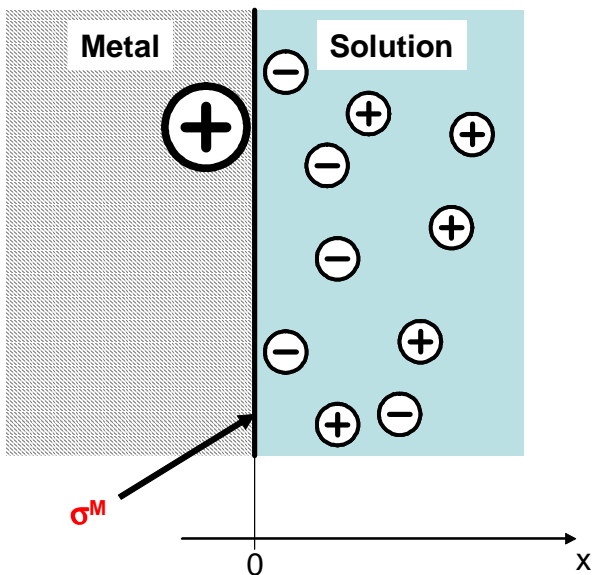


Gouy-Chapman model (1910)

The double layer is not as compact as in Helmholtz rigid layer.

Consider **thermal motions of ions**:

Tendency to increase the **entropy** and make the layer **diffuse** (while **electrostatic attraction** tends to keep ions close to interface and make the layer more **rigid**).



Distribution of ions: determined by electrostatics and stat. mechanics

Assumptions:

- Ions: point ions, highly mobile
- Solvent: dielectric continuum
- Metal: perfect conductor

Distribution of ions with distance x from interface:

apply **Boltzmann statistics**

$$n_i = n_i^0 \exp \left[-\frac{z_i F (\varphi(x) - \varphi^s)}{RT} \right]$$

n_i : particle density (#particles/cm³)

Regions of large $\varphi(x)$: reduced density of positive ions, enhanced density of anions (compared to bulk).

Charge density involving all ionic species:

$$\begin{aligned}\rho(x) &= \sum_i n_i z_i e_0 \quad \text{with} \quad e_0 = 1.602 \cdot 10^{-19} \text{ C} \\ &= \sum_i n_i^0 z_i e_0 \exp \left[-\frac{z_i F (\varphi(x) - \varphi^S)}{RT} \right]\end{aligned}$$

Galvani potential in solution obeys **Poisson's equation**:

$$\frac{d^2 \varphi(x)}{dx^2} = -\frac{\rho(x)}{\epsilon \epsilon_0}$$

Resulting expressions is the **Poisson-Boltzmann equation**:

$$\frac{d^2 \varphi_\Delta}{dx^2} = -\frac{1}{\epsilon \epsilon_0} \sum_i n_i^0 z_i q \exp \left[-\frac{z_i F \varphi_\Delta(x)}{RT} \right], \quad \text{where } \varphi_\Delta(x) = \varphi(x) - \varphi^S$$

Note: This equation is precisely equal to the Debye-Hückel theory of ionic interactions in dilute solutions, which determines the charge distribution around a central ion.

Next: Let's consider a z-z-electrolyte

$$(*) \quad \rho(x) = n^0 z q \left\{ \exp \left[-\frac{z F \varphi_\Delta(x)}{RT} \right] - \exp \left[\frac{z F \varphi_\Delta(x)}{RT} \right] \right\}$$

Debye-Hückel approximation

Let's further assume that the potential variation is small,

$$\frac{zF \varphi_{\Delta}(x)}{RT} \ll 1$$

i.e. potential variations are $\varphi_{\Delta} \ll 25 \text{ mV}$ at room-T. This well-known approximation corresponds to the so-called

Debye-Hückel approximation.

If we use this approximation in the charge distribution (*) of the z-z electrolyte and then insert this charge distribution into the Poisson-Boltzmann equation, then we arrive at the **linear Poisson-Boltzmann equation**:

$$\frac{d^2 \varphi_{\Delta}}{dx^2} = \kappa^2 \varphi_{\Delta}$$

Here, κ is the **inverse Debye-length**,

$$\kappa = \left(\frac{2(zF)^2 c^0}{\epsilon \epsilon_0 RT} \right)^{1/2} = \frac{1}{L_D},$$

c^0 : bulk electrolyte concentration (far away from interface)

κ or its inverse L_D are important characteristics of the electrolyte.

Debye-length L_D : quantitative measure of width of space charge region within which $\varphi(x)$ decreases from φ^M to φ^S – tremendous importance in electrochemistry and biology.

The following effects are important to remember:

➤ Larger electrolyte concentration $c^0 \rightarrow$ smaller L_D

i.a.w: the double layer becomes less diffuse

➤ Higher temperature \rightarrow larger L_D

i.a.w.: the double layer becomes more diffuse

Potential and charge distribution in the electrolyte solution are given in **Debye-Hückel approximation** by:

$$\varphi_{\Delta}(x) = \frac{\sigma^M}{\epsilon\epsilon_0\kappa} \exp(-\kappa x)$$

$$\rho(x) = -\sigma^M \kappa \exp(-\kappa x)$$

i.e. they are **exponential functions of the distance from the interface**, i.e. the excess surface charge density σ^M on the metal is balanced by an exponentially decaying space-charge layer in solution.

The double layer capacity in this approximation is given by

$$C_{d,DH} = \epsilon\epsilon_0\kappa = \frac{\epsilon\epsilon_0}{L_D}$$

i.e. it is given by the plate capacitor formula with the Debye length as the effective plate separation.

**Table: Debye length at various electrolyte concentrations
(1-1 electrolyte)**

$c^0 / \text{mol l}^{-1}$	10^{-4}	10^{-3}	10^{-2}	10^{-1}
$L_D / \text{Å}$	304	96	30.4	9.6

Higher concentrations:

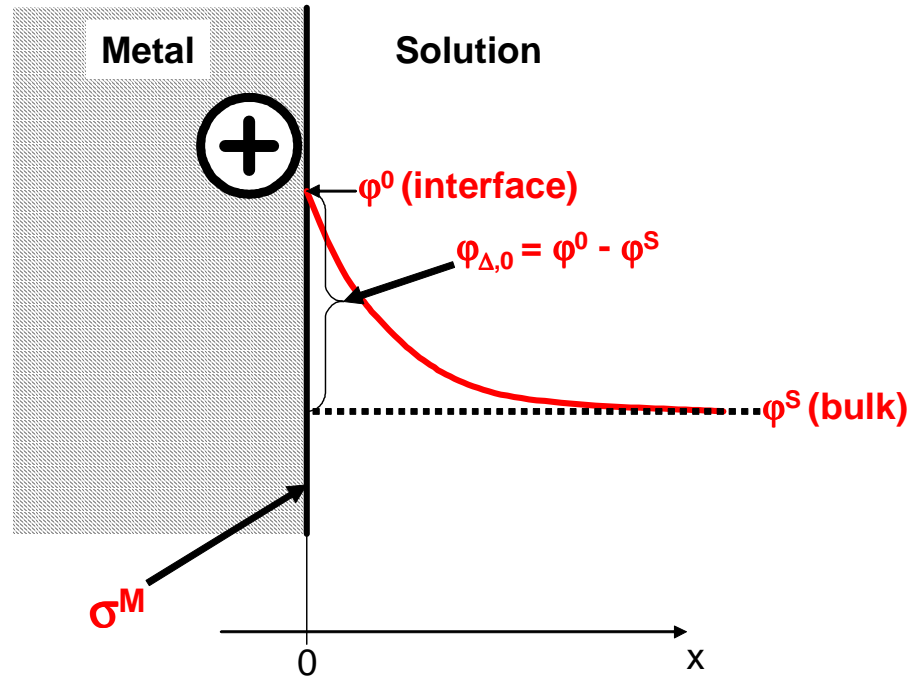
- steeper potential drop in solution
- narrower space charge region, smaller L_D
- higher double layer capacities, $C_{d,DH}$

In practice: The Debye-Hückel (DH) approximation is not valid at large electrolyte concentration. It works well as long as the potential variation does not exceed $\varphi_\Delta \approx 80 \text{ mV}$.

General Case: Nonlinear Poisson-Boltzmann-equation

For a z-z-electrolyte with concentration c^0 the Poisson-Boltzmann equation has an explicit solution. This will be added as an appendix. Here only the main results will be given.

Potential distribution in solution



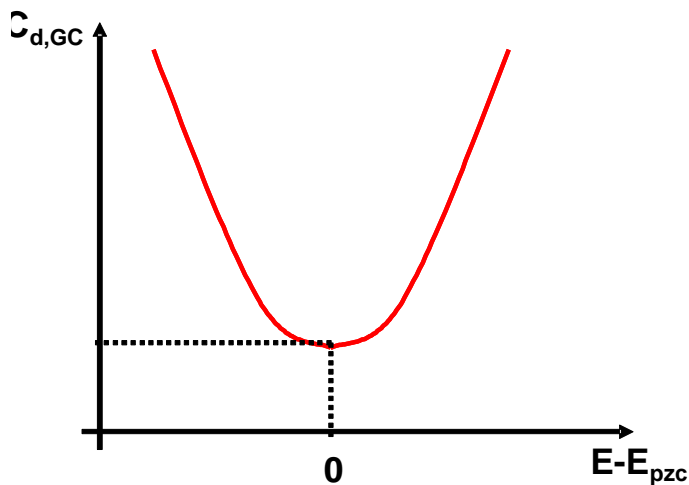
The relation between potential and charge density of the diffuse layer is given by

$$\sigma^M = \varepsilon\varepsilon_0 \left(\frac{d\varphi_{\Delta}}{dx} \right)_{x=0} = (8RT\varepsilon\varepsilon_0 c^0)^{1/2} \sinh\left(\frac{zF\varphi_{\Delta,0}}{2RT}\right)$$

Differentiating this expression gives the differential capacity in the Gouy-Chapman model:

$$C_{d,GC} = \left(\frac{\partial\sigma^M}{\partial\varphi_{\Delta,0}} \right) = \frac{\varepsilon\varepsilon_0}{L_D} \cosh\left(\frac{zF\varphi_{\Delta,0}}{2RT}\right), \text{ where } \varphi_{\Delta,0} = E - E_{pzc}$$

The variation of this capacitance with electrode potential E is thus given by



This model predicts correctly the minimum in capacity at the pzc. For large E , it predicts an unlimited rise of the capacity.

Why would the DL capacity rise unlimitedly in this approach?
Which assumption is responsible for this unphysical behaviour?

It is assumed that ions are point charges, which could approach the electrode surface arbitrarily close with increasing E . This leads to a very small charge separation (consider the plate capacitor as an analogue!). **The capacity rises without limit.**

What is the solution out of this “capacity catastrophe”???

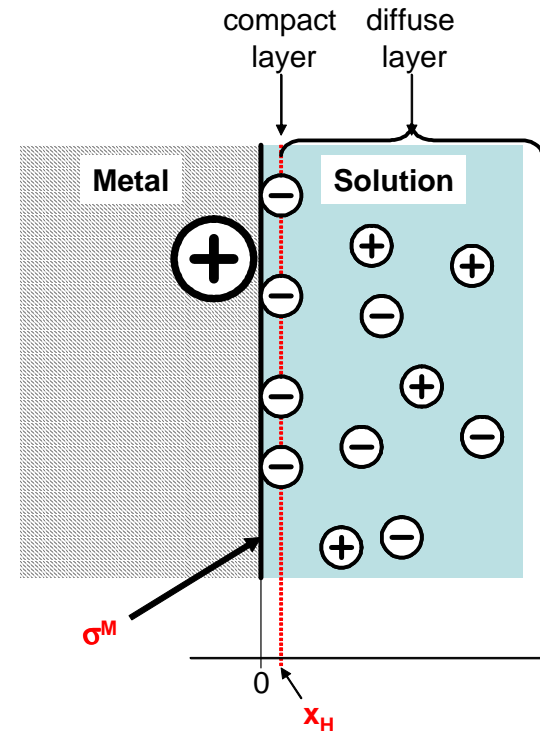
Ions have a finite size! Arbitrarily close approach is not possible. Ions are stopped from approaching the electrode at distances that correspond to their radii.

A further refinement of the double layer models takes this effect into account.

The Stern Model (1924)

- accounts for finite size of ions
- combines the Helmholtz and Gouy-Chapman models
- two parts of double layer:
 - (a) compact layer (“rigid layer”) of ions at distance of closest approach
 - (b) diffuse layer.

The compact layer, $x < x_H$, is charge-free (linear variation of potential)!



Mathematically: two capacitors in series with total capacity

$$\frac{1}{C_d} = \frac{1}{C_{\text{diff,H}}} + \frac{1}{C_{\text{diff,GC}}} = \frac{x_H}{\epsilon\epsilon_0} + \frac{L_D}{\epsilon\epsilon_0 \cosh\left(\frac{zF\phi_{\Delta,0}}{2RT}\right)}$$

- Far from E_{pzc} (large $\phi_{\Delta,0} = E - E_{\text{pzc}}$):

$$C_{\text{diff,H}} \ll C_{\text{diff,GC}} \Rightarrow C_d \cong C_{\text{diff,H}} \quad \square \quad \text{Helmholtz, rigid}$$

- Close to E_{pzc} (small $\phi_{\Delta,0} = E - E_{\text{pzc}}$):

$$C_{\text{diff,H}} \gg C_{\text{diff,GC}} \Rightarrow C_d \cong C_{\text{diff,GC}} \quad \square \quad \text{Gouy-Chapman, diffuse}$$

Remember: the smaller guy always wins (well, not always, but here)!

Effect of electrolyte concentration:

smaller electrolyte concentration

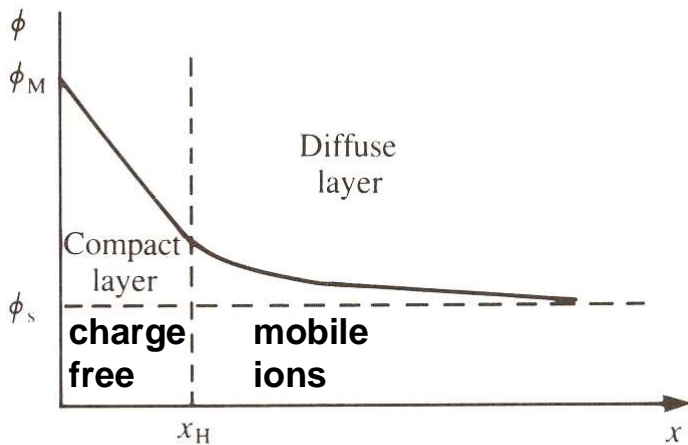
- smaller κ (L_D larger), double is more diffuse!
- $C_{diff,GC}$ becomes more important

The **Stern model** reproduces gross features of real systems.

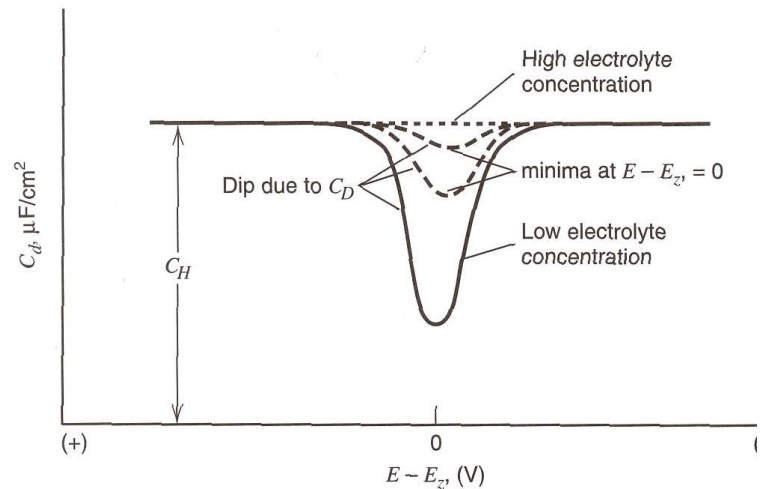
Potential distribution in interfacial layer and capacity variation with E are shown in the figures below.

What happens upon increasing the electrolyte concentration?

Potential distribution



Double layer capacitance



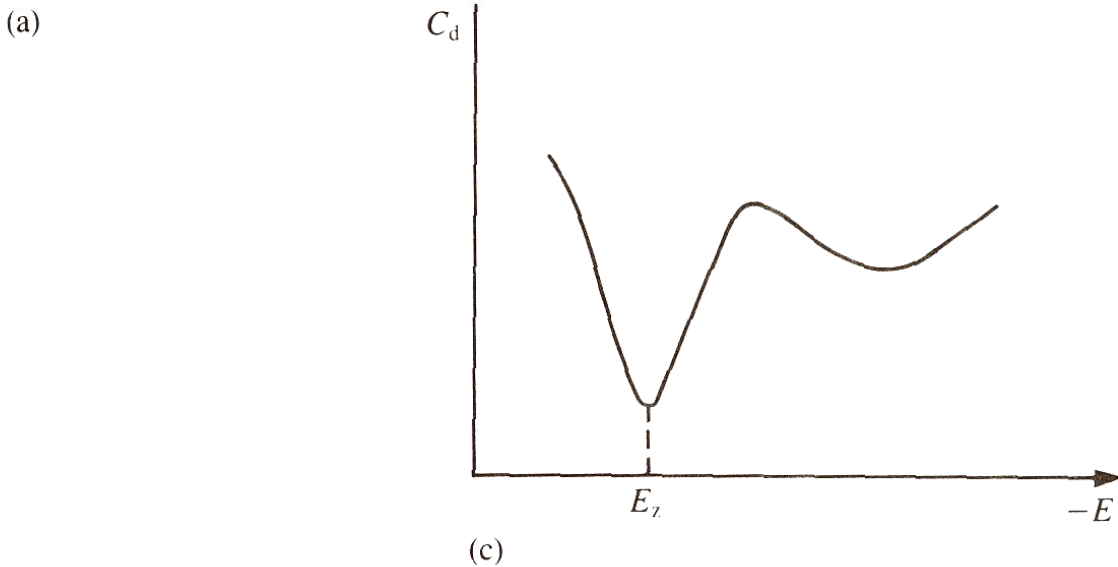
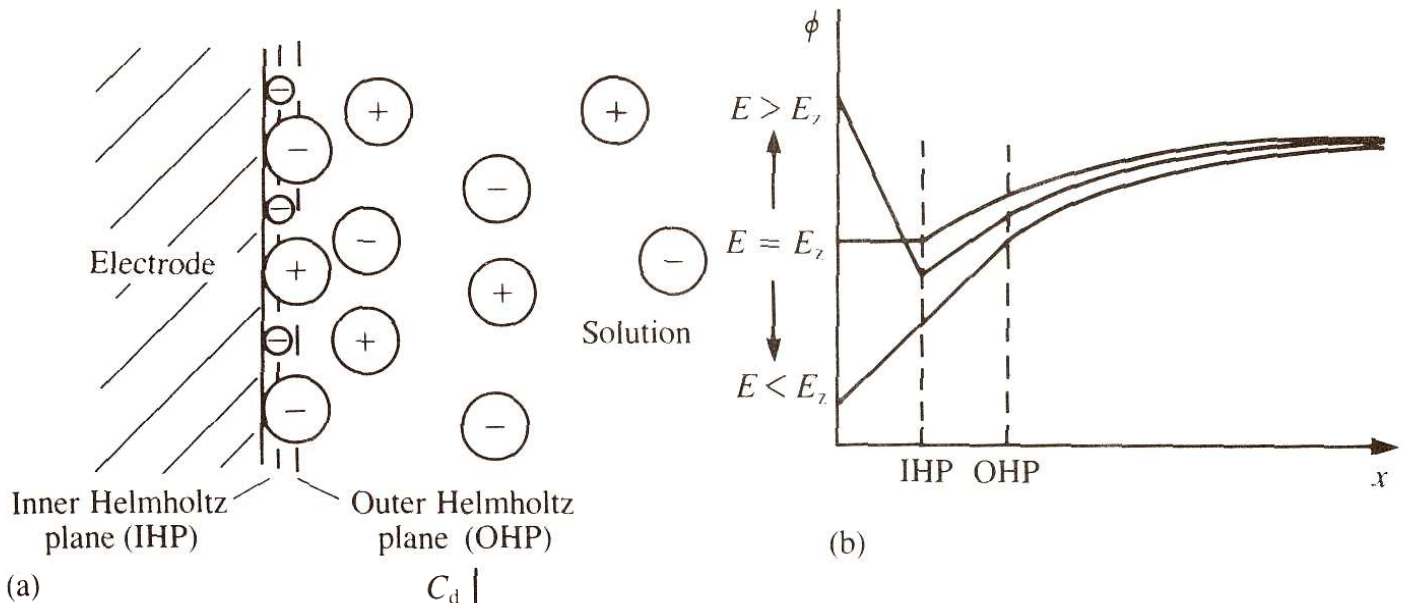
Further refinement: Grahame model (1947)

Some ions (usually anions) lose hydration shell – smaller radii!

Ions of smaller radii could approach the electrode closer.

Distinguish **three different regions!**

- **Inner Helmholtz plane (IHP):** through centers of small, partially solvated ions
- **Outer Helmholtz plane (OHP):** through centers of fully solvated ions
- **Outside OHP:** diffuse layer



This is the best model so far. It shows good correspondence to the experimental data.

Why are the potential distributions (in (b)) different for positive and negative E ?

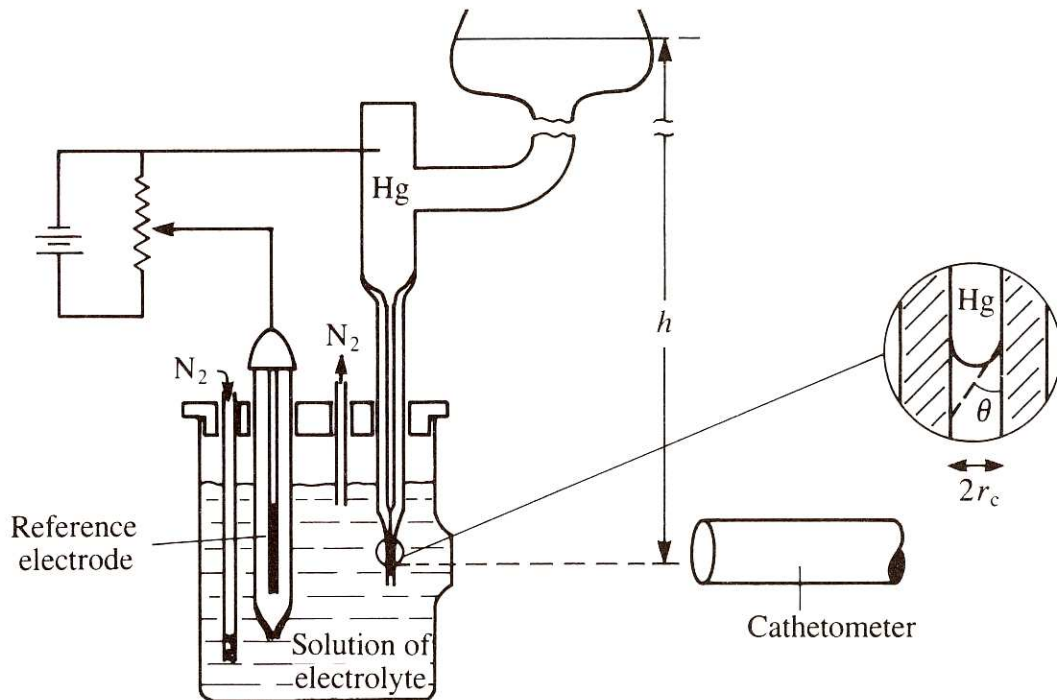
This is due to a difference between anions and cations. Anions have a less rigid solvation shell. They become more easily desolvated. Thus, desolvated anions could form the IHP. This happens at positive E . Cations keep their solvation shell. They, thus, cannot approach the electrode closer than to the OHP.

Appendix: Electrocapillary measurements

Only applicable to liquid electrodes (metals), based on measurement of surface tension (Lippmann's method). The method was developed specifically for mercury electrodes.

This is a **null-point technique**, i.e. the measurement of a physical property is performed when the system has reached an equilibrium state. Such measurements are rather accurate. Balanced forces: Surface tension of mercury in the capillary counterbalances the force of gravity

$$2\pi r_c \gamma \cos \theta = \pi r_c^2 \rho_{\text{Hg}} h g$$



r_c is the capillary radius,

γ is the surface tension,

θ is the contact angle

h is the height of the capillary column of Hg.

In the measurement, the contact angle θ is measured with a microscope. Above relation then provides values of the surface tension γ . As the experimental parameter, the electrode potential E can be varied.

What happens upon changing E ?

When the system is balanced (reaching a new equilibrium – minimum of Gibbs free energy!), the change in surface energy is exactly balanced by the electrical work,

$$-A_s d\gamma = QdE$$

where A_s is the surface area and Q is the excess charge on the surface.

Therefore, the charge density on the Hg electrode is given by

$$\sigma^M = \frac{Q}{A_s} = -\frac{d\gamma}{dE}.$$

It is, thus, possible to measure the surface charge as a function of E .