Electroanalytical Chemistry

techniques covered to date

- Potentiometry – based on galvanic cell
- Controlled Potential Electrolysis – electrolytic
- Chronoamperometry – electrolytic cell
- Chronopotentiometry – electrolytic cell
- Coulometry (potential or current) - electrolytic
- Voltammetry (stirred & unstirred) - electrolytic
- DC Polarography – electrolytic cell
Polarography (DC or direct current)

- Same as voltammetry in unstirred solution except, use Dropping Mercury Electrode (DME)
- Vary potential linearly with time
- Measure current vs time

Theory

- assume $\text{Ox} + n \text{e}^- \leftrightarrow \text{Red}$
- both Ox & Red are soluble or Ox soluble & Red dissolves in mercury electrode
- reversible reaction (electrochemically)
Realistic diagram of a DME for polarography

Slow flow of Hg through tubing → drop forms, expands and falls off → new drop forms
Advantages of DME

1) A new electrode surface forms every few seconds preventing buildup of impurities or reaction products $\rightarrow$ clean surface

2) Metallic products dissolve or amalgamate with Hg leaving surface clean also

3) High hydrogen overvoltage allows more negative potentials than other electrodes

4) Expansion of drop area and decrease in diffusion limited current counteract each other
Disadvantages of DME

1) Hg is easily oxidized which prevents the use of more positive (oxidizing) potentials
2) DME is cumbersome to set up and use
3) DME is fragile, not rugged
4) Hg is highly toxic & has measurable vapor pressure
5) Continual Hg dropping becomes costly
6) Hg must be highly pure
7) Hg can air oxidize and the oxide can clog the capillary tube where the drop forms
Static Mercury Drop Electrode & Controlled Growth Electrode
As drop forms:

1) Concentration polarization occurs at the electrode surface as described by Cottrell Eq.

\[ I = nF A c_0 \sqrt{\frac{D}{\pi t}} \]

\( \text{The Cottrell equation} \)

2) Size of drop increases \( \Rightarrow \) area increases

\[ A = (4\pi)^{1/2} \left( \frac{3 \times 10^{-3}}{\rho_{\text{Hg}}} \right)^{2/3} (m \ t)^{2/3} \]

area

density of Hg

mass flow rate (mg/sec)

drop time

drop time = time for 1 drop
The two effects, concentration polarization which decreases current, and the area increase which increases current, tend to cancel each other out.

Combining equations gives the Ilkovic Eq.

\[ I = 708 \, n \, D^{1/2} \, m^{2/3} \, t^{2/3} \, C \]  
max current

\[ I = 607 \, n \, D^{1/2} \, m^{2/3} \, t^{2/3} \, C \]  
average current
Two name changes occur in polarography

- The limiting current becomes $I_d$ for the diffusion current.
- The capacitive current is $I_{Cap}$.
- The residual current is $I_{Res}$. 
Polarogram for $5 \times 10^{-4}$ M Cd$^{2+}$ in 1 M HCl

max current

$E_{1/2}$

HALF-WAVE POTENTIAL

DIFFUSION CURRENT $I_d$
or average current

Scan for 1 M HCl alone

$E_{d.e.}$ VOLTS vs. S.C.E.
Remember for LSV

$$E_{\text{DME}} = E_{1/2} - \frac{RT}{nF} \ln \frac{I_d - I}{I}$$

A plot of log $\frac{I_d - I}{I}$ vs. E yields a straight line

With slope of 0.059/n if process is reversible

- This plot is used to establish reversibility & to determine “n”

- $E_{1/2}$ is characteristic of species reduced

- $I_d$ is used for quantitative analysis
Effect of complexation on $E_{1/2}$ for metal ion reduction

- Electrochemical methods measure free ion
- Metals bound in complexes are not measured

$$
M^{n+} + xL \rightleftharpoons ML_x \quad K_f = \frac{[ML_x^{n+}]}{[M][L]^x}
$$

- However, voltammetric methods, like polarography, actually remove metal ion from solution at the electrode surface

$$
M^{n+} + n e^- \rightleftharpoons M(Hg)
$$

- Two effects 1) it takes more energy to do this
  2) it shifts equilibrium to left, releasing metal ion
1) Extra energy required to reduce metal from a complex results in an $E_{1/2}$ that is more negative than $E_{1/2}$ for metal ion alone

$$\Delta E_{1/2} = E_{1/2M} - E_{1/2M}$$

Plot $\Delta E_{1/2}$ vs. $\ln C_L$ to get $K$ & $x$ for complex

2) Equilibrium shift caused by release of metal ion from complex can cause errors in analysis depending on complex kinetics
Operational Aspects of Polarography

1) Oxygen dissolved in solutions can be reduced and cause an oxygen wave

\[ \text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2\text{O}_2 \]

Routinely bubble an inert gas through solution to displace \( \text{O}_2 \), usually \( \text{N}_2 \), \( \text{He} \), \( \text{Ar} \)

2) Polarographic maxima (= interfering peaks) sometimes form in polarogram due to convection currents resulting from drop expansion and dislodging
Can minimize using a small amount of surfactant added to solution (0.0001%) Triton X-100
Summary of DC Polarography

- Polarography is good for many metals
- Works well even at high salt concentrations
- Applicable to many organic functional groups
- Can be used to study metal complexation
- In practice DC Polarography has been replaced by other polarographic variations
- Particularly variations that handle capacitive current better
- Working range $10^{-3}$ M to $10^{-5}$ M
- Precision 1 – 2 %
Summary of DC Polarography (cont.)

• Can do 3 or 4 metals simultaneously if concentrations are compatible
• Still difficult to measure one species in the presence of a large excess of a second species because waves don’t stack well
• Can have problems with complex matrices like wastewater, sludge, biological samples that foul the electrode
• DC polarography is a fundamental technique which has many variations and improvements
Calibration Methods for Electrochemistry

1) Absolute Calibration – use theoretical relationship for current to calculate conc. 
e.g., \( I = 708 \, n \, D^{1/2} \, m^{2/3} \, t^{2/3} \, C \)
Measure \( m \) and \( t \) and look up \( n \) and \( D \)
Solve Ilkovic equation for \( C \)

This is not the most reliable method because it requires very accurately measured values of \( m \) & \( t \) as well as reliable info on \( D \) which varies with solution composition, also \( I_{\text{cap}} \) is problem
2) Calibration curve – construct plot of current vs. concentration for several standard solutions

![Graph showing a linear relationship between current (I) and concentration.](image.png)

Each point represents a separate solution introduced into the electrochemical cell and analyzed.

Calibration curves are sometimes used in electrochemistry for calibration, but they are not the most common method.
3) Internal Standard (Pilot Ion) – add a more easily reduced species to both the unknown sample & the standard solution

\[
\frac{I_{\text{unk}}}{I_{\text{pilot}}} = \frac{708 \ n \ D^{1/2} (m^{2/3} t^{2/3})}{708 \ n \ D^{1/2} (m^{2/3} t^{2/3})} \frac{C_{\text{unk}}}{C_{\text{pilot}}}
\]

Response ratio of ion in unknown sample to pilot ion is equal to ratio of concentrations
Compensates for variations in solution matrix
4) Standard Additions – spike a small volume \( (V_s) \) of standard solution of known concentration \( (C_s) \) into original volume of sample \( (V_o) \) measuring first the current for the current for the original sample \( (I_o) \), then the current for the spiked sample \( (I_s) \)

\[
C_u = \frac{I_o V_s C_s}{(I_s V_s) + (I_s - I_o) V_o}
\]

where \( C_u \) is concentration of the unknown