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Polarographic Studies of Nucleic Acids by Dropping Mercury Electrode

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ABSTRACT: Polarography is a type of voltammetry where the working electrode is a dropping mercury electrode (DME) or a static mercury drop electrode (SMDE), which are useful for their wide cathodic ranges and renewable surfaces. It was invented in 1922 by Czech chemist Jaroslav Heyrovský, for which he won the Nobel prize in 1959.[1] The main advantages of mercury as electrode material are as follows: 1) a large voltage window: ca. from +0.2 V to -1.8 V vs reversible hydrogen electrode (RHE). Hg electrode is particularly well-suited for studying electroreduction reactions. 2) very reproducible electrode surface, since mercury is liquid. 3) very easy cleaning of the electrode surface by making a new drop of mercury from a large Hg pool connected by a glass capillary.

Polarography played a major role as an experimental tool in the advancement of both Analytical Chemistry and Electrochemistry until the 1990s (see figure below), when it was supplanted by other methods, that did not require the use of mercury

KEYWORDS: polarography, mercury drop, electrode, electroreduction, analytical chemistry, cathodic

I. INTRODUCTION

Polarography is an electrochemical voltammetric technique, that employs (dropping or static) mercury drop as a working electrode. In its most simple form polarography can be used to determine concentrations of electroactive species in liquids by measuring their mass-transport limiting currents. In such an experiment the potential of the working mercury drop electrode is linearly changed in time, and the electrode current is recorded at a certain time just before the mercury drop dislodges from a glass capillary, where a stream mercury comes from. A plot of the current vs. potential in a polarography experiment shows the current oscillations corresponding to the drops of Hg falling from the capillary. If one connected the maximum current of each drop, a sigmoidal shape would result. The limiting current (the plateau on the sigmoid), called the diffusion-limited current because diffusion is the principal contribution to the flux of electroactive material at this point of the Hg drop life. More advanced varieties of polarography produce peaks (which allow for a better resolution of different chemical species) rather than waves of the classical polarography, as well as improve the detection limits, which is some cases can be as low as 10^-9 M[1]

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Heyrovský's Polarograph

There are limitations in particular for the classical polarography experiment for quantitative analytical measurements. Because the current is continuously measured during the growth of the Hg drop, there is a substantial contribution from capacitive current. As the Hg flows from the capillary end, there is initially a large increase in the surface area. As a consequence, the initial current is dominated by capacitive effects as charging of the rapidly increasing interface occurs. Toward the end of the drop life, there is little change in the surface area which diminishes the contribution of capacitance changes to the total current. At the same time, any redox process which occurs will result in faradaic current that decays approximately as the square root of time (due to the increasing dimensions of the Nernst diffusion layer). The exponential decay of the capacitive current is much more rapid than the decay of the faradaic current; hence, the faradaic current is proportionally larger at the end of the drop life. [2] Unfortunately, this process is complicated by the continuously changing potential that is applied to the working electrode (the Hg drop) throughout the experiment. Because the potential is changing during the drop lifetime (assuming typical experimental parameters of a 2 mV/s scan rate and a 4 s drop time, the potential can change by 8 mV from the beginning to the end of the drop), the charging of the interface (capacitive current) has a continuous contribution to the total current, even at the end of the drop when the surface area is not rapidly changing. As such, the typical signal to noise of a polarographic experiment allows detection limits of only approximately 10^{-5} or 10^{-6} M.[3]

Heyrovský's Polarograph and DME

Dramatically better discrimination against the capacitive current can be obtained using the tast and pulse polarographic techniques. These have been developed with introduction of analog and digital electronic potentiostats. A first major improvement is obtained, if the current is only measured at the end of each drop lifetime (tast polarography. An even greater enhancement has been the introduction of differential pulse polarography. Here, the current is measured before the beginning and before the end of short potential pulses. The latter are superimposed to the linear potential-time-function of the voltammetric scan. Typical amplitudes of these pulses range between 10 and 50 mV, whereas pulse duration is 20 to 50 ms. The difference between both current values is that taken as the analytical signal. This technique results in a 100 to 1000-fold improvement of the detection limit[4], because the capacitive component is effectively subtracted.

II. DISCUSSION

Qualitative information can also be determined from the half-wave potential of the polarogram (the current vs. potential plot in a polarographic experiment). The value of the half-wave potential is related to the standard potential for the redox reaction being studied.

This technique and especially the differential pulse anodic stripping voltammetry (DPASV) method can be used for environmental analysis, and especially for marine study for characterisation of organic matter and metals interactions[5]

The Ilkovic equation is a relation used in polarography relating the diffusion current (I_d) and the concentration of the depolarizer (c), which is the substance reduced or oxidized at the dropping mercury electrode. The Ilkovic equation has the form

where:

Id=KnD1/3mr2/3t1/6C

- k is a constant which includes π and the density of mercury, and with the Faraday constant F has been evaluated at 708 for maximal current and 607 for average current
- D is the diffusion coefficient of the depolarizer in the medium (cm^2/s)
- n is the number of electrons exchanged in the electrode reaction, m is the mass flow rate of Hg through the capillary (mg/s)
- t is the drop lifetime in seconds,
- c is depolarizer concentration in mol/cm^3.

The equation is named after the scientist who derived it, the Slovak chemist Dionýz Ilkovič (1907–1980).[6]

A liquid metal electrode is an electrode that uses a liquid metal, such as mercury, Galinstan, and NaK. They can be used in electrocapillarity, voltammetry, and impedance measurements.[1] The dropping mercury electrode (DME) is a working electrode made of mercury and used in polarography. Experiments run with mercury electrodes are referred to as forms of polarography even if the experiments are identical or very similar to a corresponding voltammetry experiment which uses solid working electrodes. Like other working electrodes these electrodes are used in electrochemical studies using three electrode systems when investigating reaction mechanisms related to redox chemistry among other chemical phenomena. A flow of mercury passes through an insulating capillary producing a droplet which grows from the end of the capillary in a reproducible way. Each droplet grows until it reaches a diameter of about a millimeter and releases. The released droplet is no longer in contact with the working electrode whose contact is above the capillary. As the electrode is used mercury collects in the bottom of the cell. In some cell designs this mercury pool is connected to a lead and used as the cell's auxiliary electrode. Each released drop is immediately followed by the formation of another drop. The drops are generally produced at a rate of about 0.2 Hz. A major advantage of the DME is that each drop has a smooth and uncontaminated surface free from any adsorbed analyte or impurity. The self-renewing electrode does not need to be cleaned or polished like a solid electrode. This advantage comes at the cost of a working electrode with a constantly changing surface area. Since the drops are produced predictably the changing surface area can be accounted for or even used advantageously. In addition, the drops' growth causes more and more addition of capacitive current to the faradaic current. These changing current effects combined with experiments where the potential is continuously changed can result in noisy traces. In some experiments the traces are continually sampled, showing all the current deviation resulting from the drop growth. Other sampling methods smooth the data by sampling the current at the electrode only once per drop at a specific size. The DME's periodic expansion into the solution and hemispherical shape also affects the way the analyte diffuses to the electrode surface. The DME consists of a fine capillary with a bore size of 20–50 µm.

The hanging mercury drop electrode (HMDE) is a working electrode variation on the dropping mercury electrode (DME). Experiments run with dropping mercury electrodes are referred to as forms of polarography. If the experiments are performed at an electrode with a constant surface (like the HMDE) it is referred as voltammetry.[7]

Like other working electrodes these electrodes are used in electrochemical studies using three electrode systems when investigating reaction mechanisms related to redox chemistry among other chemical phenomenon

Hanging mercury drop electrode

The hanging mercury drop electrode produces a partial mercury drop of controlled geometry and surface area at the end of a capillary in contrast to the dropping mercury electrode which steadily releases drops of mercury during an experiment. The disadvantages a DME experiences due to a constantly changing surface are not experienced by the HMDE since it has static surface area during an experiment. The static surface of the HMDE means it is more likely to suffer from the surface adsorption phenomenon than a DME. Unlike solid electrodes which need to be cleaned and polished between most experiments, the self-renewing HMDE can simply release the contaminated drop and grow a clean drop between each experiment. The working electrode is the electrode in an electrochemical system on which the reaction of interest is occurring.[1][2][3] The working electrode is often used in conjunction with an auxiliary electrode, and a reference electrode in a three electrode system.[8] Depending on whether the reaction on the electrode is a reduction or an oxidation, the working electrode is called cathodic or anodic, respectively. Common working electrodes can consist of materials ranging from inert metals such as gold, silver or platinum, to inert carbon such as glassy carbon, boron doped diamond[4] or pyrolytic carbon, and mercury drop and film electrodes.[5] Chemically modified electrodes are employed for the analysis of both organic and inorganic samples.

Electrode potential appears at the interface between an electrode and electrolyte due to the transfer of charged species across the interface, specific adsorption of ions at the interface, and specific adsorption/orientation of polar molecules, including those of the solvent.

In an electrochemical cell, the cathode and the anode have a certain electrode potential independently and the difference between them is the cell potential:

$$E_{cell} = E_{cathode} - E_{anode}.$$

The electrode potential may be either that at equilibrium at the working electrode ("reversible potential"), or a potential with a non-zero net reaction on the working electrode but zero net current ("corrosion potential", "mixed potential"), or a potential with a non-zero net current on the working electrode (like in galvanic corrosion or voltammetry). Reversible potentials can be sometimes converted to the standard electrode potential for a given electroactive species by extrapolation of the measured values to the standard state.

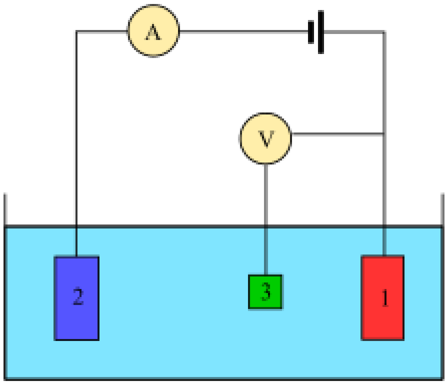
The value of the electrode potential under non-equilibrium depends on the nature and composition of the contacting phases, and on the kinetics of electrode reactions at the interface (see Butler–Volmer equation).

An operational assumption for determinations of the electrode potentials with the standard hydrogen electrode involves this reference electrode with hydrogen ion in an ideal solution having is "zero potential at all temperatures" equivalently to standard enthalpy of formation of hydrogen ion is also "zero at all temperatures".[9]

The measurement is generally conducted using a three-electrode setup (see the drawing):

1. working electrode,
2. counter electrode,
3. reference electrode (standard hydrogen electrode or an equivalent).

In case of non-zero net current on the electrode, it is essential to minimize the ohmic IR-drop in the electrolyte, e.g., by positioning the reference electrode near the surface of the working electrode (e.g., see Luggin capillary), or by using a supporting electrolyte of sufficiently high conductivity. The potential measurements are performed with the positive terminal of the electrometer connected to the working electrode and the negative terminal to the reference electrode.[10]



Three-electrode setup for measurement of electrode potential

III. RESULTS AND CONCLUSIONS

Historically, two conventions for sign for the electrode potential have formed:[2]

1. convention "Nernst–Lewis–Latimer" (sometimes referred to as "American"),
2. convention "Gibbs–Ostwald–Stockholm" (sometimes referred to as "European").

In 1953 in Stockholm[3] IUPAC recognized that either of the conventions is permissible; however, it unanimously recommended that only the magnitude expressed according to the convention (2) be called "the electrode potential". To avoid possible ambiguities, the electrode potential thus defined can also be referred to as Gibbs–Stockholm electrode potential. In both conventions, the standard hydrogen electrode is defined to have a potential of 0 V. Both conventions also agree on the sign of E for a half-cell reaction when it is written as a reduction.

The main difference between the two conventions[4] is that upon reversing the direction of a half-cell reaction as written, according to the convention (1) the sign of E also switches, whereas in the convention (2) it does not. The logic behind switching the sign of E is to maintain the correct sign relationship with the Gibbs free energy change, given by $\Delta G = -nFE$ where n is the number of electrons involved and F is the Faraday constant. It is assumed that the half-reaction is balanced by the appropriate SHE half-reaction. Since ΔG switches sign when a reaction is written in reverse, so too, proponents of the convention (1) argue, should the sign of E. Proponents of the convention (2) argue that all reported electrode potentials should be consistent with the electrostatic sign of the relative potential difference.[9]

Potential of a cell assembled of two electrodes can be determined from the two individual electrode potentials using

$$\Delta V_{cell} = E_{red,cathode} - E_{red,anode}$$

or, equivalently,

$$\Delta V_{cell} = E_{red,cathode} + E_{oxy,anode}.$$

This follows from the IUPAC definition of the electric potential difference of a galvanic cell,[5] according to which the electric potential difference of a cell is the difference of the potentials of the electrodes on the right and the left of the galvanic cell. When ΔV_{cell} is positive, then positive electrical charge flows through the cell from the left electrode (anode) to the right electrode (cathode).[10]

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