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9. 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 **Gouy-Chapman theory** Stern's modification **Specific adsorption** Studies at solid electrodes **Double layer at solids Single-crystal electrode surfaces** Solid metal-solution interface **Extent & rate of specific adsorption** Nature of specific adsorption **Adsorption isotherms Rate of adsorption Effect of adsorption of electroinactive species**

A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001.

Double layer structure & adsorption

Understanding interfaces Surface electrochemistry Electrocatalysis Supercapacitors Charged particles: colloids And so on

<u>Thermodynamics of the double layer</u> 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) $n^{\circ} = n^{S} - n^{R}$



 $n_i^{\sigma} = n_i^{S} - n_i^{R}$ 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 $\rightarrow 1^{\text{st}}$ two terms can be dropped $(\partial \overline{G}^{R}/\partial n_{i}^{R}) = \overline{\mu}_{i}$ (electrochemical potential) \rightarrow const at equilibrium

$$\overline{\mu_i} = (\partial \overline{\mathbf{G}}^{\mathbb{R}} / \partial \mathbf{n}_i^{\mathbb{R}}) = (\partial \overline{\mathbf{G}}^{\mathbb{S}} / \partial \mathbf{n}_i^{\mathbb{S}})$$

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

Differential excess free energy

$$d\overline{G}^{\circ} = d\overline{G}^{S} - d\overline{G}^{R} = \chi dA + \sum \overline{\mu}_{i} d(n_{i}^{S} - n_{i}^{R})$$

$$d\overline{G}^{\circ} = \chi dA + \sum \overline{\mu}_{i} dn_{i}^{\circ}$$

Euler's theorem for variables, A and n_i (const T and P) $\overline{G}^{\circ} = (\partial \overline{G}^{\circ} / \partial A)A + \sum (\partial \overline{G}^{\circ} / \partial n_i^{\circ})n_i^{\circ}$ $\overline{G}^{\circ} = \forall A + \sum \overline{\mu}_i n_i^{\circ}$

$$\Rightarrow \qquad d\overline{G}^{\circ} = \forall dA + \sum \overline{\mu}_{i} dn_{i}^{\circ} + Ad\forall + \sum n_{i}^{\circ} d\overline{\mu}_{i}$$
$$Ad\forall + \sum n_{i}^{\circ} d\overline{\mu}_{i} = 0$$

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

 $-dy = \sum \Gamma_i d\overline{\mu_i}$

Gibbs adsorption isotherm: importance of surface tension for interfacial structure

Electrocapillary equation

Consider

Cu'/Ag/AgCl/K+, Cl-, M/Hg/Ni/Cu

M: neutral species

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

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

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

Some linkages: $\overline{\mu}_{e}^{Hg} = \overline{\mu}_{e}^{Cu}$ $\overline{\mu}_{KC1} = \mu_{KC1} = \overline{\mu}_{K^{+}} + \overline{\mu}_{C1}$ $\overline{\mu}_{H20} = \mu_{H20}$ $\overline{\mu}_{M} = \mu_{M}$ $d\overline{\mu}_{Hg} = d\overline{\mu}_{Hg}^{0} = 0$ $-d\chi = \Gamma_{e}d\overline{\mu}_{e}^{Cu} + (\Gamma_{K^{+}}d\overline{\mu}_{KC1} - \Gamma_{K^{+}}d\overline{\mu}_{C1^{-}} + \Gamma_{C1}d\overline{\mu}_{C1^{-}}) + (\Gamma_{M}d\mu_{M} + \Gamma_{H20}d\mu_{H20})$ From the equilibrium at the reference interface $\overline{\mu}_{AgC1} + \overline{\mu}_{e}^{Cu'} = \overline{\mu}_{Ag} + \overline{\mu}_{C1}$. Since $d\overline{\mu}_{AgC1} = d\overline{\mu}_{Ag} = 0$, $d\mu_{e}^{Cu'} = d\mu_{C1}$.

 $-d \chi = \Gamma_e d \overline{\mu_e}^{Cu} - (\Gamma_{K^+} - \Gamma_{Cl^-}) d \overline{\mu_e}^{Cu'} + \Gamma_{K^+} d \mu_{KCl} + \Gamma_M d \mu_M + \Gamma_{H2O} d \mu_{H2O}$

Excess charge density on the metallic side of the interface

$$\sigma^{M} = -F\Gamma_{e}$$

Opposite charge density on the solution side

$$\sigma^{S} = -\sigma^{M} = F(\Gamma_{K^{+}} - \Gamma_{Cl^{-}})$$
$$d\mu_{e}^{Cu} - d\mu_{e}^{Cu'} = -Fd(\phi^{Cu} - \phi^{Cu'}) = -FdE_{-}$$

E: potential of the mercury electrode with respect to the reference

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

Gibbs-Duhem relation at const T and P

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

Xi: mole fraction

$$X_{H2O}d\mu_{H2O} + X_{KCI}d\mu_{KCI} + X_Md\mu_M = 0$$

Remove dµ_{H2O}

 $-d\chi = \sigma^{M}dE_{-} + [\Gamma_{K^{+}} - (X_{KCI}/X_{H2O})\Gamma_{H2O}]d\mu_{KCI} + [\Gamma_{M} - (X_{M}/X_{H2O})\Gamma_{H2O}]d\mu_{M}$

Relative surface excess: measurable parameters

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 H₂O positive excess: K⁺ > H₂O Water: reference component Dilute solutions: negligible (X_i/X₈)Γ₈

Electrocapillary equation

 $-d\chi = \sigma^{M}dE_{-} + \Gamma_{K+(H2O)}d\mu_{KC1} + \Gamma_{M(H2O)}d\mu_{M}$

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

Excess charge and capacitance

From electrocapillary equation,

$$\sigma^{M} = (\partial \gamma / \partial E_{-})_{\mu KC1, \mu M}$$

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



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

→ potential at maximum: "electrocapillary maximum (ECM)"

 \rightarrow curve slope = 0 at ECM \rightarrow "potential of zero charge" (PZC)

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

At more negative potentials \rightarrow the electrode surface has a negative excess charge At more positive potentials \rightarrow positive surface charge

→ Plots of surface charge can be made by differentiating electrocapillary curves



The capacitance of the interface → its ability to store charge in response to a perturbation in potential

 $C_d = (\partial \sigma^M / \partial E)$

<u>Differential capacitance</u>: the slope of the plot of σ^{M} vs. E



Integral capacitance, C_i (or K): ratio of total charge density (𝔅^M) at potential E to the total potential difference

$$C_i = \sigma^{M}/(E - E_Z)$$

E_Z: PZC

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

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

$$\chi = \int \int C_d dE$$

Relative surface excesses

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

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

Since $\mu_{\text{KC1}} = \mu_{\text{KC1}}^0 + \text{RT} \ln a_{\text{KC1}}$

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

→ relative surface excess Γ_{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



Fig. 13.2.6: 0.1 M KBr At potentials positive of E_Z (i.e., for σ^M > 0)→ surface excess of K⁺: positive → specific adsorption of Br⁻ on mercury



<u>Models for double layer structure</u> 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

 $\partial \sigma / \partial V = C_d = \epsilon \epsilon_0 / d$

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

 \rightarrow 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 $\rho(x) = \sum n_i z_i e = \sum n_i^0 z_i e \exp(-z_i e \varphi/kT)$ $\rho(x)$ is related to the potential at distance x by the Poisson equation $\rho(x)=-\epsilon\epsilon_0(d^2\varphi/dx^2)$

Poisson-Boltzmann equation

$$\begin{split} d^2\varphi/dx^2 &= -(e/\epsilon\epsilon_0)\sum n_i{}^0z_i exp(-z_ie\varphi/kT) \\ d^2\varphi/dx^2 &= (1/2)(d/d\varphi)(d\varphi/dx)^2 \end{split}$$

 $\rightarrow \qquad (d\phi/dx)^2 = (2kT/\varepsilon\varepsilon_0)\sum n_i^0 [exp(-z_ie\phi/kT) - 1]$

For z:z electrolyte $d\phi/dx = -(8kTn^0/\epsilon\epsilon_0)^{1/2}\sinh(ze\phi/2kT)$

(a) Potential profile in the diffusion layer

For dilute aqueous solution ($\varepsilon = 78.49$) at 25°C $\kappa = (3.29 \text{ x } 10^7)\text{zC}^{*1/2}$ 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 $(tanh(ze\phi/kT) \sim ze\phi/kT) = \frac{\phi}{\phi_0} = e^{-\kappa x}$

Good approximation for $\phi_0 \leq 50/z \text{ mV}$ at $25^{\circ}C$



Reciprocal of κ : unit of distance and characterizes the spatial decay of potential \rightarrow kind of characteristic thickness of the diffusion layer

→ thicker as conc of electrolyte falls

(b) Relation between σ^{M} and ϕ



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

Gauss law, charge

 $q = \varepsilon \varepsilon_0 \int_{\text{surface}} E \cdot dS$ = $\varepsilon \varepsilon_0 A (d\phi/dx)_{x=0}$ Using $q/A = \sigma^S$ and $d\phi/dx = -(8kTn^0/\varepsilon \varepsilon_0)^{1/2} \sinh(ze\phi/2kT)$ $\sigma^{S} = \textbf{-}\sigma^{M} = (8kTn^{0}\epsilon\epsilon_{0})^{1/2} sinh(ze\varphi_{0}/2kT)$

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 $C_d = d\sigma^{M/d\varphi_0} = (2z^2 \epsilon \epsilon_0 n^{0/k}T)^{1/2} \cosh(ze\varphi_0/2kT)$

For dilute aqueous solutions at 25°C $C_d = 228zC^{*1/2}\cosh(19.5z\phi_0)$ where C_d is in μ F/cm²

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

Smaller in experiment than in prediction

Resemble at low conc and near PZC



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

X₂: outer Helmholtz plane (OHP)



Poisson-Boltzmann equation for $x \ge x_2$

 $\frac{\tanh(ze\varphi/4kT)/\tanh(ze\varphi_2/4kT)}{=e^{-\kappa(x-x^2)}}$ Where φ_2 is the potential at x_2 Field strength at x_2 , $(d\varphi/dx)_{x=x^2} = -(8kTn^0/\epsilon\epsilon_0)^{1/2}\sinh(ze\varphi_2/2kT)$

Total potential drop across the double layer

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

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

 $\sigma^{M} = (8kTn^{0}\epsilon\epsilon_{0})^{1/2}sinh[ze/2kT(\varphi_{0} - \sigma^{M}x_{2}/\epsilon\epsilon_{0})]$

Differential capacitance

$$\begin{split} \mathrm{C}_{d} &= d\sigma^{M}\!/d\varphi_{0} = (2z^{2}\epsilon\epsilon_{0}n^{0}\!/kT)^{1/2} \mathrm{cosh}(ze\varphi_{2}\!/2kT)/[1 + (x_{2}\!/\epsilon\epsilon_{0})(2\epsilon\epsilon_{0}z^{2}e^{2}n^{0}\!/kT)^{1/2} \mathrm{cosh}(ze\varphi_{2}\!/2kT)] \end{split}$$

 $1/C_{d} = x_{2}/\varepsilon\varepsilon_{0} + 1/[(2\varepsilon\varepsilon_{0}z^{2}e^{2}n^{0}/kT)^{1/2}\cosh(ze\varphi_{2}/2kT)]$

Two components

$1/C_{d} = 1/C_{H} + 1/C_{D}$

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

Gouy-Chapman-Stern model



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 $\rightarrow C_D$ is so large $\rightarrow C_H$

→ 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 \rightarrow <u>specific adsorption</u> of anions: their center: *inner Helmholtz plane* (IHP), x₁



Fig.13.2.6 Br-

(i) Specifically adsorbed ion \rightarrow considering the slopes of $z_i F \Gamma_{i(H2O)}$ vs. $\sigma^M = -[F \Gamma_{K+(H2O)} - F \Gamma_{Br-(H2O)}]$

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

Concentration, E_7 , Table by "Grahame" V vs. NCE^{b} Electrolyte M \rightarrow shift : linear with *ln*[activity] 1.0 -0.472NaF 0.1 -0.472 \rightarrow slope: Esin-Markov coefficient at $\sigma^{M} = 0$ 0.01 -0.480(non-specific adsorption: EM coeff = 00.001 -0.4821.0 -0.556NaCl 0.3 -0.524 $(1/\text{RT})(\partial E_{\pm}/\partial \ln a_{\text{salt}})_{\sigma M} = (\partial E_{\pm}/\partial \mu_{\text{salt}})_{\sigma M}$ 0.1 -0.5051.0 -0.65KBr 0.1 -0.58-0.540.01 KI 1.0 -0.820.1 -0.72-0.660.01 0.001 -0.59

Studies at solid electrodes

Double layer at solids

Most measurements on mercury

→ 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
- \rightarrow low-index crystal faces: stable, polishable
- \rightarrow higher-index planes: more edges, step & kink sites

Reconstruction: minimize surface energy

Carbon: highly oriented pyrolytic graphite (HOPG)





Face-centered cubic (FCC) structure

Potential of zero charge

Hg	Sb	Bi	Bi(111)	Sn	Pb	In	In(Ga)	Tl	Tl(Ga)	Ga	Cd	Zn
-0.19	-0.17	-0.38	-0.41	-0.39	-0.60	-0.65	-0.67	-0.71	-0.69	-0.69	-0.75	-0.91

Table 1. Potentials of zero charge of sp metals, $E_{\sigma=0}$ (V) vs. the standard hydrogen electrode (SHE).^a

^aThe uncertainty varies mostly between 0.01 and 0.02 V, but it is higher for d metals and lower (0.001 V) for Hg. (Reproduced from Trasatti and Lust (1999)^[16] by permission of Plenum.)

Table 2.	Potentials of 2	ptentials of zero charge of sd metals, $E_{\sigma=0}$ (V) vs. SHE. ^a							
Ag	Ag(111)	Ag(100)	Ag(110)	Au	Au(111)	Au(100)	Au(110)	Cu	Cu(110)
-0.70	-0.45	-0.62	-0.74	0.20	0.56	0.32	0.20	-0.64	-0.69

^aAs per Table 1.

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), \rightarrow -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 KPF₆ and NaF (top to bottom 100, 40, 20, 10, and 5 mM) Independence of min in capacitance \rightarrow 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) $\sim +0.7$ 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/cm² on Au(111), spacing 2.9 Å

 \rightarrow if adsorbate atoms on atop sites: (1 x 1) superlattice (2.5 x 10⁻⁹ mol/cm²)

Iodine or 4-aminothiophenol: $(\sqrt{30} \times \sqrt{30})R30^\circ \rightarrow 1/3$ Au (8.3 x 10⁻¹⁰ mol/cm²) Lower coverage for larger molecules





Roughness factor: actual area/projected area ($\sim 1.5 - 2$ for smooth electrode)

Adsorption isotherms

Equal electrochemical potentials for bulk & adsorbed species i at equilibrium

$$\mu_{i}^{A} = \mu_{i}^{b}$$

$$\mu_{i}^{0,A} + \text{RT} \ln a_{i}^{A} = \mu_{i}^{0,b} + \text{RT} \ln a_{i}^{b}$$

Standard free energy of adsorption

$$\Delta G_i^{\ 0} = \mu_i^{\ 0,A} - \mu_i^{\ 0,b}$$
$$a_i^{\ A} = a_i^{\ b} e^{-\Delta Gi0/RT} = \beta_i a_i^{\ b}$$
$$\beta_i = exp(-\Delta G_i^{\ 0}/RT)$$

Where

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, $\theta = \Gamma_i / \Gamma_s$

$$\theta/(1-\theta) = \beta_i a_i^t$$

$$\Gamma_{i} = \Gamma_{s}\beta_{i}C_{i}/(1+\beta_{i}C_{i})$$

If two species i & j are adsorbed competitively,

$$\Gamma_{i} = \Gamma_{i,s}\beta_{i}C_{i}/(1 + \beta_{i} + \beta_{j})$$

$$\Gamma_{j} = \Gamma_{j,s}\beta_{j}C_{j}/(1 + \beta_{i} + \beta_{j})$$

<u>Logarithmic Temkin isotherm</u> Interactions between adsorbed species $\Gamma_i = (RT/2g)\ln(\beta_i a_i^b) \quad (0.2 < \theta < 0.8)$

<u>Frumkin isotherm</u>

Electrochemical free energy of adsorption is linearly related to Γ_i $\Delta G_i^{0}(Frumkin) = \Delta G_i^{0}i(Langmuir) - 2g\Gamma_i$

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

g: J/mol per mol/cm² \rightarrow increased coverage changes the adsorption E of i Positive g: interactions between adsorbed molecules are attractive Negative g: repulsive interactions As g \rightarrow 0, Frumkin isotherm approaches the Langmuir isotherm

Rate of adsorption When $\beta_i C_i \ll 1$, $\Gamma_i = \Gamma_s \beta_i C_i = b_i C_i$ Where $b_i = \beta_i \Gamma_s$ $\Gamma_i(t) = b_i C_i(0,t)$ $C_i(x,0) = C_i^*$, $\lim C_i(x,t) = Ci^*$ $\Gamma_i(t) = \int D_i [\partial C_i(x,t)/\partial x]_{x=0} dt$ $\rightarrow \qquad \Gamma_i(t)/\Gamma_i = 1 - \exp(D_i t/b_i^2) \operatorname{erfc}[(D_i t)^{1/2}/b_i]$

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



Effect of adsorption of electroinactive species

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

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

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 $(\mu_i) = (\partial G / \partial n_i)$: const at equilibrium

Surface tension $(\gamma) = (\partial G/\partial A)$: 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: $-d\gamma = \sigma^{M}dE + \Sigma\Gamma_{i}d\mu_{i}$

for electrochemical interface

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

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

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



Additional Notes

Charged Interfaces

Reference: Duncan J. Shaw, Introduction to Colloid and Surface Chemistry, John Wiley (ch.7)

Origin of the charge at colloidal surfaces

1. Ionization

- Proteins acquire their charge by ionization of –COOH and NH₂ group.
- The degree of ionization, hence the charge, is pH-dependent.
- Isoelectric point (pH) : the pH at which the net charge is zero
- Experimentally measured electrophoretic mobility can provide information on the sign and magnitude of the surface charge

Isoelectric	Isoelectric point (pH)				
Myoglobin	7.0				
Gliadin					
β-Lactoglobulin	5.2				
Ovalbumin	4.55				
Haemoglobin (horse)	6.9				
Serum albumin (horse)	4.8				
Serum globulin (horse)					
Fibrinogen (bovine)	5.2				
Myosin	5.4				
Bushy stunt virus	4.1				



proteins

high pH: -COOH \rightarrow -COO⁻ + H⁺ (-)charge low pH: -NH₂ + H⁺ \rightarrow -NH₃ + (+)charge



a) HC oil droplet, b) Sulfonated PS

c) Arabic acid (carboxylated polymer),

d) Serum albumin adsorbed on to oil droplets

2. Ion adsorption

- Unequal adsorption of (+) and (-) ions at colloid surfaces form the bulk solution.
- lons may be electrolytes, the ubiquitous H⁺ and OH⁻ present in the solution.
 - *(+) ions are usually small and so more hydrated than (-) ions.
 - * (-) ions are less hydrated and easily polarized.
- Larger hydrated (+) ions have a smaller adsorption tendency: weaker electrostatic interaction with the surface.
- Surfaces in contact with aqueous media are more often (-)ly charged than (+)ly charged.
- Hydrocarbon oil droplets and even air bubbles in aqueous media are (-)ly charged.



3. Ion dissolution

• Ionic substances can acquire a surface charge by unequal dissolution of (+) and (-) ions.

- Ex: AgI(s) \leftrightarrow Ag⁺(aq) + I⁻(aq) : K_{sp} = [Ag⁺][I⁻] ~ 10⁻¹⁶ at RT.
- * Zero point of charge is achieved at pAg = $5.5 \rightarrow [Ag^+] = 3.16 \times 10^{-6} \text{ M}$
- * The smaller Ag⁺ ion is less strongly bound than I⁻ ion in AgI(s) and so it is mobile.
- The smaller ion has a stronger tendency of solvation (hydration) than a larger ion. Ag⁺(s) \rightarrow Ag⁺(aq); ΔG_{Aq} and I⁻(s) \rightarrow I⁻(aq); $\Delta G_{I} > \Delta G_{Aq}$ (more negative).
- Additionally added Ag⁺ or I⁻ ions can modify the surface charge by via adsorption.
 * Thus, Ag⁺ or I⁻ is called the potential-determining ion.
- H+ and OH- ions are the potential-determining ions for hydrous metal oxide sols. * -M-OH + H⁺ \rightarrow -M-OH₂⁺
- * -M-OH + OH⁻ \rightarrow -M-O⁻ + H₂O



Diffuse (electrical) double layer

- Electrolytes present in the solution.
- Electrical neutrality.
- Coions and counter ions
- Coions are repelled and counter-ions are attracted by the surface charges.
- How are these ions distributed near the charged surface ?

Helmholtz model

- Simplest model but it does not accurately represent the actual double layer.
- Inner Helmholtz plane: charged surface
- Outer Helmholtz plane: fixed distance from the surface equal to the radius of a solvated counter-ion.
- Inner region: only solvent molecules present.
- Outside OHP: random distribution of both ions.
- Electrical potential variation as show in the right figure.





Gouy-Chapman model

Assumptions

- 1. Uniformly charged flat surface of infinite extent.
- 2. lons in the diffuse layer are point charges.
- 3. Symmetrical ions of z^+z^- type.

Boltzmann distribution law.

$$n_{+} = n_{0} \exp\left[\frac{-ze\psi}{kT}\right] \qquad n_{-} = n_{0} \exp\left[\frac{+ze\psi}{kT}\right]$$

$$\rho = ze(n_{+} - n_{-}) = zen_{0}\left(\exp\left[\frac{-ze\psi}{kT}\right] - \exp\left[\frac{+ze\psi}{kT}\right]\right) = -2zen_{0} \sinh\frac{ze\psi}{kT}$$

$$\frac{d^{2}\psi}{dx^{2}} = -\frac{\rho}{\epsilon} \qquad \frac{d^{2}\psi}{dx^{2}} = \frac{2zen_{0}}{\epsilon} \sinh\frac{ze\psi}{kT}$$
Poisson-Boltzmann equation

Boundary conditions: $\psi(0) = \psi_0$ at the flat surface and $d\psi/dx = 0$ at $x = \infty$.

$$\psi = \frac{2kT}{ze} \ln\left(\frac{1 + \gamma \exp[-\kappa x]}{1 - \gamma \exp[-\kappa x]}\right) \qquad \gamma = \frac{\exp[ze\psi_0 / 2kT] - 1}{\exp[ze\psi_0 / 2kT] + 1}$$
$$\kappa = \left(\frac{2e^2n_0z^2}{\epsilon kT}\right)^{\nu_2} = \left(\frac{2e^2N_Acz^2}{\epsilon kT}\right)^{\nu_2} = \left(\frac{2F^2cz^2}{\epsilon RT}\right)^{\nu_2} \qquad 1/\kappa = \text{Debye screening} = \text{avg. EDL} \text{ (shielding) length thickness}$$



Debye-Hückel approximation

If $ze\psi_0/2kT \ll 1$ (kT/e = 25.6 mV at 25°C) $n_{+} = n_0 \exp\left[\frac{-ze\psi}{kT}\right] = n_0(1 - ze\psi/kT)$ $n_{-} = n_0 \exp\left[\frac{+ze\psi}{kT}\right] = n_0(1+ze\psi/kT)$ $\rho = ze(n_+ - n_-) = -2zen_0 \frac{ze\psi}{kT}$ $\frac{d^2 \psi}{dx^2} = -\frac{\rho}{\epsilon} = (2n_0 z^2 e^2 / \epsilon kT) \psi = \kappa^2 \psi$ $\frac{\mathrm{d}^2 \psi}{\mathrm{d}x^2} - \kappa^2 \psi = 0 \longrightarrow \psi = \psi_0 \exp[-\kappa x]$

 ψ = ψ₀ exp(κ x) was discarded because of dψ/dx = 0 at x = ∞.

$$\sigma_0 = -\int_0^\infty \rho \mathrm{d}x \to \sigma_0 = \epsilon \kappa \psi_0$$



Surface charge vs. surface potential

 $\sigma_0 = \epsilon \kappa \psi_0$

- Meaning of 1/ κ : thick of diffuse double layer.
- ψ_0 determined by σ_0 and κ or σ_0 determined by ψ_0 and κ

Two cases

For a symmetrical electrolyte at 25 °C $\kappa = 0.329 \times 10^{10} \left(\frac{cz^2}{\text{mol dm}^{-3}}\right)^{\frac{1}{2}} \text{m}^{-1}$ $\frac{1}{\kappa} \sim 1 \text{ nm for } \text{c} = 0.1 \text{ M and}$ $\frac{1}{\kappa} \sim 10 \text{ nm for } \text{c} = 10^{-3} \text{ M}$ of 1:1 electrolyte

- 1) ψ_0 fixed and σ_0 adjusted:
- When the surface charge is due to adsorption of potential-determining ion. ex: Agl sol. $\rightarrow \psi_0$ is determined by the concentration of Ag⁺ (and I⁻) ions in solution.
- Addition of inert electrolyte increases κ and results in more adsorption of ion to keep ψ_0 approximately constant.
- 2) σ_0 fixed and ψ_0 adjusted:
- The charge density at an ionogenic surface remains constant upon adding an inert electrolyte and ψ_0 decreases.
 - ex: protein solution

Gouy-Chapman model for spherical interface

$$\nabla^2 \psi = \frac{1}{r^2} \frac{\mathrm{d}}{\mathrm{d}r} \left(\frac{r^2 \mathrm{d}\psi}{\mathrm{d}r} \right) = \frac{2zen_0}{\epsilon} \sinh \frac{ze\psi}{kT} \qquad (7.11)$$

within Debye-Hückel approximation

$$\nabla^2 \psi = \kappa^2 \psi$$

Boundary conditions

$$\psi = 0, \, d\psi/dr = 0 \text{ at } r = \infty$$

 $\psi = \psi_0 \, \frac{a}{r} \, \exp[-\kappa (r - a)]$



 Debye-Hückel approximation (zeψ << ~ 25 meV) is often not a good one for colloid and surface phenomena. Unapproximated, numerical solution to eq.(7.11) can be computed.

Stern model

Modification of the Gouy-Chapman model by considering

- 1. Finite size of ion: ions cannot approach the surface (Stern plane) within the radius of hydrated ion.
- 2. Specific ion adsorption in the Stern layer is included.
- 3. EDL is divided into two parts: inner part + diffuse DL, the boundary of which is the Stern plane.
- 4. Surface of shear is located outside of the Stern plane because of the hydrated ions
- 5. The potential at the shear plane is called electrokinetic or zeta (ζ) potential, which can be measured experimentally.

Inner part of EDL(Stern layer)

- Thickness of δ ~ 5 Å
- Specifically adsorbed ions may be present.
- Oriented solvent molecules in the Stern layer has a smaller $\epsilon'(\sim 5 10) < \epsilon(= 78.5 \text{ for } H_2O)$ due to mutual depolarization.





Specific ion adsorption

- Counter-ion adsorption in Stern plane
- I(bulk) + S(surf) ↔ I(surf) + S(bulk); solvent =1, ion = 2
 K' = a₂^s a₁^b/ a₁^s a₂^b
- Assuming a 2D ideal solution for the adsorbed layer
- $a_i \sim c_i = n x_i$; n = total moles/unit surface area, x_i = mole fraction
- $a_2^s / a_1^s = x_2^s / x_1^s = x_2^s / (1 x_2^s)$
- K' $a_2^{b} / a_1^{b} = a_1^{s} / a_2^{s} = x_2^{s} / (1 x_2^{s})$
- Solving for x_2^s , $x_2^s = K' (a_2^b / a_1^b) / {(1 + K'(a_2^b / a_1^b))} = 1/ {1 + (a_1^b / K' a_2^b)}$
- Since $\mathbf{x}_2^s + \mathbf{x}_1^s = 1$, $\mathbf{x}_2^s = \mathbf{\theta}$ (coverage).
- Letting K' $/a_1^{b} = K$ (a new constant), $\theta = K a_2^{b} / (1 + K a_2^{b})$.
- This is one form of the Langmuir adsorption isotherm.
 cf: for gas adsorption θ = Kp/ (1+Kp)
- $\Delta G^0 = RT \ln K$
- $\Delta G^0 = \Delta H^0 T\Delta S^0 \sim \Delta H^0 = \Delta E^0$ (no PV term involved) = $N_{\Delta} (ze \psi_d + \Phi) \rightarrow K = exp\{-N_{\Delta}(ze \psi_d + \Phi)/RT\}$

 $(\Phi = van der Waals term)$

- The electrical interaction is the dominant term at RT.
- Let σ_1 is the surface charge density due to specifically adsorbed ions.
- $x_2^s = \sigma_1 / \sigma_m = 1 / \{1 + (a_1^b / Ka_2^b)\} \sim 1 / \{1 + (c_1^b / Kc_2^b)\}$
- $c_1^{b}/c_2^{b} = (1/V_m) / (n_0/N_A)$, where V_m is the molar volume of solvent.

 $\cdot \sigma_1 = \sigma_m / [1 + (N_A / V_m n_0) \exp\{(ze\psi_d + \Phi)/kT\}]$





- a) Reversal of charge due to the adsorption of surface-active or polyvalent counter-ions.
- b) Adsorption of surface-active co-ions.

Capacitance of EDL

- Usually counter-ion adsorption is dominant.
- Adsorption of polyvalent ions can result is charge reversal.

I. If there is no specifically adsorbed ions

$$C_1 = \frac{\sigma_0}{\psi_0 - \psi_d}$$
 and $C_2 = \frac{\sigma_0}{\psi_d} \rightarrow \psi_d = \frac{C_1 \psi_0}{C_1 + C_2}$

II. If specifically adsorbed ions are present

$$\sigma_{0} + \sigma_{1} + \sigma_{2} = 0 ; \text{ electrical neutrality}$$

$$\sigma_{0} = \frac{\epsilon'}{\delta} (\psi_{0} - \psi_{d}), \ \sigma_{1} = \frac{\sigma_{m}}{1 + \frac{N_{A}}{n_{0}v_{m}} \exp\left[\frac{ze\psi_{d} + \phi}{kT}\right]}$$

$$\sigma_{0} + \sigma_{1} + \sigma_{2} =$$

$$\frac{\epsilon}{\delta}(\psi_0 - \psi_d) + \frac{\sigma_m}{1 + \frac{N_A}{n_0 V_m} \exp\left[\frac{ze\psi_d + \phi}{kT}\right]} - (8n_0\epsilon kT)^{1/2}\sinh\frac{ze\psi_d}{2kT} = 0$$

$$\begin{array}{c}
0 \\
\psi_{d} \\
\psi_{0} \\
\psi_{0} \\
\hline
\end{array}
\begin{array}{c}
1/\kappa \\
\sigma_{1} \\
\sigma_{0} \\
\sigma_{0} \\
\sigma_{0} \\
\sigma_{0} \\
\hline
\end{array}
\begin{array}{c}
-\sigma_{2} \\
\sigma_{2} \\
\sigma_{2} \\
\sigma_{0} \\
\sigma_{0} \\
\sigma_{0} \\
\sigma_{0} \\
\sigma_{0} \\
\hline
\end{array}
\begin{array}{c}
C2 \\
C2 \\
C1 \\
\hline
\end{array}$$

- $\frac{\overline{C} \overline{C_1} C_2}{\psi_d} = \epsilon \kappa = 2.28 \left(\frac{cz^2}{\text{mol dm}^{-3}} \right)^{\frac{1}{2}} \text{F m}^{-2} \text{ for aqueous electrolyte at } 25^{\circ}\text{C}$ (1) • For Hg- aqueous electrolyte interfaces C can be measured from electrocapillary measurements and
- for Agl- aqueous electrolyte interfaces from potentiometric measurements.
- C_2 can be calculated from the eq.(1) above.
- Then, from $C_1 = \epsilon'/\delta$ (Stern layer capacitance) can be obtained.
- For the AgI- aqueous electrolyte interface C1! 0.1- 0.2 Fm⁻².
- Taking $\delta = 5$ Å, one gets $\epsilon' = 5-10$ (<< $\epsilon = 78.5$ for H₂O at RT) \rightarrow ordering of H₂O in the Stern layer.



Electrocapilarity

Lippmann apparatus

- Ideally non-polarizable normal calomel electrode (reference)
- Hg electrode in contact with nonreactive salt solution (ideally polarizable electrode).
- When a potential Φ is to the Hg electrode, charge accumulates at its surface.
- Simultaneously, the γ of Hg changes to cause a shift of the meniscus, which is observed with a microscope.
- dG = γ dA + Φ dQ at fixed T,P, and μ .
- Similarly to the Gibbs-Duhem equation, A dy + Q d $\Phi = 0 \rightarrow (\partial \gamma / \partial \Phi)_{T,P,u} = - Q/A = \sigma$
- The capacitance of the EDL is $C = (\partial Q / \partial \Phi) / A = - (\partial^2 \gamma / \partial \Phi^2); \text{ constant} \rightarrow \text{ parabolic } \gamma - \Phi \text{ curve.}$
- γ is maximum when the surface is not charged.
- For an inert electrolyte such as K_2CO_3 , γ_{max} occurs at Φ Φ_{NCE} = 0.48 V.
- For other electrolytes the maximum shifts due to specific ion adsorption.
 Ex: ion adsorption (OH⁻, Cl⁻, Br⁻, CNS⁻ etc.) as shown in the Figure.



Lippmann apparatus



electrocapillary curve

Surface potentials

- The measurable electric potential difference φ between the solid interior and the bulk solution varies according to the Nernst equation; E = E^o RT lnQ/ vF Ex: For a Agl-aqueous electrolyte interface dφ /d(pAg) = 2.303 RT/F (= 59 mV at 25 C)
- $\phi = \psi + \chi$, where χ is due to adsorbed ions and orientation dipolar solvent.

• Experimentally,
$$\left(\frac{d\zeta}{d(pAg)}\right)_{\zeta \to 0} = -40 \text{ mV}$$
 at RT was found.

•
$$\left(\frac{\mathrm{d}\zeta}{\mathrm{d}(\mathrm{pAg})}\right)_{\zeta \to 0} = \left(\frac{\mathrm{d}\psi_0}{\mathrm{d}(\mathrm{pAg})}\right) \left(\frac{\mathrm{d}\psi_d}{\mathrm{d}\psi_0}\right)_{\zeta \to 0} = -59 \frac{C_1}{C_1 + C_2} \mathrm{mV}$$
 (1)

- The measures C₁ and C₂ values are qualitatively consisten with the above eq.(1)
- The Stern layer model and the assumptions made are qualitatively correct.





Electrokinetic Phenomena

Relative motion between charged surface and diffuse double layer

- 1. Electrophoresis: $\mathscr{E} \rightarrow$ charge particle movement.
- 2. Electro-osmosis: $\mathscr{E} \rightarrow DL$ layer movement against fixed surface charge.
- 3. Streaming potential: DL layer movement $\rightarrow \mathscr{E}$ generation.
- 4. Sedimentation potential: charge particle movement $\rightarrow \mathscr{C}$ generation.

- All arising from the relative movement of particle with respect to the liquid.
- \mathscr{F} field \rightarrow relative motion: Electrophoresis, electro-osmosis
- relative motion $\rightarrow \mathscr{E}$ field: Streaming potential,

sedimentation potential