Double layer structure & adsorption (Ch. 13)

- Thermodynamics of the double layer
- Experimental evaluation of surface excesses & electrical parameters
- Models for double layer structure
- Helmholtz model
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Thermodynamics of the double layer

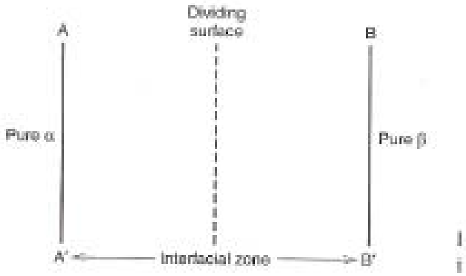
Gibbs adsorption isotherm

Suppose an interface of surface area A separating two phases, α & β

→ interfacial zone (~ 100 Å)

→ *excesses* and *deficiencies*

in the concentration of components



Surface excess (in # of moles of any species)

$n_i^{\sigma} = n_i^S - n_i^R$

n_i^{σ}: excess quantity (any extensive variable, e.g., electrochemical free energy),

n_i^S & n_i^R: # of moles of species i in interfacial region for actual & reference systems

Electrochemical free energy

For the reference system, $\overline{G}^R = \overline{G}^R(T, P, n_i^R)$

For the actual system, $\overline{G}^S = \overline{G}^S(T, P, A, n_i^S)$

$$d\overline{G}^R = (\partial\overline{G}^R/\partial T)dT + (\partial\overline{G}^R/\partial P) + \sum(\partial\overline{G}^R/\partial n_i^R)dn_i^R$$

$$d\overline{G}^S = (\partial\overline{G}^S/\partial T)dT + (\partial\overline{G}^S/\partial P)dP + (\partial\overline{G}^S/\partial A)dA + \sum(\partial\overline{G}^S/\partial n_i^S)dn_i^S$$

At const T & P → 1st two terms can be dropped

$(\partial\overline{G}^R/\partial n_i^R) = \overline{\mu}_i$ (electrochemical potential) → const at equilibrium

$$\overline{\mu}_i = (\partial \overline{G}^R/\partial n_i^R) = (\partial \overline{G}^S/\partial n_i^S)$$

$(\partial \overline{G}^S/\partial A) = \gamma$ (surface tension): a measure of the energy required to produce a unit area of new surface

Differential *excess free energy*

$$d\overline{G}^\sigma = d\overline{G}^S - d\overline{G}^R = \gamma dA + \sum \overline{\mu}_i d(n_i^S - n_i^R)$$

$$d\overline{G}^\sigma = \gamma dA + \sum \overline{\mu}_i dn_i^\sigma$$

Euler's theorem for variables, A and n_i (const T and P)

$$\overline{G}^\sigma = (\partial \overline{G}^\sigma/\partial A)A + \sum (\partial \overline{G}^\sigma/\partial n_i^\sigma) n_i^\sigma$$

$$\overline{G}^\sigma = \gamma A + \sum \overline{\mu}_i n_i^\sigma$$

→ $$d\overline{G}^\sigma = \gamma dA + \sum \overline{\mu}_i dn_i^\sigma + A d\gamma + \sum n_i^\sigma d\overline{\mu}_i$$

$$A d\gamma + \sum n_i^\sigma d\overline{\mu}_i = 0$$

Surface excess concentration, $\Gamma_i = n_i^\sigma/A$ (excesses per unit area of surface)

$$-d\gamma = \sum \Gamma_i d\overline{\mu}_i$$

Gibbs adsorption isotherm: importance of surface tension for interfacial structure

Electrocapillary equation

Consider

$$\mathrm{Cu'/Ag/AgCl/K^+,\ Cl^-,\ M/Hg/Ni/Cu}$$

M: neutral species

Gibbs adsorption isotherm; components of Hg electrode, ions, neutral

$$-d\gamma = (\Gamma_{Hg} d\bar{\mu}_{Hg} + \Gamma_{e} d\bar{\mu}_{e}^{Hg}) + (\Gamma_{K+} d\bar{\mu}_{K+} + \Gamma_{Cl-} d\bar{\mu}_{Cl-}) + (\Gamma_{M} d\bar{\mu}^{M} + \Gamma_{H2O} d\bar{\mu}_{H2O})$$

$\bar{\mu}_e^{Hg}$: electrons in the mercury phase

Some linkages:

$\bar{\mu}_e^{Hg} = \bar{\mu}_e^{Cu}$
$\bar{\mu}_{KCl} = \mu_{KCl} = \bar{\mu}_{K+} + \bar{\mu}_{Cl-}$
$\bar{\mu}_{H2O} = \mu_{H2O}$
$\bar{\mu}_{M} = \mu_{M}$
$d\bar{\mu}_{Hg} = d\bar{\mu}_{Hg}^{0} = 0$

$$-d\gamma = \Gamma_{e} d\bar{\mu}_{e}^{Cu} + (\Gamma_{K+} d\bar{\mu}_{KCl} - \Gamma_{K+} d\bar{\mu}_{Cl-} + \Gamma_{Cl-} d\bar{\mu}_{Cl-}) + (\Gamma_{M} d\mu_{M} + \Gamma_{H2O} d\mu_{H2O})$$

From the equilibrium at the reference interface

$\bar{\mu}_{AgCl} + \bar{\mu}_e^{Cu'} = \bar{\mu}_{Ag} + \bar{\mu}_{Cl-}$

Since $d\bar{\mu}_{AgCl} = d\bar{\mu}_{Ag} = 0$, $d\mu_e^{Cu'} = d\mu_{Cl-}$

$$-d\gamma = \Gamma_e d\bar{\mu}_e^{Cu} - (\Gamma_{K+} - \Gamma_{Cl-}) d\bar{\mu}_e^{Cu'} + \Gamma_{K+} d\mu_{KCl} + \Gamma_M d\mu_M + \Gamma_{H2O} d\mu_{H2O}$$

Excess charge density on the metallic side of the interface

$$\sigma^M = -F\Gamma_e$$

Opposite charge density on the solution side

$$\sigma^S = -\sigma^M = F(\Gamma_{K+} - \Gamma_{Cl-})$$

$$d\bar{\mu}_e^{Cu} - d\bar{\mu}_e^{Cu'} = -F d(\phi^{Cu} - \phi^{Cu'}) = -F dE_-$$

E_-: potential of the mercury electrode with respect to the reference

$$-d\gamma = \sigma^M dE_- + \Gamma_{K+} d\mu_{KCl} + \Gamma_M d\mu_M + \Gamma_{H2O} d\mu_{H2O}$$

Gibbs-Duhem relation at const T and P

$$\sum X_i d\mu_i = 0$$

Xi: mole fraction

$$X_{H2O} d\mu_{H2O} + X_{KCl} d\mu_{KCl} + X_M d\mu_M = 0$$

Remove $d\mu_{H2O}$

$$-d\gamma = \sigma^M dE_- + [\Gamma_{K+} - (X_{KCl}/X_{H2O})\Gamma_{H2O}]d\mu_{KCl} + [\Gamma_M - (X_M/X_{H2O})\Gamma_{H2O}]d\mu_M$$

Relative surface excess: measurable parameters

$$\Gamma_{K+(H2O)} = \Gamma_{K+} - (X_{KCl}/X_{H2O})\Gamma_{H2O}$$

$$\Gamma_{M(H2O)} = \Gamma_M - (X_M/X_{H2O})\Gamma_{H2O}$$

Cannot measure absolute surface excess of K^+, but only excess relative to water
e.g., zero excess: same mole ratio of adsorption of K^+ and H_2O
positive excess: $K^+ > H_2O$
Water: reference component
Dilute solutions: negligible $(X_i/X_S)\Gamma_S$

Electrocapillary equation

$$-d\gamma = \sigma^M dE_- + \Gamma_{K+(H2O)}d\mu_{KCl} + \Gamma_{M(H2O)}d\mu_M$$

→ all measurable parameters

Experimental evaluation of surface excesses & electrical parameters

Electrocapillarity and the DME

For DME,

$$t_{max} = 2\pi r_c \gamma / mg$$

t_{max}: drop lifetime

→ t_{max} vs. E has same shape as the electrocapillary curve

Excess charge and capacitance

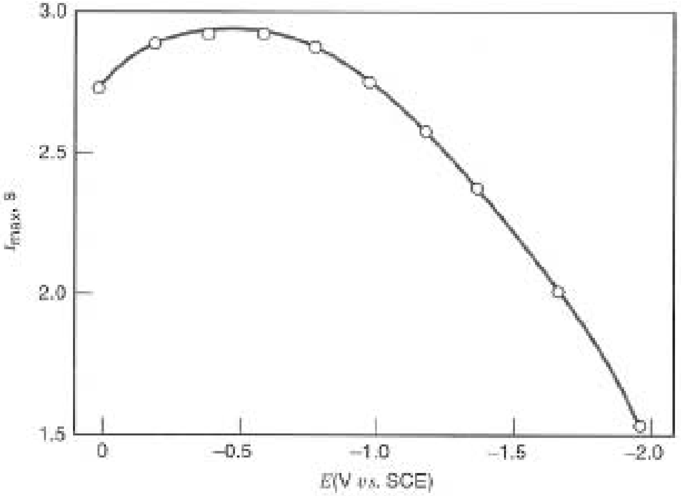
From electrocapillary equation,

$$\sigma^M = (\partial \gamma / \partial E_-)_{\mu KCl, \mu M}$$

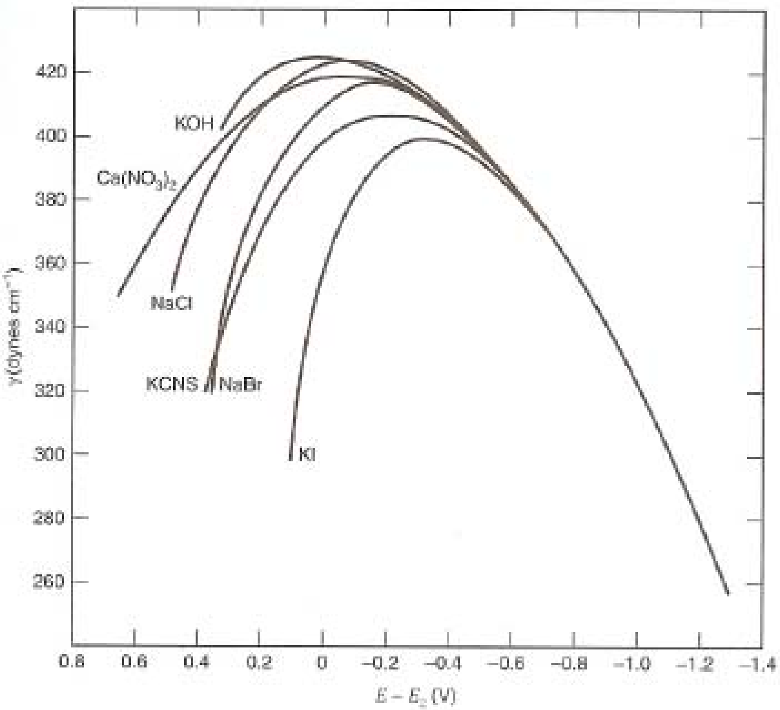
the excess charge on the electrode

→ slope of electrocapillary curve at any E

Drop time of a DME in 0.1 M KCl vs. E



Electrocapillary curve in different electrolyte



→ the existence of a <u>maximum</u> in surface tension

→ potential at maximum: <u>"electrocapillary maximum (ECM)"</u>

→ curve slope = 0 at ECM → **"potential of zero charge"** (PZC)

$$\sigma^M = \sigma^S = 0$$

$$C_i = \int \quad C_d dE / \int \quad dE$$

Average of C_d over the potential range from E_Z to E

Differential capacitance is the more useful quantity, in part it is precisely measurable by impedance techniques

Capacitance can be obtained from the electrocapillary curves by double differentiation

$$\gamma = \iint \quad C_d dE$$

Relative surface excesses

From electrocapillary equation, relative surface excess of K^+ at the interface

$$\Gamma_{K+(H2O)} = -(\partial \gamma / \partial \mu_{KCl})_{E-,\mu}$$

Since $\mu_{KCl} = \mu^0_{KCl} + RT\,ln\,a_{KCl}$

$$\Gamma_{K+(H2O)} = -(1/RT)(\partial \gamma / \partial\, ln\, a_{KCl})_{E-,\mu M}$$

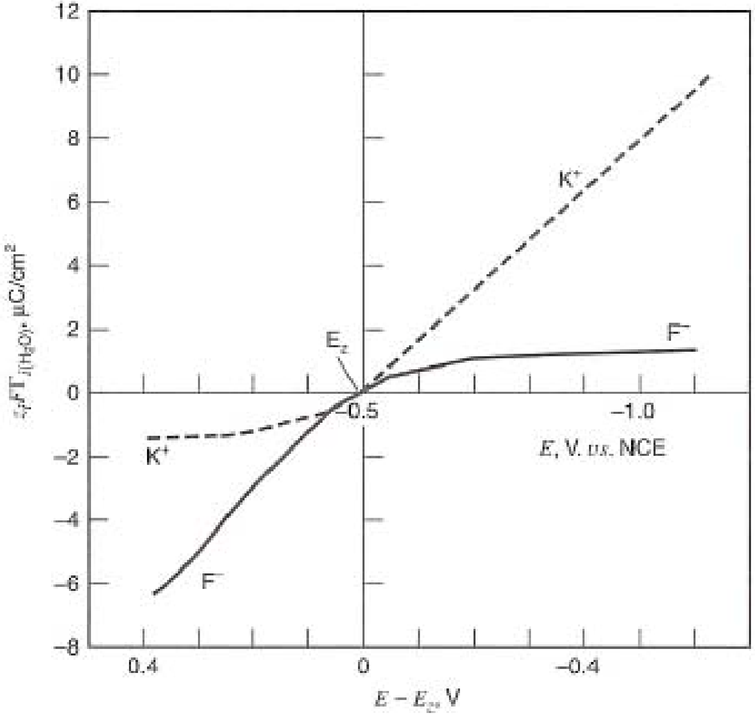
→ relative surface excess $\Gamma_{K+(H2O)}$ at any potential E- by measuring surface tension for several KCl activities (at const M)

Relative surface excess of Cl^-: from the charge balance ($\sigma^S = -\sigma^M = F(\Gamma_{K+} - \Gamma_{Cl-}$)

Fig. 13.2.9: relative surface excess of 0.1 M KF in contact with mercury

At potentials positive of E_Z → surface excess of K^+: negative → K^+ conc in the interface is smaller than in the bulk (reverse for Cl^-)

At potentials negative of E_Z → opposite



Models for double layer structure

The Helmholtz model

Two sheets of charge, having opposite polarity, separated by a distance of molecular order → equivalent to a parallel-plate capacitor

Relation of stored charge density, σ, and voltage drop V between the plate

$$\sigma = (\varepsilon\varepsilon_0/d)V$$

ε: dielectric const of the medium, ε_0: permittivity of free space, d: spacing

Differential capacitance

$$\partial\sigma/\partial V = C_d = \varepsilon\varepsilon_0/d$$

Weakness of this model: predict C_d is const

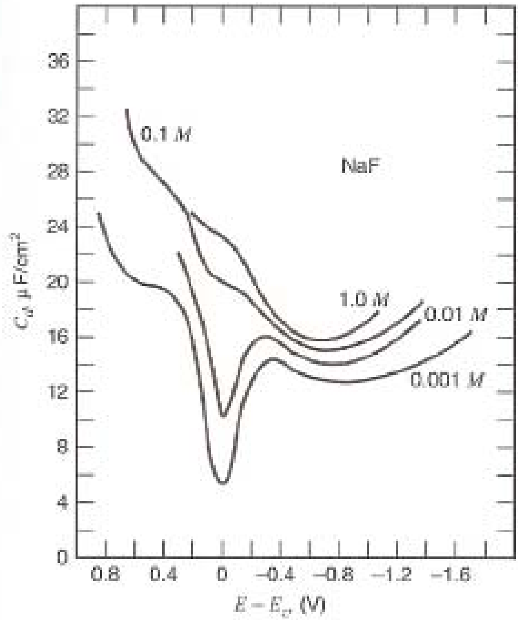
e.g., Fig. 13.3.1

Differential capacitance vs. E

in Hg/NaF interface

→ potential dependence

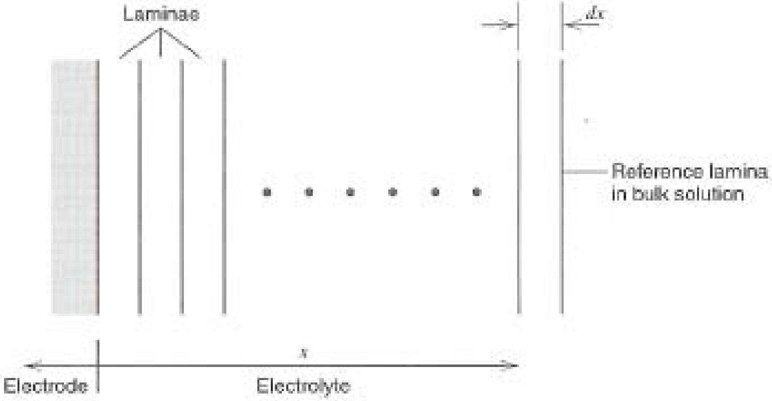
→ more sophisticated model needed



The Gouy-Chapman theory

Charge on the electrode is confined to the surface

Charge in the solution: *diffusion layer*



Population in any lamina (number concentration of species)

$$n_i = n_i^0 \exp(-z_i e\phi/kT)$$

n_i^0: bulk concentration, ϕ: electrostatic potential (ϕ measured with respect to the bulk)

Total charge per unit volume in any lamina

$$\rho(x) = \sum n_i z_i e = \sum n_i^0 z_i e \exp(-z_i e\phi/kT)$$

$\rho(x)$ is related to the potential at distance x by the Poisson equation

$$\rho(x) = -\varepsilon\varepsilon_0(d^2\phi/dx^2)$$

Poisson-Boltzmann equation

$$d^2\phi/dx^2 = -(e/\varepsilon\varepsilon_0)\sum n_i^0 z_i \exp(-z_i e\phi/kT)$$

$$d^2\phi/dx^2 = (1/2)(d/d\phi)(d\phi/dx)^2$$

→ $$(d\phi/dx)^2 = (2kT/\varepsilon\varepsilon_0)\sum n_i^0[\exp(-z_i e\phi/kT) - 1]$$

For z:z electrolyte $\quad d\phi/dx = -(8kTn^0/\varepsilon\varepsilon_0)^{1/2}\sinh(ze\phi/2kT)$

(a) Potential profile in the diffusion layer

ϕ_0: potential at x = 0 relative to the bulk solution

= potential drop across the diffusion layer

$$\tanh(ze\phi/4kT)/\tanh(ze\phi_0/4kT) = e^{-\kappa x}$$

Where $\quad \kappa = (2n^0z^2e^2/\varepsilon\varepsilon_0 kT)^{1/2}$

For dilute aqueous solution ($\varepsilon = 78.49$) at 25°C

$$\kappa = (3.29 \times 10^7)zC^{*1/2}$$

C^*: bulk z:z electrolyte conc in mol/L, κ: cm^{-1}

Potential profile for several different ϕ_0: potential decay away from the surface

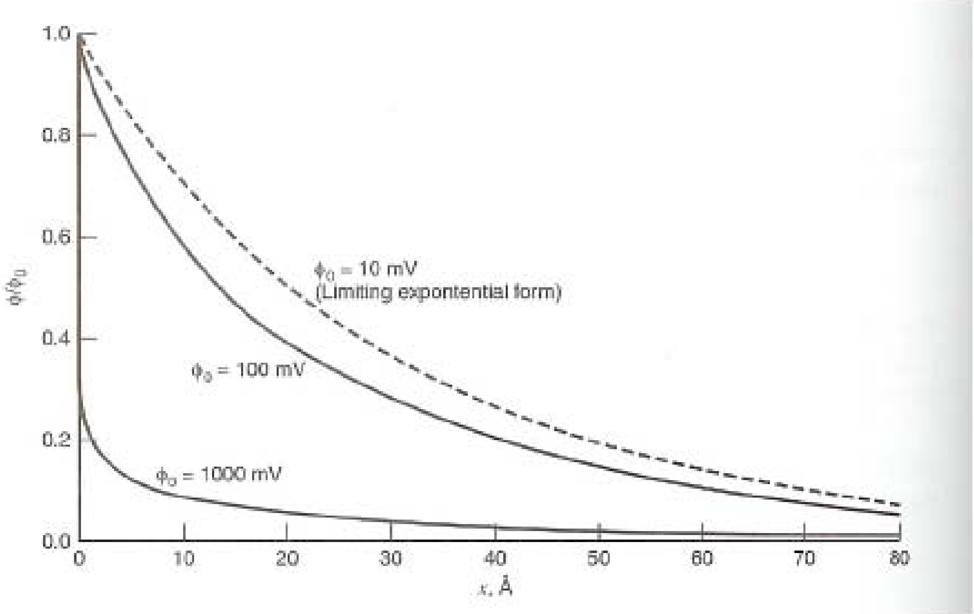
At large ϕ_0 (a highly charged electrode), the drop is precipitous because the diffusion layer is relatively compact

As ϕ_0 smaller, the decline is more gradual

If ϕ_0 is sufficiently low ($\tanh(ze\phi/kT) \sim ze\phi/kT$)

$$\phi/\phi_0 = e^{-\kappa x}$$

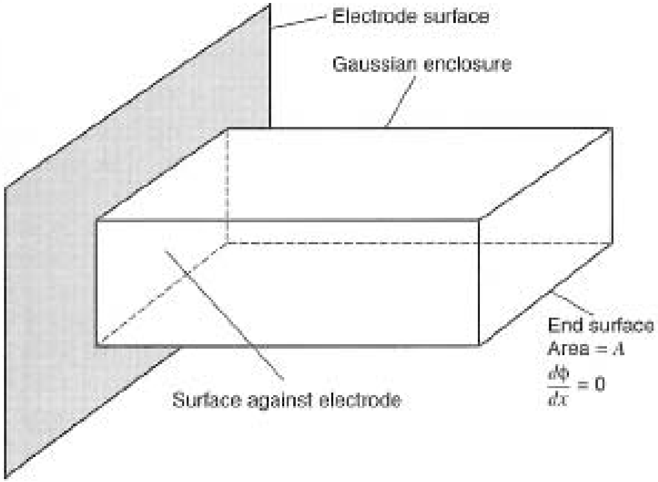
Good approximation for $\phi_0 \leq 50/z$ mV at 25°C



Reciprocal of κ: unit of distance and characterizes the spatial decay of potential
→ kind of characteristic thickness of the diffusion layer
→ thicker as conc of electrolyte falls

$C^*(M)^b$	$1/\kappa$(Å)
1	3.0
10^{-1}	9.6
10^{-2}	30.4
10^{-3}	96.2
10^{-4}	304

(b) Relation between σ^M and ϕ
Suppose Gaussian surface



Gauss law, charge

$$q = \varepsilon\varepsilon_0 \int_{\text{surface}} \boldsymbol{E} \cdot d\mathbf{S}$$
$$= \varepsilon\varepsilon_0 A (d\phi/dx)_{x=0}$$

Using $q/A = \sigma^S$ and $d\phi/dx = -(8kTn^0/\varepsilon\varepsilon_0)^{1/2}\sinh(ze\phi/2kT)$

$$\sigma^S = -\sigma^M = (8kTn^0\varepsilon\varepsilon_0)^{1/2}\sinh(ze\phi_0/2kT)$$

For dilute solution at 25°C

$$\sigma^M = 11.7C^{*1/2}\sinh(19.5z\phi_0)$$

Where C^* is in mol/L for σ^M in $\mu C/cm^2$

(c) Differential capacitance

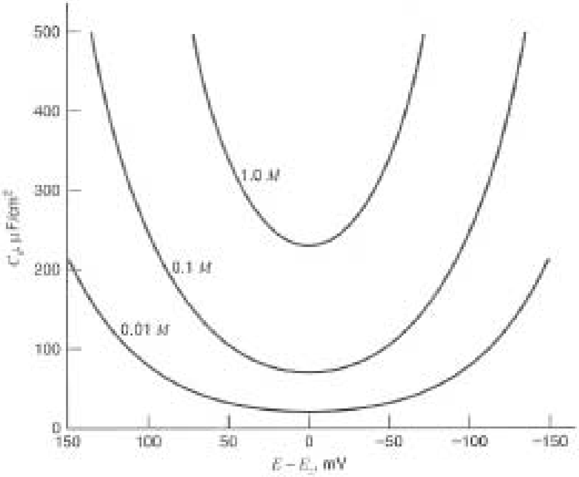
$$C_d = d\sigma^M/d\phi_0 = (2z^2e^2\varepsilon\varepsilon_0 n^0/kT)^{1/2}\cosh(ze\phi_0/2kT)$$

For dilute aqueous solutions at 25°C

$$C_d = 228zC^{*1/2}\cosh(19.5z\phi_0)$$

where C_d is in $\mu F/cm^2$

Predicted plot (V-shape) vs. observed one
i) low conc & near PZC에서만 유사
ii) 실험치가 예측치보다 훨씬 작음
→ need better theory!



Stern's modification

Gouy-Chapman model: unlimited rise in differential capacitance with ϕ_0

→ ions are not restricted with respect to location in solution phase
(point charge can approach the surface arbitrarily closely)

→ not realistic: ions have a finite size & cannot approach the surface any closer than the ionic radius. If solvated, larger radius. Solvent layer should be considered

X_2: outer Helmholtz plane (OHP)

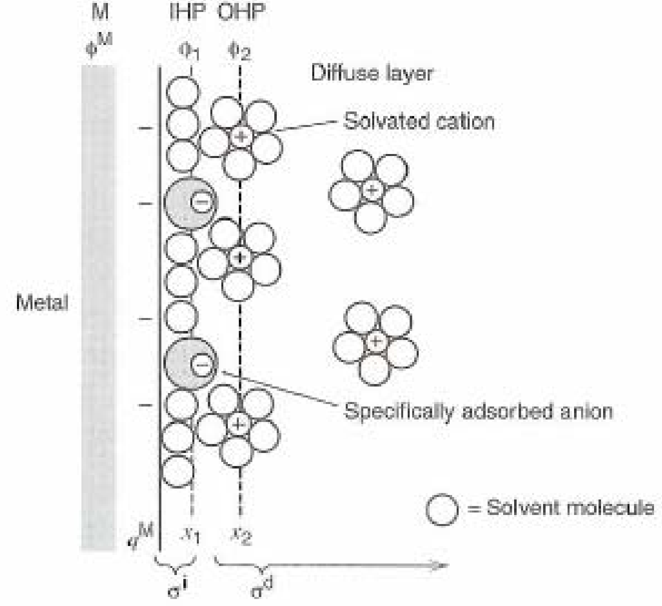


Figure 1.2.3 Proposed model of the double-layer region under conditions where anions are specifically adsorbed.

Poisson-Boltzmann equation for $x \geq x_2$

$$\tanh(ze\phi/4kT)/\tanh(ze\phi_2/4kT) = e^{-\kappa(x-x2)}$$

Where ϕ_2 is the potential at x_2

Field strength at x_2, $(d\phi/dx)_{x=x2} = -(8kTn^0/\varepsilon\varepsilon_0)^{1/2}\sinh(ze\phi_2/2kT)$

Total potential drop across the double layer

$$\phi_0 = \phi_2 - (d\phi/dx)_{x=x2}x_2$$

$$\sigma^M = -\sigma^S = -\varepsilon\varepsilon_0(d\phi/dx)_{x=x2} = (8kTn^0\varepsilon\varepsilon_0)^{1/2}\sinh(ze\phi_2/2kT)$$

$$\sigma^M = (8kTn^0\varepsilon\varepsilon_0)^{1/2}\sinh[ze/2kT(\phi_0 - \sigma^M x_2/\varepsilon\varepsilon_0)]$$

Differential capacitance

$$C_d = d\sigma^M/d\phi_0 = (2z^2e^2\varepsilon\varepsilon_0 n^0/kT)^{1/2}\cosh(ze\phi_2/2kT)/[1 + (x_2/\varepsilon\varepsilon_0)(2\varepsilon\varepsilon_0 z^2e^2n^0/kT)^{1/2}\cosh(ze\phi_2/2kT)]$$

$$1/C_d = x_2/\varepsilon\varepsilon_0 + 1/[(2\varepsilon\varepsilon_0 z^2e^2n^0/kT)^{1/2}\cosh(ze\phi_2/2kT)]$$

Two components

$$1/C_d = 1/C_H + 1/C_D$$

C_D: capacitance of the charge at OHP, C_D: truly diffuse charge

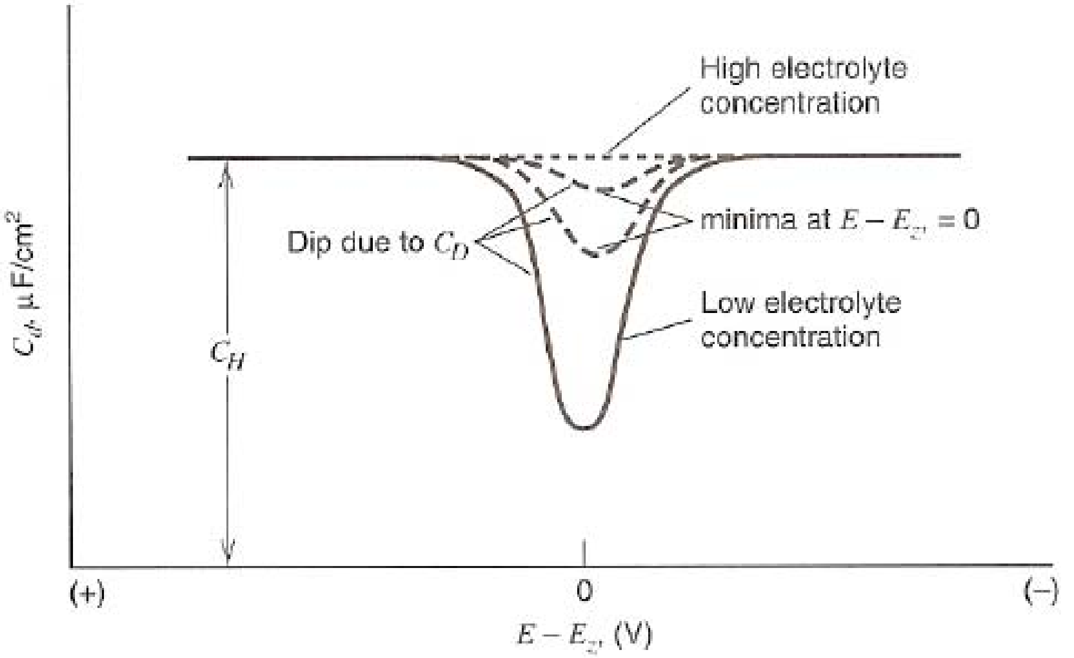
C_H: independent of potential

C_D: varies in V-shaped depending potential

C_d: V-shaped near PZC with low electrolyte conc (characteristic of C_D)

At large electrolyte conc or large polarization → C_D is so large → C_H

→ Gouy-Chapman-Stern (GCS) model



Specific adsorption

Fig.13.2.2

Potential more negative than PZC: decline & same regardless composition (GCS model)

Potential more positive than PZC: depend specifically on the composition

→ *<u>specific adsorption</u>* of anions: their center: *inner Helmholtz plane* (IHP), x_1

Fig.13.2.6 Br^-

(i) Specifically adsorbed ion → considering the slopes of $z_i F\Gamma_{i(H2O)}$ vs. σ^M

$$\sigma^M = -[F\Gamma_{K+(H2O)} - F\Gamma_{Br-(H2O)}]$$

In the absence of specific adsorption: charge on the electrode is counterbalanced by the excess of one ion and a deficiency of the other (Fig.13.2.5)

→ Fig. 13.2.6: more positive than PZC → superequivalent adsorption of bromide (considering slopes & compare with Fig. 13.2.5)

(ii) Esin-Markov effect: shift in PZC with change in electrolyte conc

Table by “Grahame”

→ shift : linear with *ln*[activity]

→ slope: Esin-Markov coefficient at $\sigma^M = 0$

(non-specific adsorption: EM coeff = 0

$$(1/RT)(\partial E_{\pm}/\partial \ln a_{salt})_{\sigma M} = (\partial E_{\pm}/\partial \mu_{salt})_{\sigma M}$$

Studies at solid electrodes

Double layer at solids

대부분 **mercury**에 대에 집중

→ solid electrode: difficulty to reproduce same & clean surface, not atomically smooth…

Well-defined single crystal electrode surfaces

Different crystal faces exhibit different properties (e.g., PZC, work function..)

Pt, Pd, Ag, Ni, Cu: FCC crystal structures

→ low-index crystal faces: stable, polishable

→ higher-index planes: more edges, step & kink sites

Reconstruction: minimize surface energy

Carbon: highly oriented pyrolytic graphite
(HOPG)

Potential of zero charge

cf. Pt: 0.18 V, Ni: -0.33 V

Different crystal faces exhibit different properties (e.g., PZC, work function..)
e.g., PZC on Ag(111) (-0.69 V vs. SCE), Ag(110) (-0.98 V),
→ -0.8 V: carry negative charge in (111), positive charge in (110)

Different catalytic & adsorption properties
e.g., different CV in Pt (0.5 M H_2SO_4)

Solid metal-solution interface

Information on PZC & interface from capacitance measurements

Capacitance curves for Ag(100) at different conc of KPF_6 and NaF

(top to bottom 100, 40, 20, 10, and 5 mM)

Independence of min in capacitance → weakly specificallyadsorbed on Ag

PZC from capacitance minimum

PZC depends upon crystal faces (e.g., Ag)

calculated: polycrystalline (46% (110), 23% (100), 31% (111))

Another complication: surface reconstruction
Au(100): reconstructed (5 x 20) during flame heating
< +0.5 V: maintained (5 x 20)
~+0.7 V: converted to original (100)

Extent and rate of specific adsorption

Nature and extent of specific adsorption

Commensurate: molecules adsorb in exact corresponding pattern with surface atoms
e.g., 1.5×10^{15} Au atoms/cm^2 on Au(111), spacing 2.9 Å
→ if adsorbate atoms on atop sites: (1 x 1) superlattice (2.5×10^{-9} mol/cm^2)

Iodine or 4-aminothiophenol: $(\sqrt{30} \times \sqrt{30})R30^\circ$ → 1/3 Au (8.3×10^{-10} mol/cm^2)
Lower coverage for larger molecules

Roughness factor: actual area/projected area (~1.5 – 2 for smooth electrode)

Adsorption isotherms

Equal electrochemical potentials for bulk & adsorbed species i at equilibrium

$$\mu_i^A = \mu_i^b$$

$$\mu_i^{0,A} + RT\, \mathit{ln}\, a_i^A = \mu_i^{0,b} + RT\, \mathit{ln}\, a_i^b$$

Standard free energy of adsorption

$$\Delta G_i^0 = \mu_i^{0,A} – \mu_i^{0,b}$$

$$a_i^A = a_i^b\, e^{-\Delta Gi0/RT} = \beta_i a_i^b$$

Where $\beta_i = \exp(-\Delta G_i^0/RT)$

Langmuir isotherm

Assumption:

(a) No interactions between the adsorbed species on the electrode surface

(b) No heterogeneity of the surface

(c) At high bulk activities, saturation coverage of the electrode by adsorbate (e.g., to form a monolayer) of amount of Γ_s

$$\Gamma_i/(\Gamma_s – \Gamma_i) = \beta_i a_i^b$$

Fractional coverage, $\Theta = \Gamma_i/\Gamma_s$

$$\Theta/(1 – \Theta) = \beta_i a_i^b$$

$$\Gamma_i = \Gamma_s \beta_i C_i/(1 + \beta_i C_i)$$

If two species i & j are adsorbed competitively,

$$\Gamma_i = \Gamma_{i,s} \beta_i C_i/(1 + \beta_i + \beta_j)$$
$$\Gamma_j = \Gamma_{j,s} \beta_j C_j/(1 + \beta_i + \beta_j)$$

Logarithmic Temkin isotherm

Interactions between adsorbed species

$$\Gamma_i = (RT/2g)\ln(\beta_i a_i^b) \quad (0.2 < \Theta < 0.8)$$

Frumkin isotherm

Electrochemical free energy of adsorption is linearly related to Γ_i

$$\Delta G_i^0(\text{Frumkin}) = \Delta G_i^0 i\ (\text{Langmuir}) – 2g\Gamma_i$$

$$\beta_i a_i^b = [\Gamma_i/(\Gamma_s - \Gamma_i)]\exp(-2g\Gamma_i/RT)$$

g: J/mol per mol/cm^2 → increased coverage changes the adsorption E of i

Positive g: interactions between adsorbed molecules are attractive

Negative g: repulsive interactions

As g → 0, Frumkin isotherm approaches the Langmuir isotherm

Rate of adsorption

When $\beta_i C_i << 1$, $\Gamma_i = \Gamma_s \beta_i C_i = b_i C_i$

Where $b_i = \beta_i \Gamma_s$

$$\Gamma_i(t) = b_i C_i(0,t)$$

$C_i(x,0) = C_i^*$, lim $C_i(x,t) = Ci^*$

$$\Gamma_i(t) = \int D_i[\partial C_i(x,t)/\partial x]_{x=0}\, dt$$

→ $\Gamma_i(t)/\Gamma_i = 1 – \exp(D_i t/b_i^2)\mathrm{erfc}[(D_i t)^{1/2}/b_i]$

$\Gamma_i(t)/\Gamma_i$ is independent of C_i^*, but actually depend on.

bC^*/Γ_s

Effect of adsorption of electroinactive species

→ such adsorption inhibit (or poison) an electrode reaction or accelerate the electrode reaction (e.g., hydrogen or oxygen)

$$k^0 = k_{\Theta=0}^0(1 - \Theta) + k_c^0\Theta$$

Where $k_{\Theta=0}^0$ is the standard rate const at the bare surface & k_c^0 that at the filmed portions

For completer blockage by the film, $k_c^0 = 0$

For catalysis by the filmed area, $k_c^0 > k_{\Theta=0}^0$

Effect of adsorbed substances

Hydrogen & oxygen

CO & organics

Summary

Electrochemical potential (μ_i) = ($\partial G/\partial n_i$): const at equilibrium

Surface tension (γ) = ($\partial G/\partial A$): a measure of the energy required to produce a unit area of new surface

Surface excess concentration (Γ_i) = n_i/A: excess per unit area of surface

Gibbs adsorption isotherm: $-d\gamma = \Sigma \gamma_i d\mu_i$ **<u>for general interface</u>**

Electrocapillary equation: $-d\gamma = \sigma^M dE + \Sigma \Gamma_i d\mu_i$

<u>for electrochemical interface</u>

The excess charge density on the metallic side of interface: $\sigma^M = -\sigma^S$

→ **surface tension (γ) vs. charge density: $\sigma^M = -(\partial \gamma/\partial E)_\mu$**

Surface tension (γ) vs. charge density: $\sigma^{M} = (\partial \gamma / \partial E)_{\mu}$

Curve slope = 0: "potential of zero charge"(pzc)

$$\sigma^{M} = \sigma^{S} = 0$$

- excess charge

Exp.

$$C_{d} = (\partial \sigma^{M} / \partial E)$$