Lecture #17 of 20+

The Double Layer

Chapter 13

Q: What's in this set of lectures?
A: B&F Chapter 13 main concepts:

- Section 1.2.3: Double layer structure
- Sections 13.1 & 13.2: Gibbs adsorption isotherm, Gibbadsorption isotherm,\[\text{Electrocapillarity},\text{Surface excess, Lippmann's equation, Point of Zero Charge}\]
- Section 13.3: Models: Helmholtz, Gouy–Chapman (Poisson–Boltzmann), Gouy–Chapman–Stern
- Section 13.5: Specific adsorption
the electronic and ionic charge on an electrode, \( q_M \), is compensated by the accumulation of oppositely charged ions in solution: \( q_M = -q_S \)

... this sounds just like a Donnan equilibrated membrane interface due to having a species confined to one side of the membrane (\( R^- \) is like \( e^- \) in metals)

... the bulk solution is called "quasi-neutral"

... anyway, we should understand the details of how these electrified interfaces are structured... and metal–solution interfaces are well understood

This sort of looks like a parallel plate capacitor

What is the potential difference between the two sides? \( E_{app} \)

What is the potential difference between one side and near the middle? \( \approx E_{app}/2 \)

Does a solution reactant located within the double layer "feel" \( E_{app} \) or \( E_{app} \)?

\( < E_{app} \) mind = blown!

... anyway... in polar solvents, all charged electrode surfaces possess a common structure...

inner Helmholtz (IHP) (AKA compact layer, Helmholtz layer, or Stern layer)

specifically adsorbed anion; also called contact adsorption; polarized with \( \delta^+ \) near the electrode

anion (e.g. \( Cl^- \))
... cations have strongly coordinated waters that exchange slowly...

... the (second) layer of solution extending from the OHP that has a composition perturbed from bulk is called the diffuse layer

... follows a Poisson–Boltzmann distribution...

... this is the same idea behind the derivation of the Debye–Hückel equation (to obtain activity coefficients based on the ionic strength) and the Donnan equation (to obtain the electric potential difference across a membrane/solution interface)...

... the general idea for each is that diffusive (thermal) transport (Boltzmann) is equal and opposite to drift (electrostatic) transport (Poisson/Gauss)

Notice particularly the following:
1) A layer of oriented waters covers the surface...
   ... water orientation (O or H) is dictated by the surface charge

2) Anions shed their primary hydration layers and directly adsorb onto the surface. This is called "specific adsorption"...
   ... with F⁻ being an exception

3) In general, cations do not specifically adsorb; their primary hydration layers are too strongly attached (by the ion–dipole interaction) to be shed at room temperature. This is an example of "nonspecific adsorption"...
   ... with (CH₃)₄N⁺ being an exception
The persistence of water molecules within the first hydration layer is illustrated by the water exchange rate from ions... (Girault, *Analytical and Physical Electrochemistry*, Marcel Dekker, 2004, Figure 3.13)

\[
\sigma^M = -\sigma^S
\]

charge (density) on metal excess charge (density) in solution

The electrode carries a charge, \( q^M \), and a surface change density \( \sigma^M \) \((\sigma^M = q^M / A)\). The total charge (density) of the system is zero, and so...

\[
\sigma^M = -\sigma^S
\]

The electrode carries a charge, \( q^M \), and a surface change density \( \sigma^M \) \((\sigma^M = q^M / A)\). The total charge (density) of the system is zero, and so...

\[
\sigma^M = -\sigma^S
\]

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 1.2.2
... now, what is excess solution charge? There is a technical name for this... it is called the (Gibbs) Surface Excess, \( \Gamma \)

\[
\Gamma = \frac{\Delta \gamma_i}{A} \quad \text{(mol cm}^{-2}\text{)}
\]

**Fig. 7.46.** The distinction between the amount of adsorbed material (hatched area) in the interphase region and the surface excess (shaded area).

Bockris and Reddy, Vol. 2, Plenum Publishing, 1977, Figure 7.46

... now put it all together, and what do we have? ...

\[
d\tilde{G}^R = \left( \frac{\partial \tilde{G}^S}{\partial T} \right) + \left( \frac{\partial \tilde{G}^S}{\partial P} \right) + \sum_i \left( \frac{\partial \tilde{G}^S}{\partial n_i} \right) d\tilde{n}_i
\]

\[
d\tilde{G}^S = \left( \frac{\partial \tilde{G}^R}{\partial T} \right) + \left( \frac{\partial \tilde{G}^R}{\partial P} \right) + \left( \frac{\partial \tilde{G}^R}{\partial A} \right) dA + \sum_i \left( \frac{\partial \tilde{G}^R}{\partial n_i} \right) d\tilde{n}_i
\]

... where \( R \) is in a reference system, and \( S \) is in the actual system

... and at constant temperature and constant pressure, but variable \( A \)...

\[
d\tilde{G}^R = d\tilde{G}^S - d\tilde{G}^R = \gamma dA + \sum_i \bar{\mu}_i d(n_i^S - n_i^R)
\]

\[
d\tilde{G}^S = \gamma dA + \sum_i \bar{\mu}_i d\tilde{n}_i + A d\gamma + \sum_i n_i^R d\bar{\mu}_i
\]

... now put it all together, and what do we have? ...

... and setting the two forms of the differential equation equal to each other...

\[
-d\gamma = \sum_i \Gamma_i \, d\bar{\mu}_i
\]

**Gibbs Adsorption Isotherm**

\[
d\tilde{G}^R = d\tilde{G}^S - d\tilde{G}^R = \gamma dA + \sum_i \bar{\mu}_i d(n_i^S - n_i^R)
\]

\[
d\tilde{G}^S = \gamma dA + \sum_i \bar{\mu}_i d\tilde{n}_i + A d\gamma + \sum_i n_i^R d\bar{\mu}_i
\]
... now put it all together, and what do we have?  
... recasting the difference in electric potential ($d\phi$) as the change in applied potential ($dE$)...  
... we have the electrocapillary equation (B&F pp. 537–538)...  
Recall $\mu = \mu + zF \phi$  
\[-dy = \sigma M dE + \sum_i \Gamma_i d\mu_i\]  
the surface tension (units: energy/area, typically J m$^{-2}$ or N m$^{-1}$... these are identical)  
\[
\gamma = \frac{\partial G}{\partial A}  
\]

---  

... now put it all together, and what do we have?  
... recasting the difference in electric potential ($d\phi$) as the change in applied potential ($dE$)...  
... we have the electrocapillary equation (B&F pp. 537–538)...  
Recall $\mu = \mu + zF \phi$  
\[-dy = \sigma M dE + \sum_i \Gamma_i d\mu_i\]  
the surface excess concentration of species $i$ (units: moles/area), and sometimes called the Gibbs surface excess  

---  

... now put it all together, and what do we have?  
... recasting the difference in electric potential ($d\phi$) as the change in applied potential ($dE$)...  
... we have the electrocapillary equation (B&F pp. 537–538)...  
Recall $\mu = \mu + zF \phi$  
\[-dy = \sigma M dE + \sum_i \Gamma_i d\mu_i\]  
the chemical potential of species $i$  

... but where is the electric potential ($\phi$) term?
... now put it all together, and what do we have? 
... recasting the difference in electric potential (d\(\phi\)) as the change in applied potential (dE)... 
... we have the electrocapillary equation (B&F pp. 537–538)... 
Recall \(\bar{\mu} = \mu + zF\phi\)

\[-dy = \sigma^M dE + \sum_i \Gamma_i d\mu_i\]

the change in potential between the WE and the RE

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... now put it all together, and what do we have? 
... recasting the difference in electric potential (d\(\phi\)) as the change in applied potential (dE)... 
... we have the electrocapillary equation (B&F pp. 537–538)... 

\[-dy = \sigma^M dE + \sum_i \Gamma_i d\mu_i\]

so measurement of the surface tension (\(\gamma\)) of a variable-area electrode as a function of its potential (\(E\)) is a direct way to get at its surface charge (density), \(\sigma^M\). This is called Lippmann’s Equation:

\[\sigma^M = -\left(\frac{d\gamma}{dE}\right)\mu_i\]

Key Point: Measuring \(\gamma\) is easy if the electrode is a liquid...

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... thus, our window into the double layer structure is the dropping mercury electrode (DME)... Seriously!

\[q_m = \text{mass flow rate (kg/s)}\]

http://gmwgroup.harvard.edu

... since drop moves slowly, \(F_j = F_{\text{gravity}}\) (recall that \(F_j = mg = (q_m t_{\text{max}})g\))

\[t_{\text{max}} = \frac{2\pi r_c}{q_m g} \gamma\]

acceleration due to gravity

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... now, in a dropping mercury electrode, as the name implies...

[Diagram]

... now, in a dropping mercury electrode, as the name implies...

[Diagram]

... now, in a dropping mercury electrode, as the name implies...

[Diagram]
what do we measure during this process?

\[ r = 1 \text{ mm} \]

suppose the electrode is at a potential where \( \sigma^M = q^M/A = 25 \, \mu \text{C/cm}^2 \)

what is the surface charge, \( q^M \)?

\[ q^M = (25 \times 10^{-6} \text{C/cm}^2)(4\pi r^2) \]
\[ = (25 \times 10^{-6} \text{C/cm}^2)4\pi(0.1)^2 \]
\[ = (25 \times 10^{-6} \text{C/cm}^2)(0.126\text{cm}^2) \]
\[ = 3.14 \times 10^{-6} \text{C} = 3.14 \mu \text{C} \]

what happens as the electrode grows?

so even though the potential is constant,
... and even though no Faradaic electrochemistry is occurring,
... the Hg droplet grows (surface area increases),
... and thus current flows to its surface...
... and this current is proportional to \( q^M \)
... what happens as the electrode grows?

... after it falls, off, the current drops to a small value...

... and then the process repeats...

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... okay, so let’s do an experiment... scan the potential (E) while we measure the current in 0.1 M HCl...

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Question: Why do the current oscillations stop at -0.60V?

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Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 7.1.5

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the potential at the point of zero charge (pzc)

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Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 7.1.5
... okay, so let’s do an experiment... scan the potential (E) while we measure the current in 0.1 M HCl...

notice also that the phase of the current oscillation inverts as E crosses the PZC...

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 7.1.5

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... a linear scan voltammogram acquired with a DME (and therefore called a polarogram)
... DMEs are "self-cleaning"

\[
\text{Cr}_2O_7^{2-} + 3e^- + 4H_2O \rightleftharpoons \text{Cr(OH)}_3 + 5OH^-
\]

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... look familiar? ... It’s just this:

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Figure 1.4.2 (a) Current-potential curve for a nernstian reaction involving two soluble species with only oxidant present initially. (b) log(|i|/|i_0|) vs E for this system.
Okay, now going back to the case of 0.10 M HCl, let’s measure the drop time, \( t_{\text{max}} \), as a function of potential...

The potential at the point of zero charge (pzc)...

... this huge kinetic overpotential for \( \text{H}_2 \) evolution helps to minimize Faradaic reactions...

Bard & Faulkner, 2nd Ed., Wiley, 2001, Figure 7.1.5

... take the \( t_{\text{max}} \) versus \( E \) data and make a plot... and voila!...

Clearly proportional to \( \gamma \)...

... and recall...

\[
\sigma^M = \frac{dy}{dE} \mu
\]

Why is the surface tension largest when the surface charge is smallest?

\[ t_{\text{max}} = \frac{2\pi r_c}{mg} \gamma \]

... the intermolecular cohesive forces between solvent molecules is large but...

... like charges repel!

E_pzc
... okay, what can we do with this information? Well, a plot of charge (q) versus potential (E) has a slope of... What? Capacitance (C)

\[ \frac{q}{E} = C \]

... but this is the integral / total capacitance... the capacitance that applies for a given applied potential versus \( E_{\text{pzc}} \). For a real capacitor, C is virtually E-independent, but that may not be (and in fact, is not) true for an electrical double layer.

... in anticipation of this, let's define a differential capacitance (\( C_d \)), which is the correct term to use, as follows:

\[ C_d = \left( \frac{\partial \sigma^M}{\partial E} \right) = -\left( \frac{\partial^2 \gamma}{\partial E^2} \right) \mu_i \]

Let's compare total capacitance (C) and differential capacitance (\( C_d \)) as follows:

![Graph showing the relationship between charge density and potential](image)

\( E_z \) is the potential at the pzc

... if we can measure \( \gamma \), we can determine \( \sigma_{\text{pzc}} \).

... and if we can determine \( \sigma_{\text{pzc}} \), we can determine C...

... and all of this only works for liquid electrodes whose surface areas change over time... Crazy!

\[ \sigma^M = -\left( \frac{d\gamma}{dE} \right) \mu_i \]

\[ C_d = \left( \frac{\partial \sigma^M}{\partial E} \right) \]

Aside: One can determine \( E_{\text{pzc}} \) of a solid electrode using its capacitance
...here’s what the $C$ vs. $E$ data actually look like as a function of concentration, for aqueous KF at a DME...

Fig. 5.13 Capacity of a mercury electrode in a KF solution (pzc = 0.43 V) with the respective Gouy-Chapman capacity [Paolo Gallino, EPFL thesis].
H.H. Girault, Analytical and Physical Electrochemistry, EPFL Press, 2004, Figure 5.13

...data for aqueous NaF from B&F is qualitatively similar...

Flat? ... Eh, not really.

Why were both of these measured using fluoride salts?

In order to minimize specific adsorption!

Figure 13.3.1 Differential capacitance vs. potential for NaF solutions in contact with mercury at 25°C. [Reprinted with permission from D.C. Grahame, Chem. Rev., 41, 441 (1947), Copyright 1947, American Chemical Society.]

Grahame, Chem. Rev., 1947, 41, 441

For the purposes of this class, we want to understand the microscopic origin of the most prominent features of these $C_d$ vs. $E$ data:

a) A minimum in $C_d$ exists at the pzc.

b) $C_d$ is quasi-constant at potentials well positive and well negative of the pzc.

c) This quasi-constant $C_d$ is larger when $E$ is (+) of pzc than when it is (–) of pzc.

d) $C_d$ increases with salt concentration at all potentials, and the "dip" near the pzc disappears.
... do you want to understand the details of $C_d$ away from the pzc?
Do you want to understand the hump? There is a book for that...

Three traditional models for double layer structure:
1) Helmholtz
2) Gouy–Chapman (GC)
3) Gouy–Chapman–Stern (GCS)

... let's take a look at each of these...

Models of Electrical Double Layer:
1) The Helmholtz Model: this is the simplest possible model. It postulates that ions (anions and cations) occupy a plane located a distance, $d$, from the electrode surface, and that the effective "dielectric constant" operating in the double layer is potential independent:

$$C_d = \frac{\varepsilon \varepsilon_0}{d}$$

... for a parallel plate capacitor, $C$ is independent of $E$ because the permittivity of the capacitor, $\varepsilon_\varepsilon_0$, and its spacing, $d$, are both independent of applied potential...
... the Helmholtz model says that the electrical double layer acts like, and looks like (rare in EChem), a parallel plate capacitor...

\[ C_d = \frac{\varepsilon \varepsilon_0}{d} \]

... \( C_d \) is therefore independent of \( E \) because the permittivity of the capacitor, \( \varepsilon \varepsilon_0 \), and its spacing, \( d \), are both independent of applied potential...

... Question: What value for \( C_d \) do we calculate by plugging in to this model the known "dielectric constant" (permittivity = IUPAC) of water?

... recall, here's what the double layer really looks like...

... and here's what the double layer looks like in the Helmholtz approximation...
... first, what’s $\varepsilon_r$ for water? Well, that depends… can it rotate? (BRIEFLY)

For water at 20 °C...

![Diagram of dielectric properties](image)

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… and here’s what the double layer looks like in the Helmholtz approximation...

Answer: $\varepsilon_r \approx 78$ (static relative permittivity)

$C_d = \frac{\varepsilon \varepsilon_0}{d}$

$4 \text{Å} = 0.4 \times 10^{-9} \text{m}$

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… and here’s what the double layer looks like in the Helmholtz approximation...

$C_d = \frac{\varepsilon \varepsilon_0}{d}$

$= (78)(8.854 \times 10^{-12} \text{F/m})$

$= 0.4 \times 10^{-9} \text{m}$

$= 1.73 \text{F/m}^2$

$= 1.73 \text{F/m} \times \frac{10^6 \mu \text{F/m}^2}{100 \text{cm}^2}$

$= 172.6 \mu \text{F/cm}^2$

Is this what is observed? Nope!… OK, now what?

$4 \text{Å} = 0.4 \times 10^{-9} \text{m}$

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... now, what if the water dielectric is saturated, and thus fixed? 

... so that water cannot rotate...

\[ C_d = \frac{\varepsilon \varepsilon_0}{d} \]

\[ \epsilon = 6 \]

\[ C = \frac{6(8.854 \times 10^{-12} F/m)}{0.4 \times 10^{-9} m} = 0.133 F/m^2 \]

\[ \frac{0.133 F/m^2}{F/100^2 cm} = 13.3 \mu F/cm^2 \]

... much more reasonable!

... if the Helmholtz model is correct, we'd get this exactly: (BRIEFLY)

\[ \sigma^M = \left( \frac{d\gamma}{dE} \right) \mu_i \]

\[ C_d = \left( \frac{\partial \sigma^M}{\partial E} \right) \]

... here are electrocapillary data for various electrolytes... (BRIEFLY)

... hey, you can already see that the Helmholtz Model fails a little...

... mostly on the left...
Notwithstanding, notice particularly the following:

a) the $\gamma$ vs. $E$ parabola is independent of salt... 
   ... at potentials negative of the $pzc$...

b) ... but strongly dependent on salt positive of $pzc$...

c) ... and $pzc$ itself depends on the electrolyte... 
   ... we'll get to this shortly...