from a Cambridge pH potentiometer (with the galvanometer shorted off) used as a potential divider. The voltage output of the potentiometer across YZ can be varied at will, the resistance R_4 being 225 ohms per volt of D.C. voltage.

When the pulsating (A.C. superimposed on D.C.) potential is incident on the dropping electrode, a pulsating current is produced. Our present interest is to measure the A.C. component of the pulsating current. For measuring this, the arrangement used is as follows:—A valve amplifier system (Fig. 1) working on the non-linear portion of the characteristic curves of the valves, partially rectifies and amplifies any incident alternating potential. This amplified current is incident on a Leeds and Northrup galvanometer (period: 14·5 sec.; resistance: 1,182 ohms; shunt: 99 ohms). The tapping key K connects the amplifier system to the potential drop across R_3 in the rest position P, and to that across R_5 when the key is depressed to the position P_2. First, the resistance R_3 is reduced to zero, thereby making the input to the amplifier system zero. The current passing through the galvanometer under these conditions is compensated by the potentiometer. Then the resistance R_3 is increased to 3 ohms, thereby making the input to the

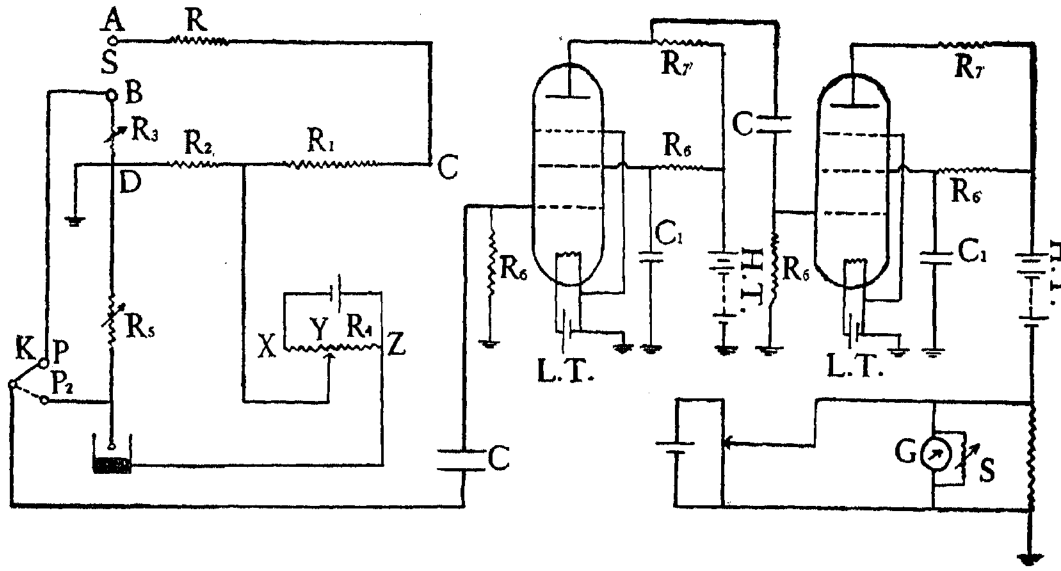

FIG. 1

$R = 600\,\Omega$
$R_1 = 13{,}000\,\Omega$
$R_2 = 58\,\Omega$
$R_3 = 0{\cdot}3\,\Omega$
$R_4 = 225\,\Omega$ per volt of D.C.
$R_5 = 0-2{,}500\,\Omega$ (according to the current)

$C = 0{\cdot}25\,\mu F$
$C_1 = 0{\cdot}1\,\mu F$
L.T. $= 1{\cdot}5$ V
H.T. $= 45$ V
$S = 99\,\Omega$
$R_6 = 5\,M\Omega$
$R_7 = 1\,M\Omega$

amplifier equal to 2·3 mv. The galvanometer gets deflected. The reading on the galvanometer scale is noted. Any current passing through the dropping electrode passes through the resistance R_5. The potential drop thus obtained across R_5 is applied to the amplifier system by depressing the tapping key to the position P_2. In this position R_5 is adjusted so as to give the same deflection of the galvanometer as was obtained for a potential of 2·3 mv. (*i.e.*, in the position P, of the tapping key). By knowing the value of the resistance R_5, the current can be calculated. The condenser serves to filter off the D.C. component of the pulsating current.

This arrangement for measuring the current has the following advantages: (1) The measurement is not affected by any changes with time in the characteristics of the amplifying system. (2) It is also unaffected by the variation of the characteristics of the amplifier with the change in frequency of the A.C.

The dropping electrode has the following characteristics:

m: 0·69 mg./sec.

t : 5·3 sec. in 0·1 M — KCl_{aq}. in open circuit.

The experiment is first performed with IM KCl containing no other dischargeable ions. Hydrogen, obtained from a Kipp after purification by passing through mercuric chloride, lead acetate and distilled water is passed in the solution for 15 minutes to remove traces of oxygen. The A.C. passing through the dropping electrode at the different D.C. potentials are measured as explained above and the results are represented in Fig. 2. The experiments are carried out at different frequencies of the A.C.

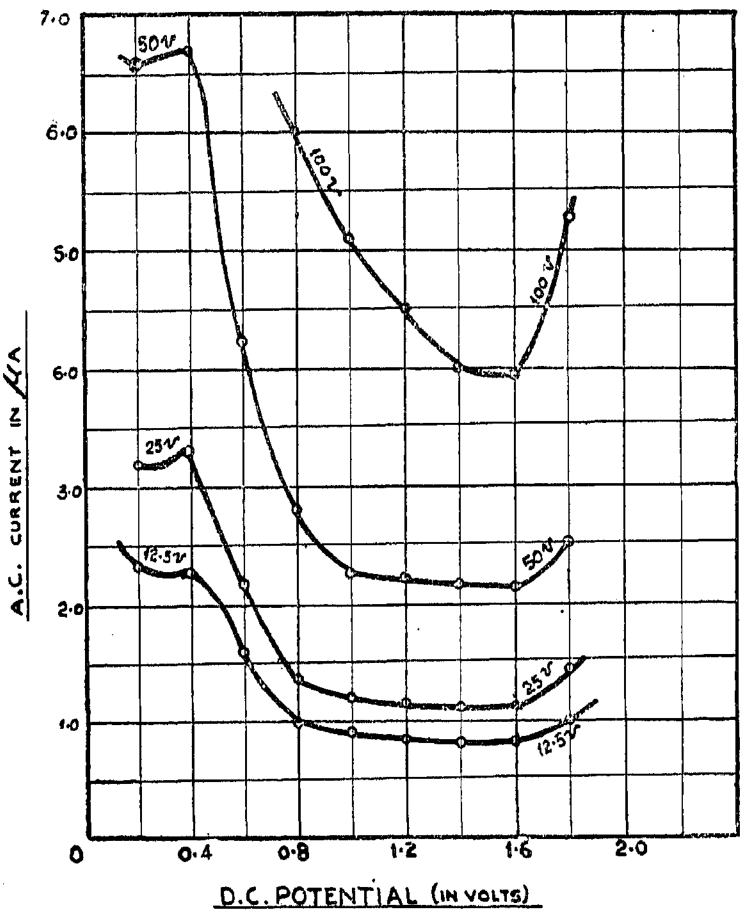

FIG. 2

The experiment is repeated with IM KCl containing $3 \cdot 27 \times 10^{-3}$ M nickel ions (in the form of nickel chloride) and the results are represented in Fig. 3.

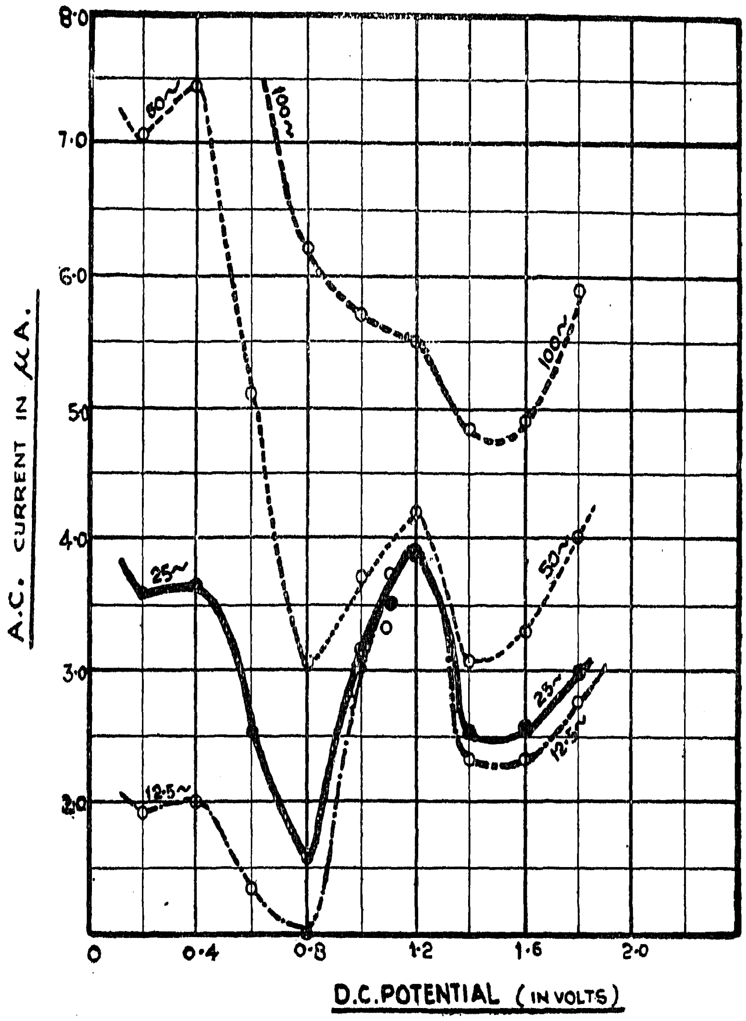

FIG. 3

Fig. 4 represents the polarographic curve of nickel obtained with the same dropping electrode.

DISCUSSION

Our results confirm in general the observation made by Breyer and Gutman[1] that a maximum in the alternating current occurs nearly at the half-wave potential of the system in question. Fig. 4 shows the polarographic curve from which the half-wave potential comes out to be at about 1·1 volt. The alternating current maximum from Fig. 3, comes out to 1·2 volt, which is nearly the half-wave potential. The D.C. potential at which the a.c. maximum occurs is independent of the frequency of the a.c. field. This is in agreement with the observation made by Doss and Agarwal (*loc. cit.*). There is one important difference, however, between these curves and the curve obtained by Doss and Agarwal. Whereas the value for the alternating current at the maximum in their system was nearly independent of the frequency, with nickel it is found that there is a large stepping up of the a.c. current as the frequency is changed from 50 to 100 cycles per second. This difference in behaviour can be explained as follows:

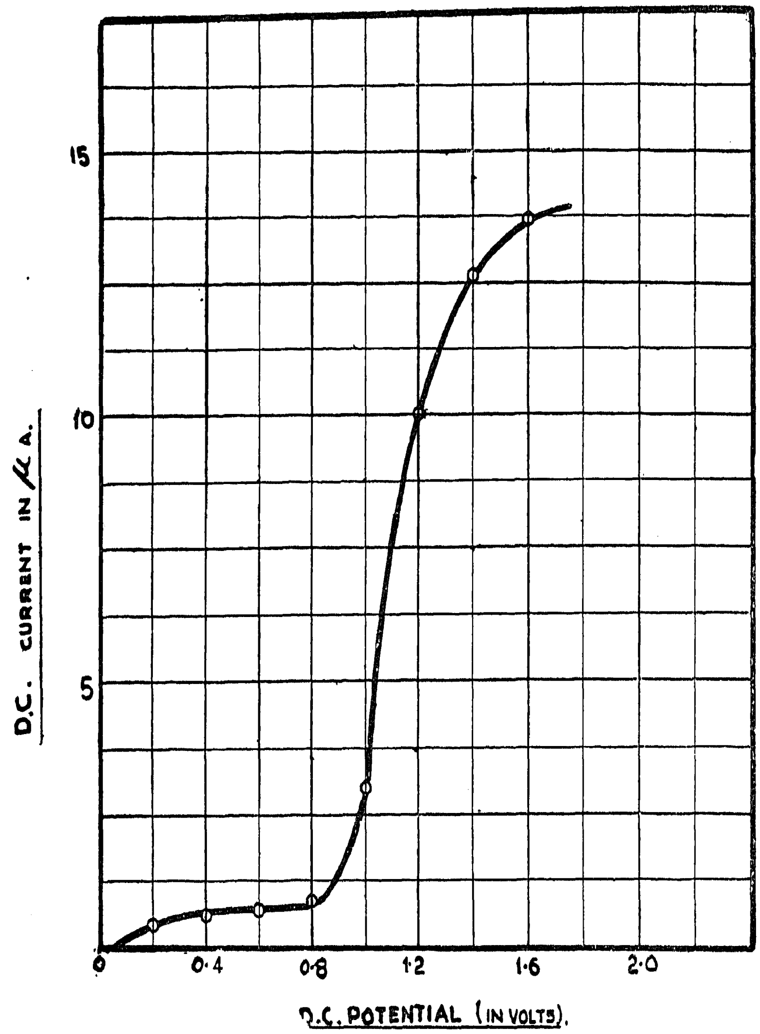

FIG. 4. *Polarographic current : Nickel*

The dropping mercury electrode in contact with the solution of the electrolyte presents an electric double layer which behaves like a capacity in absence of any reducing ions. The increase in the a.c. current with increase in frequency (Fig. 2) is due to the diminution of the capacitative impedance. The effect of the presence of the reducible ions is equivalent to shorting the electric double layer capacity by a resistance, or more generally by an impedance consisting of a resistance and a capacity in parallel the value of which decreases with the increase in the intensity of the discharge of the reducible ions. The effect of this is to reduce the overall capacitative impedance. At the half-wave potential of the reducible ions the discharge is maximum and hence there is a maximum in the alternating current. It appears that in the system dealt with by Doss and Agarwal, this maximum capacitative impedance becomes a very small fraction of the total impedance of the system so that the change of frequency has no marked effect on the overall impedance of the system at the a.c. maximum. With the system dealt with in this paper, however, the minimum capacitative impedance is yet comparable with the total impedance of the system and hence an increase in the frequency has a marked effect on the value of the a.c. current at the half-wave potential.

Breyer and Gutman have worked out a quantitative theory to explain the form of the curves. One of the assumptions that they have started is that the alternating current at any instant would be equal to the polarographic current corresponding to the potential incident on the electrode at that instant. We have worked out the theoretical curve relating the a.c. current with the d.c. voltage on the basis of the above assumption alone. This is shown in Fig. 5 (Curve I). The experimentally observed curve (Curve II) is given in the same figure for comparison. The above assumption of Breyer

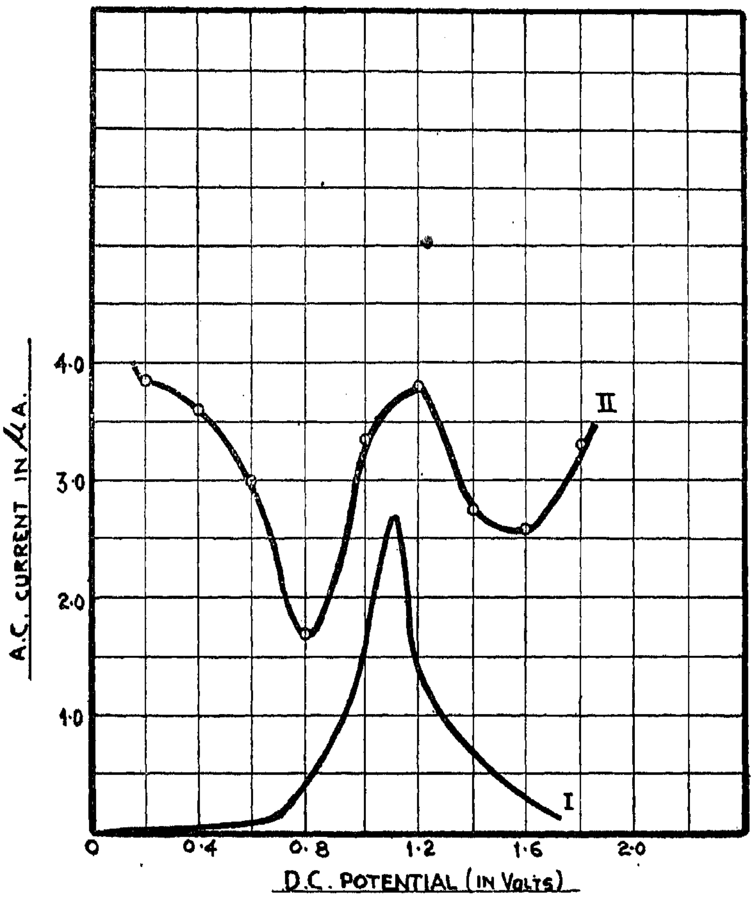

FIG. 5. *I. Theoretical Curve.* *II. Experimental Curve.*

and Gutman approaches nearest to the experiment at near the half-wave potential for this system at the frequencies of 12·5 and 25 cycles per second. At other frequencies and potentials, however, there are large deviations, the experimental values being much higher than the theoretical values. This divergence is to be traced to the fact that the measured polarographic current is an average figure whereas the a.c. current is caused by the comparatively instantaneous changes in the current when the potentials are altered quickly.

A quantitative treatment of the observed phenomena appears to be possible only after more detailed and extensive experimental data on such systems become available.

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Summary

A method has been described for measuring small alternating currents. This has been applied for studying the a.c. currents induced in a dropping mercury electrode system containing nickel ions when subjected to a pulsating field at different frequencies of the field. This system has revealed interesting features which are different from the systems investigated by the previous workers.

References

1. Breyer and Gutman .. *Faraday Soc. Discussion*, 1947, No. 1, 19.
2. Doss and Agarwal .. *Proc. Ind. Acad. Sci.*, 1951, 33, 66.