Polarography

V Lakshminarayanan

J Heyrovsky's invention of polarography in which a dropping mercury electrode is used in the electrochemical cell revolutionised electroanalysis, study of electrode kinetics and adsorption studies on mercury electrodes. Polarography has also directly contributed to the development of new and innovative ideas in electrochemical techniques, instrumentation and applications.

For many of us who were introduced to research in electrochemistry in the mid 1970s, polarography represented quintessential electrochemistry. The use of the brilliantly shining and pure liquid metal, mercury, an unlikely candidate for an electrode material ushered in a new era in electrochemistry during the last century. At a time when the solid electrode materials were dogged by the problems of irreproducibility due to surface heterogeneity and impurity, mercury, which is largely free from such malaise, became a new benchmark to study many fundamental electrochemical processes quite accurately and with great precision. While the electrochemical technique of polarography had been dominating the electroanalytical scenario for several decades since its discovery by J Heyrovsky in the 1920s, the impact of this technique in electrochemistry extended far beyond the routine electroanalysis. With the discovery of this technique the face of electrochemistry, which was mostly referred to in the context of ionic equilibria, Debye-Huckel theory and solution electrochemistry in general, started changing. Polarography extended its influence in the study of such diverse phenomena as electrocatalysis, electrochemical energy sources, batteries, fuel cells, biological processes such as ion transport across membranes, solar cells, etc. The technique had a major impact in the study of the mechanism of electrode reactions and consequent theoretical developments of electrode processes such

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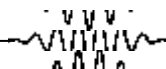
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as studies of electrolytic diffusion processes and other transport phenomena.

Modern polarography is quite a sensitive and relatively rapid analytical technique. It has the capability to provide information on several parameters of interest to electrochemists in several areas including inorganic, organic and pharmaceutical chemistry research. Polarography has gone long past the era of old galvanometers and the X-Y recorders. Instead, with the development of modern electronic instrumentation and PC control, it has acquired the ability to study new and interesting processes occurring at the metal –solution interface.

What is Polarography ?

In polarography, the electric potential (i.e. voltage) of a growing mercury drop in an electrolyte containing an electroactive species is varied as a function of time and the resulting current due to the electrochemical reaction is measured. The technical elegance of this method is derived from several special properties of mercury as an electrode material. The fact that mercury is a liquid metal provides several advantages such as excellent renewability and reproducibility of the surface. This metal has also a wide potential range of operation in aqueous solution due to its large hydrogen overpotential. For example, relative to the platinum electrode, the hydrogen evolution on mercury occurs at about −1.0V within the range of which many metal ions are reduced on the surface. Mercury can be easily purified as it is a liquid with an atomically smooth surface. The shape of a polarogram depends on the method and the type of periodic potential that is applied. For example, in simple DC polarography, the potential applied is a linearly varying voltage called *ramp* and the resulting current response is sigmoidal in shape as shown in *Figure* 1. This figure also shows a few selected methods of polarography where different periodic wave forms are applied to the mercury cathode. The resulting current response in each of the cases has been derived and can be related to the concentration of the species.
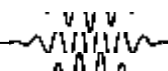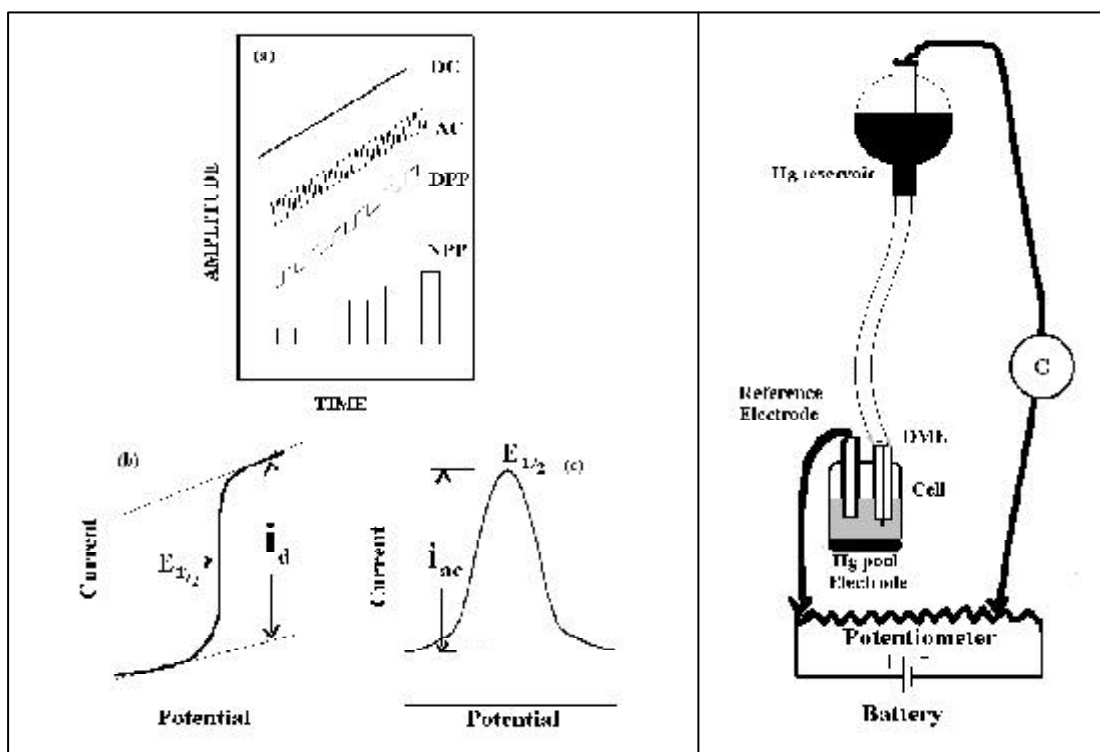
Figure 1 (left). (a) Input wave forms applied in different polarographic techniques. DC – In the conventional DC polarography the voltage ramp is applied to sweep the range of DC potential to reduce (or oxidise) the species of interest. AC – In the ac polarography , a small amplitude, typically 10-20 mV ac is superimposed over the DC potential sweep. DPP – In the differential pulse polarography (DPP), the pulses of fixed amplitude modulate the DC voltage sweep. NPP – In the normal pulse polarography (NPP), the pulse amplitude is successively increased from the same base DC potential; (b) A typical sigmoidal shape of DC polarogram. $E_{1/2}$ is the half wave potential. The NPP has a similar shape; (c) A typical ac polarogram. The DPP has a similar shape.

Figure 2 (right) A schematic diagram of a polarograph illustrating dropping mercury electrode. In the modern polarographs the potential control unit, signal conditioning and measurement systems are software controlled through a PC. DME – Dropping mercury electrode, G – Galvanometer.

The Polarographic Cell

A schematic diagram of a polarographic cell and electrode arrangement is shown in *Figure* 2. The mercury drop, which is normally a cathode of the polarographic cell flows from a glass capillary tube, which is attached to a reservoir of mercury. The
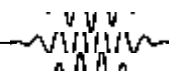
The limiting current arises essentially because the diffusion process has now attained a steady state, since the concentration of the diffusing electro-active species is almost zero near the electrode surface producing a maximum concentration gradient.

counter electrode, which is a pool of mercury into which the drop falls, acts as an anode. In the original polarograph, the cell is connected in series with a galvanometer (for measuring the flow of current) in an electrical circuit that also contains a battery or other source of direct current and a device for varying the voltage. The electroactive species which is being studied, is present in a highly conducting electrolytic medium. The concentration of this electrolyte is about 100 times higher and is electroinactive in the sense that it will not undergo charge transfer reaction on the electrode surface. Hence it is called a *supporting* or *indifferent* electrolyte. The need for such a medium is to let the majority current due to applied electric field called *migration current* be carried by the ions of the supporting electrolyte. This will allow the species of interest to follow diffusional transport towards the electrode surface as described below.

Polarographic Measurements

As the voltage is varied in small increments, the corresponding current is noted on the galvanometer. The measured current is quite small until the applied voltage reaches a critical value, which is specific for the species to be reduced at the dropping mercury electrode. The current then increases rapidly in the beginning with the applied voltage, attains a critical value and then reaches a limiting value that remains more or less constant with further increase in voltage. The plateau current I_d is called *the limiting diffusion current* and the applied potential at which this current is half its value ($I_d/2$) is known as *half wave potential* ($E_{1/2}$). This potential is independent of concentration but is characteristic of the electroactive species. The limiting current arises essentially because the diffusion process has now attained a steady state, since the concentration of the diffusing electroactive species is almost zero near the electrode surface producing a maximum concentration gradient. In practice the diffusion current is measured from a baseline which is obtained by extrapolating a small residual current flowing prior to the wave. This residual current arises from the capacitive or double layer charging current and also from trace electroactive impurities.
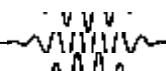
Reduction and Oxidation (Redox) Processes

The electroactive species which normally undergoes reduction forms an amalgam with the metal and the reaction can be depicted as:

$$M^{+n} + n\,e^- \leftrightarrow M\,(Hg). \tag{1}$$
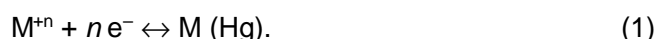
where M represents the electroactive species and M(Hg), the amalgam. The limiting diffusion current is determined by the rate of diffusion of the reducible substance on the surface of the mercury drop. This is represented by the famous Ilkovic equation:

$$I_d = 0.732\, nFCD^{1/2}m^{2/3}\, t^{1/6}, \tag{2}$$

where I_d is the limiting diffusion current, n is the number of electrons involved in the charge transfer process, F is the Faraday in coulombs, C the concentration of electroactive species in the bulk solution (mol cm^{-3}), D the diffusion coefficient cm^{2}sec^{-1}, m the mass flow rate of mercury in g sec^{-1} and t is the drop time in sec. The original Ilkovic equation above considers the linear diffusion of electroactive species to the electrode surface. More rigorous equations, for example, using spherical diffusion of the electroactive species have been derived. What is however more important is the linearity of the limiting current with concentration over a wide range, which is the corner stone of the polarographic method of analysis. For several decades, the polarographic technique as an analytical tool has been competing with and sometimes complementing the spectrochemical techniques in terms of its capabilities for trace analytical determination. As far as the detection range is concerned, the technique provides a linear response for over 6 decades of concentration and a detection limit of a few parts per trillion (ppt) (10^{-12} g/ml) has been realised relatively easily.

The dropping mercury electrode (DME) can also function as an anode and in this case the oxidation of certain oxidizable substances can be studied. When the solution under analysis

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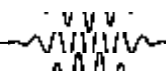
There is another class of sharply defined peaks or humps originating due to vigorous stirring of the solution near the mercury drop surface which is known as *polarographic maxima*, a phenomenon explained by an eminent Russian scientist Frumkin and his coworkers using electrocapillary effect.

contains several electroactive species, which can be reduced or oxidized at different voltages, the current-voltage curve shows several segments of S-shaped curves called polarographic waves. Though a normal DC polarogram has a sigmoidal shape, it is possible to infer from the slope of the rising portion of the curve, the relative effects of diffusion and charge transfer processes which control the electrode reaction .

Applications of Polarography

The majority of the chemical elements can be identified by polarographic analysis, and the method is also applicable to the analysis of alloys and various inorganic compounds. In addition, polarography is useful in identifying numerous types of organic compounds and in the study of chemical equilibria and the rates of reactions in solutions. The measurement of polarographic current provides a simple method for the estimation of the rate of several fast electrode reactions. The technique has contributed substantially to the study of adsorption of several surface-active molecules on a mercury surface. This method, referred to as *tensammetry,* developed by Breyer and coworkers involves the measurement of double layer capacitance of mercury–surfactant system in an electrolyte. The capacitance is strongly influenced by the presence of adsorbed species. Hence the adsorption–desorption processes produce quite pronounced and sharp peaks in the polarographic wave which can be ascribed to the presence of surface active substances even if they are not electroactive. There is another class of sharply defined peaks or humps originating due to vigorous stirring of the solution near the mercury drop surface which is known as *polarographic maxima*, a phenomenon explained by an eminent Russian scientist Frumkin and his coworkers using electrocapillary effect.

There had been several outstanding students of Heyrovsky who contributed greatly to the growth of polarography in the initial years. For example, Rudolf Brdicka, the most famous student of J Heyrovský studied extensively the biomedical applications of polarography. He carried out polarographic investigations of
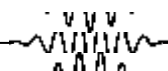
several proteins, hemes, and serum colloids. He showed the utility of polarographic techniques for the measurement of reaction rates. Peter Zuman studied mechanisms of organic reactions using polarographic measurements. These studies involved biologically important compounds that helped the development of analytical methods and a better understanding of biological activity. J Koutecky laid firm theoretical foundation notably working on the problem of polarographic kinetic current with the necessary mathematical formulation. A Sevcik and Robert Kalvoda worked on what is known as *oscillographic polarography* which finds special mention in Heyrovsky's Nobel lecture as this had further extended the technique by introducing the oscilloscope recording of the polarogram and helped to study fast electrode reactions.

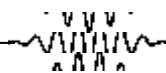## Faradaic Current and Double Layer Charging (Capacitive) Current

The total measured current in polarography consists of two major components viz., the faradaic current due to the electrochemical reaction and the charging current. This charging curent flows to charge the electrode-solution interfacial capacitor in response to the applied potential as well as to the area change. The charging current has the characteristic that it decays faster than the faradaic component, besides attaining almost zero value at the end of the drop. To study the faradaic process and to deduce reaction mechanism or for analytical purposes, it is necessary to eliminate or compensate for the double layer charging current. As the double layer charging current arises in polarography essentially due to the changing area of the electrode with the growth of the drop, and also the changing potential with time, it can be represented as

$$I_{ch} = A(E - E_z)\ (dC_{dl}/dE)\ (dE/dt) +\ C_{dl}\ A\ (dE/dt) +$$

$$(E - E_z)\ C_{dl}\ (dA/dt)\,, \tag{3}$$

where I_{ch} is the double layer charging current, A the area of the growing drop, C_{dl} the double layer capacitance, E the applied

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potential and E_z the potential of zero charge of the mercury electrode in the particular electrolytic medium. In order to reduce the double layer charging current in dc polarography, the first and second terms can be made small by slow sweep rates. Since the rate of growth of the drop is least at the end of the drop life, the term containing the area change with time may be reduced by electronically sampling the current at the end of the drop life.

The problem of improving the ratio of faradaic current to double layer charging current provided the necessary challenge needed for the advances in the technique and instrumentation pioneered by G C Barker. In a way it can be said that Barker laid the foundation for the second generation polarography. He invented the ac superimposed dc technique to correct for the double layer charging current. The square wave and pulse polarographic techniques developed by him have inherent merit in improving the faradaic to charging current ratio. These methods also provided the necessary foundation for the development of later theoretical concepts in transient electrochemical studies. In India, by some astute mathematical approach and innovative electronic design, S R Rajagopalan, S K Rangarajan and A Poojary at the National Aerospace Laboratrory, Bangalore extended these techniques to greater heights in terms of achievable analytical detection limit.

Polarography and the Development of Electro-chemical Instrumentation

It is no exaggeration to say that the popularity of polarography in the latter half of the 20th century has greatly helped in the development of electrochemical instrumentation. The advent of operational amplifiers have revolutionised the study of electrode processes and directly contributed to the growth of new electrochemical techniques. The fact that the polarography accommodates different techniques such as DC, AC and Pulse techniques have all created a need for the development of potential controlling devices with different capabilities. This
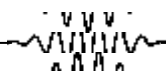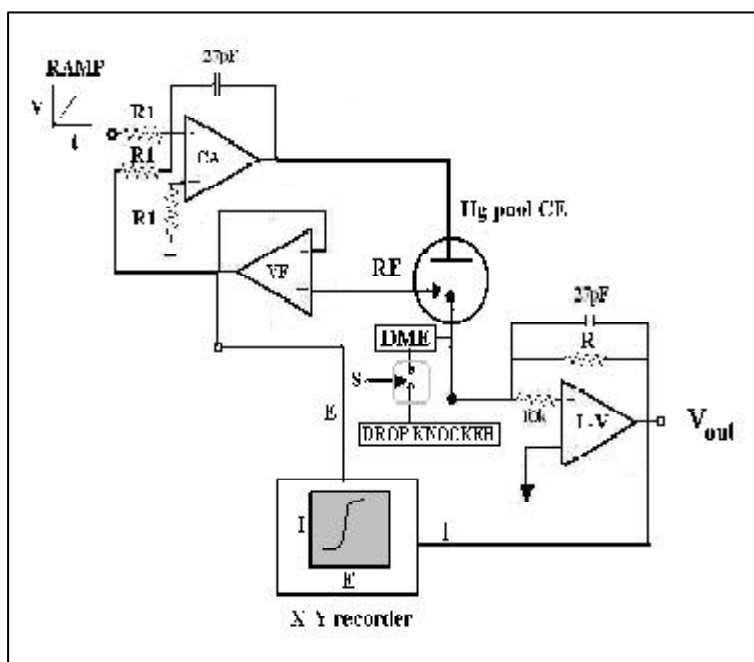
Figure 3. Block diagram of a control and measurement circuit of a polarograph. CA – control amplifier of the potentiostat (potential controlling unit); VF – voltage follower; I-V – current to voltage converter or current amplifier; S – switch which controls the mercury drop time; CE – Counter electrode; RE – Reference electrode; DME – Dropping mercury electrode; R1 – Equal and exactly matched resistors; R – current amplifier feedback resistance which determines the voltage output ($V_{out} = I_{cell} R$).

includes the development of fast potentiostats, high precision op-amp current followers and signal processing and signal conditioning devices. The need for separation of double layer charging current from faradaic current due to electrochemical process means the need for special techniques and designs that can carry out these processes effectively .

Figure 3 shows a schematic block diagram of a typical op-amp polarograph circuit .in which the control amplifier (CA) and voltage follower (VF) constitute a simple potential control circuitry called *potentiostat*. The slowly varying dc voltage (a ramp) is applied to the control amplifier op-amp. The voltage follower whose input is derived from the reference electrode of the cell which acts as a negative feedback element of the amplifier circuitry. Thus the potential at the reference electrode is maintained at the same value as that of the input voltage. The current is converted to voltage using a current amplifier, which is also known as current – voltage converter (I-V). The current and voltage values are recorded on an X–Y recorder. The periodic fall of drops is regulated by means of a drop knocker which

is controlled by an electronic switch. This is a simple description of the basic essentials of a polarograph.

Further Developments

From the original dc polarograph described above were born several other related techniques based on ac and pulse techniques mostly developed by G C Barker. These techniques later laid the foundation for some outstanding contributions by several other workers such as D E Smith, J H Sluyters, W H Reinmuth, R A Osteryoung and A M Bond. In ac polarography, a small amplitude ac voltage is superimposed over a slowly varying ramp and applied to the DME and the ac component of the cell current is measured as a function of the dc potential. The advantage of the technique is that it provides a simple means of separation of double layer charging current from the total reaction current and the method has a well-developed theory which is capable of providing kinetic information. In the pulse techniques, the total current response is sampled after a lapse of a certain time from the application of the pulse when the charging current has decayed fully as in *Figure* 4. These techniques contributed substantially to our understanding of the electrode processes and development of theoretical electrochemistry that has become an essential component of studying mechanisms of electrode reactions.

Suggested Reading

[1] A M Bond, *Modern Polarographic Methods in Analytical Chemistry*, Marcel Dekker, New York (1980).
[2] A J Bard and L R Faulkner, *Electrochemical Methods, Fundamentals and Applications*, John Wiley & Sons, New York, Second edition, (2001).
[3] L I Antropov, *Theoretical Electrochemisty*, Mir Publishers, Moscow (1972).

Influence of Polarography in Electrochemical Studies

The question often posed is whether polarography has already seen the glorious days and whether its perceived decline is irreversible. It is true that the utility of polarography as an analytical tool in recent times is declining. This is true even of other electroanalytical techniques as methods of choice for chemical analysis. This is mostly due to advances in spectroscopic techniques. However, the contribution of polarography is not limited to electoanalysis alone nor is it limited to mercury as electrode material. The increasingly popular voltammetric
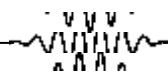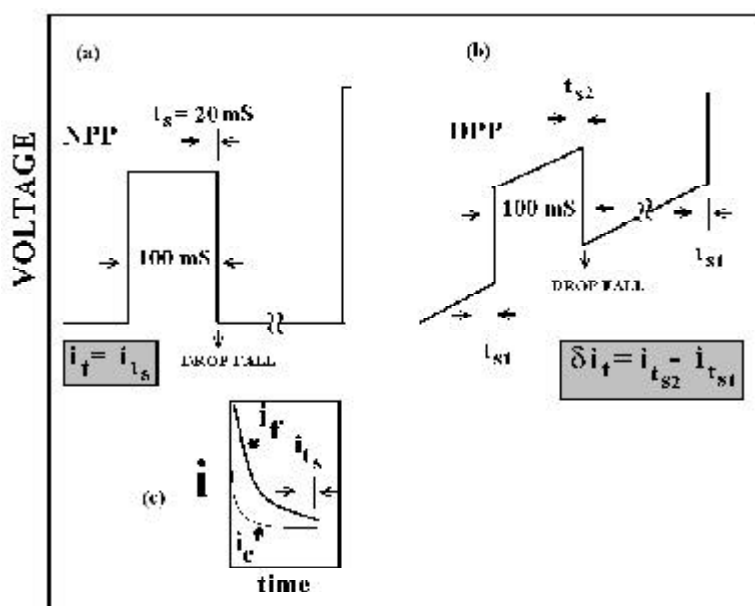
Figure 4. Schematic of pulse programme and sampling of current in NPP and DPP. (a) In the normal pulse polarogram the current is sampled at the end of the drop life (I_{ts}) at which point the charging current has decayed fully and there is measurable faradaic current. (b) In the DPP the current is first sampled just prior to the application of the pulse (I_{ts1}) and subsequently just before the drop fall (I_{ts2}) and the difference in current is measured and plotted against the potential. (c) The current response showing the decay of faradaic (I_f) and charging current (I_c) in the pulse polarography. The figure shows schematically the relative rates of decay of charging current and faradaic current responses. The current that is sampled is the total current which is the sum of the two currents (I_c anf I_f). By sampling at the end of the drop life, the charging current component is minimised.

techniques applied to solid electrodes were all enriched by the polarographic techniques. Thus, ever since its discovery in 1920s, its course had been running parallel to many other areas of electrochemistry and as such it is truly a trail blazing technique.

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