

電気二重層: Electric Double Layer

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1 Basics

The dielectric flux density \mathbf{D} (電束密度) is related to the charge density $\rho(\mathbf{r})$

$$\operatorname{div}\mathbf{D} = \rho(\mathbf{r}) \quad (1)$$

$$\mathbf{D} = \epsilon\epsilon_0\mathbf{E} = -\epsilon\epsilon_0\operatorname{grad}\phi \quad (2)$$

¹Here ϵ and ϵ_0 are the dielectric constant (with no dimension) and electric permittivity of free space [$8.854187817 \times 10^{-12} \text{ Fm}^{-1}$ ($= \text{CV}^{-1}\text{m}^{-1}$)], respectively. \mathbf{E} and ϕ is the electric field and the potential. Using the Gauss theorem

$$\int_V d\mathbf{r} \underbrace{\nabla \cdot \mathbf{D}}_{\rho} = \int_S \mathbf{D} \cdot d\mathbf{S} \quad (3)$$

In the limit that the Gauss box is very thin (thickness $\rightarrow 0$)

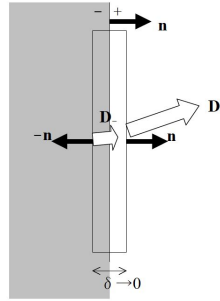


Figure 1:

$$\int_V d\mathbf{r} \rho = Q_{\text{box}} = \mathbf{n} \cdot [-\mathbf{D}_- + \mathbf{D}_+]S \quad (4)$$

where vector \mathbf{n} means the surface normal unit vector pointing from media (dark part of the Fig.1) (-) to (+).

$$\mathbf{n} \cdot [-\mathbf{D}_- + \mathbf{D}_+] = [-(\mathbf{D}_-)_z + (\mathbf{D}_+)_z] = Q_{\text{box}}/S = \sigma \quad (5)$$

where σ means the interface charge density. Using $(\mathbf{D}_+)_z = -\epsilon_0\epsilon_+ d\phi/dz|_+$, we can write

この式がポイント !!

$$\epsilon_0\epsilon_- \left. \frac{d\phi}{dz} \right|_- - \epsilon_0\epsilon_+ \left. \frac{d\phi}{dz} \right|_+ = \sigma \quad (6)$$

すなわち、ある面で分布している電荷がある時や、面の左右で誘電率が不連続であると、電位は連続になるが電位勾配は不連続（キック）になる。

¹ $\operatorname{div}\mathbf{D} = \rho$ は正（負）電荷から出（入）ていく電気力線の数はその電荷に比例するということを意味する。Appendix 参照のこと

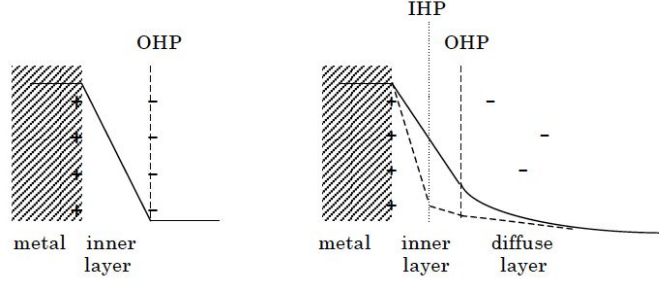


Figure 2: Electric double layer: Helmholtz model(left) and Gouy-Chapman-Stern model(right)

2 Helmholtz model

In this model the counter ion is located only at the outer Helmholtz plane(OHP) (See Fig.2 left)

$$\sigma_M + \sigma_{OHP} = 0 \quad (7)$$

There is no electric field(potential slope is zero) in the metal, thereby at the metal surface

$$-\epsilon_0 \epsilon_{\text{inner}} \left. \frac{d\phi}{dz} \right|_{M+} = \sigma_M \quad (8)$$

There is no field outside OHP because there is no charge

$$\epsilon_0 \epsilon_{\text{inner}} \left. \frac{d\phi}{dz} \right|_{OHP-} = \sigma_{OHP} \quad (9)$$

From Eq.(7)

$$\frac{d\phi}{dz} = -\frac{\sigma_M}{\epsilon_0 \epsilon_{\text{inner}}} = \text{const.} \quad \text{at inner layer} \quad (10)$$

If the thickness of the inner layer is given by d , the potential drop $\Delta\phi$ is given by

$$\Delta\phi = -\frac{\sigma_M}{\epsilon_0 \epsilon_{\text{inner}}} d \quad (11)$$

This is the analog of capacitor

$$Q = CV, \quad C = \frac{\epsilon_0 \epsilon S}{d}, \quad i = \frac{dQ}{dt} = C \frac{dV}{dt} \quad (12)$$

3 Gauss law in the diffuse layer

Now we assume the charge density of the electrolyte change in the z direction. Then we just consider z -dependence of the dielectric flux density and potential.

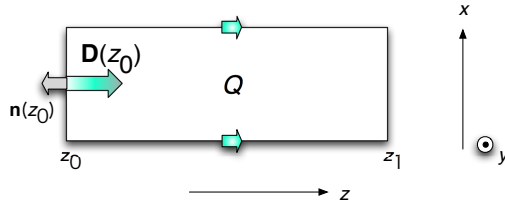


Figure 3: Gauss box of the diffuse layer

At $z = z_1$ we assume $\phi(z_1) = 0$ and $d\phi(z_1)/dz = 0$. If we apply the Gauss law to this box,

$$\int_V d\mathbf{r} \underbrace{\nabla \cdot \mathbf{D}}_{\rho} = \int_S \mathbf{D} \cdot d\mathbf{S} \quad (13)$$

There are six planes in this box, but there is only one plane where the surface normal component of the electric flux density is non-zero.

$$Q = \mathbf{D}(z_0^+) \cdot \mathbf{n}(z_0)S = -(\mathbf{D})_z|_{z_0^+}S = -\left(-\epsilon_0\epsilon\frac{d\phi}{dz}\right)\Big|_{z_0^+}S \quad (14)$$

$$\epsilon_0\epsilon\frac{d\phi}{dz}\Big|_{z_0^+} = \frac{Q}{S} \quad (15)$$

If the diffuse layer is located at the right side,

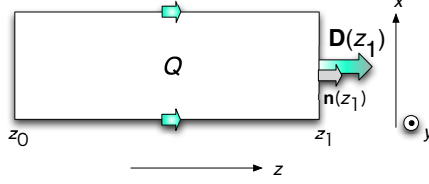


Figure 4: Gauss box of the diffuse layer. In this case the diffuse layer is located at the right side.

$$Q = \mathbf{D}(z_1^-) \cdot \mathbf{n}(z_1)S = (\mathbf{D})_z|_{z_1^-}S = -\epsilon_0\epsilon\frac{d\phi}{dz}\Big|_{z_1^-}S \quad (16)$$

$$\epsilon_0\epsilon\frac{d\phi}{dz}\Big|_{z_1^-} = -\frac{Q}{S} \quad (17)$$

4 Gouy-Chapman-Stern model with specific adsorption at inner Helmholtz plane (Fig.2 right)

To explain the experimental results the electric double layer of the series capacitor with inner and diffuse layer is used. (Gouy-Chapman-Stern model) Halogen ions such as Cl^- , Br^- , I^- adsorb on the noble metal electrode. We assume that this specific adsorption is taken place on the inner Helmholtz plane (IHP). Please note that the from the electrode to the OHP there is no charge but neutral solvent molecules can enter. Then the position OHP z_{OHP} may be given by the radius of the electrolyte ions with the smallest size. This model automatically include the cases (I) no specific adsorption $\sigma_{\text{IHP}} = 0$ (GCS), (II) no Stern layer and no adsorption (GC theory).

$$\sigma_M + \sigma_{\text{IHP}} + \sigma_{\text{OHP}} + \sigma_{\text{GC}} = 0, \quad \sigma_{\text{OHP}} = 0 \quad (18)$$

$$\frac{d\phi}{dz}\Big|_{\text{M}-} = 0 \quad (19)$$

$$\sigma_M = -\epsilon_0\epsilon_{\text{inner}}\frac{d\phi}{dz}\Big|_{\text{M}+} \quad (20)$$

$$= -\epsilon_0\epsilon_{\text{inner}}\frac{\phi_{\text{IHP}} - \phi_M}{d_{\text{IHP}}} \quad (21)$$

$$\epsilon_0\epsilon_{\text{inner}}\frac{d\phi}{dz}\Big|_{\text{IHP}-} - \epsilon_0\epsilon_{\text{inner}}\frac{d\phi}{dz}\Big|_{\text{IHP}+} = \sigma_{\text{IHP}} \quad (22)$$

$$\epsilon_0\epsilon_{\text{inner}}\frac{d\phi}{dz}\Big|_{\text{OHP}-} - \epsilon_0\epsilon_{\text{GC}}\frac{d\phi}{dz}\Big|_{\text{OHP}+} = \sigma_{\text{OHP}} = 0 \quad (23)$$

$$\sigma_{\text{GC}} = -(\sigma_M + \sigma_{\text{IHP}}) = \epsilon_0\epsilon_{\text{GC}}\frac{d\phi}{dz}\Big|_{\text{OHP}+} \quad (24)$$

At diffuse layer $z > z_{\text{OHP}}$, the GC theory can be applied

$$\text{div}\mathbf{D} = \rho, \quad \mathbf{D} = \epsilon_0\epsilon\mathbf{E}, \quad \mathbf{E} = -\nabla\phi \quad (25)$$

$$\rho = e \sum_i Z_i n_i^0 \exp\left(\frac{-Z_i e \phi(\mathbf{r})}{k_B T}\right) \quad (26)$$

$$-\epsilon_0 \nabla \cdot (\epsilon(\mathbf{r}) \nabla \phi(\mathbf{r})) = e \sum_i Z_i n_i^0 \exp\left(\frac{-Z_i e \phi(\mathbf{r})}{k_B T}\right) \quad (27)$$

$$\frac{d^2 \phi}{dz^2} = -\frac{e}{\epsilon_0 \epsilon_{GC}} \sum_i Z_i n_i^0 \exp\left(\frac{-Z_i e \phi(z)}{k_B T}\right) \quad (28)$$

$$\frac{d}{dz} \left(\frac{d\phi}{dz} \right) = \frac{d\phi}{dz} \frac{d}{d\phi} \left(\frac{d\phi}{dz} \right) = \frac{1}{2} \frac{d}{d\phi} \left(\frac{d\phi}{dz} \right)^2 \quad (29)$$

Then

$$\int d \left(\frac{d\phi}{dz} \right)^2 = -\frac{2e}{\epsilon_0 \epsilon_{GC}} \int d\phi \sum_i Z_i n_i^0 \exp\left(\frac{-Z_i e \phi(z)}{k_B T}\right) \quad (30)$$

$$\left(\frac{d\phi}{dz} \right)^2 = \frac{2k_B T}{\epsilon_0 \epsilon_{GC}} \sum_i n_i^0 \exp\left(\frac{-Z_i e \phi(z)}{k_B T}\right) + \text{constant} \quad (31)$$

$$= \frac{2k_B T}{\epsilon_0 \epsilon_{GC}} \sum_i n_i^0 \left[\exp\left(\frac{-Z_i e \phi(z)}{k_B T}\right) - 1 \right] \quad (32)$$

where we assume that $\phi = 0$ and $d\phi/dz = 0$ at $z = \infty$. **We have two solutions** $d\phi/dz = \pm \sqrt{\dots}$!!, and take "−" for $\phi = 0, d\phi/dz = 0$ at $z \rightarrow \infty$ and take "+" or $\phi = 0, d\phi/dz = 0$ at $z \rightarrow -\infty$. We will see the reason why below.

$$\frac{d\phi}{dz} = -\sqrt{\frac{2k_B T}{\epsilon_0 \epsilon_{GC}} \sum_i n_i^0 \left[\exp\left(\frac{-Z_i e \phi(z)}{k_B T}\right) - 1 \right]} \quad (33)$$

4.1 symmetric electrolyte

If the electrolyte is symmetric ($Z : Z$ electrolyte), i.e. $Z_+ = -Z_- = Z$,

(In the case of the unsymmetrical electrolytes such as 1:2, 2:1, the analytical solutions was given by David C. Grahame. JCP, 21, 1054-1060. However I recommend the numerical solution of Poisson-Boltzman equation (Eqs.27-28) in the 1D case for complicated electrolytes.)

$$\sum_i n_i^0 \left[\exp\left(\frac{-Z_i e \phi(z)}{k_B T}\right) - 1 \right] = n^0 \left[\exp\left(\frac{-Z e \phi(z)}{k_B T}\right) + \exp\left(\frac{Z e \phi(z)}{k_B T}\right) - 2 \right] \quad (34)$$

$$= 4n^0 \sinh^2\left(\frac{Z e \phi}{2k_B T}\right) \quad (35)$$

$$\sinh^2(X/2) = \left(\frac{e^{X/2} - e^{-X/2}}{2} \right)^2 = \frac{e^X + e^{-X} - 2}{4} \quad (36)$$

$$\frac{d\phi}{dz} = -\sqrt{\frac{8k_B T n^0}{\epsilon_0 \epsilon_{GC}}} \sinh\left(\frac{Z e \phi}{2k_B T}\right) \quad (37)$$

The number density n^0/m^{-3} is given by $n^0 = 1000 N_A c^*$ where the concentration of electrolyte in bulk is given by $c^*/\text{mol dm}^{-3}$, Avogadro constant N_A/mol^{-1} .

If the electrolyte is symmetric ($Z : Z$ electrolyte), i.e. $Z_+ = -Z_- = Z$,

$$\frac{d\phi}{dz} = -\sqrt{\frac{8000k_B T N_A c^*}{\epsilon_0 \epsilon_{GC}}} \sinh\left(\frac{Z e \phi}{2k_B T}\right) \quad (38)$$

Potential profiles $\phi(z)$ can be obtained by the integral

$$\int_{\phi_{\text{OHP}}}^{\phi} \frac{d\phi}{\sinh\left(\frac{Z e \phi}{2k_B T}\right)} = -\sqrt{\frac{8k_B T n^0}{\epsilon_0 \epsilon_{GC}}} \int_{z_{\text{OHP}}}^z dz \quad (39)$$

$\exp(Ze\phi/(2k_B T)) = \Phi$ とすると

$$\phi = \frac{2k_B T}{Ze} \ln \Phi, \quad d\phi = \frac{2k_B T}{Ze} \frac{d\Phi}{\Phi} \quad (40)$$

$$\int_{\Phi_{\text{OHP}}}^{\Phi} \frac{2k_B T}{Ze} \frac{2d\Phi}{\Phi(\Phi - \Phi^{-1})} = -\sqrt{\frac{8k_B T n^o}{\epsilon_0 \epsilon_{GC}}} (z - z_{\text{OHP}}) \quad (41)$$

$$\frac{2}{\Phi^2 - 1} = \frac{1}{\Phi - 1} - \frac{1}{\Phi + 1} \quad (42)$$

$$\frac{2k_B T}{Ze} \left(\ln \left| \frac{\Phi - 1}{\Phi + 1} \right| - \ln \left| \frac{\Phi_{\text{OHP}} - 1}{\Phi_{\text{OHP}} + 1} \right| \right) = -\sqrt{\frac{8k_B T n^o}{\epsilon_0 \epsilon_{GC}}} (z - z_{\text{OHP}}) \quad (43)$$

$$\begin{aligned} &= \frac{2k_B T}{Ze} \left(\ln \left| \frac{\exp(Ze\phi/(2k_B T)) - 1}{\exp(Ze\phi/(2k_B T)) + 1} \right| - \ln \left| \frac{\exp(Ze\phi_{\text{OHP}}/(2k_B T)) - 1}{\exp(Ze\phi_{\text{OHP}}/(2k_B T)) + 1} \right| \right) \\ &= \frac{2k_B T}{Ze} \ln \left[\frac{\tanh(Ze\phi/(4k_B T))}{\tanh(Ze\phi_{\text{OHP}}/(4k_B T))} \right] \end{aligned} \quad (44)$$

If the electrolyte is symmetric ($Z : Z$ electrolyte), i.e. $Z_+ = -Z_- = Z$,

$$\frac{\tanh(Ze\phi/(4k_B T))}{\tanh(Ze\phi_{\text{OHP}}/(4k_B T))} = \exp[-\kappa(z - z_{\text{OHP}})], \quad \kappa = \sqrt{\frac{2Z^2 e^2 n^o}{\epsilon_0 \epsilon_{GC} k_B T}} \quad (45)$$

The potential profile are shown in Fig.4.1.

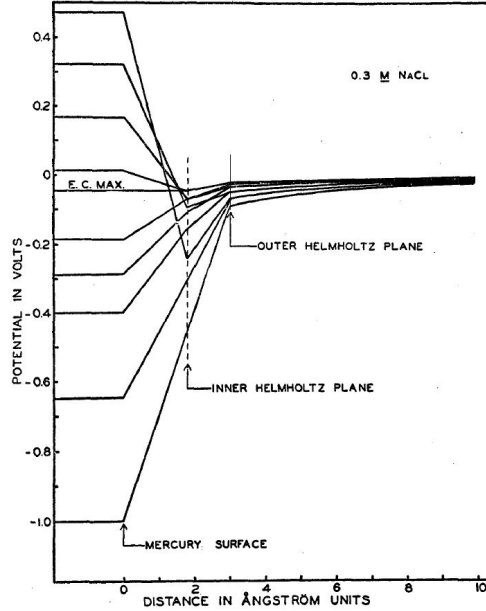


Figure 5: Calculated potential profiles in EDL for Hg in contact with 0.3 M NaCl at 298 K. At positive electrode potentials the profile has a sharp minimum at IHP because Cl^- is specifically adsorbed. D. C. Grahame, *Chem. Rev.* **1947**, **41**, 441-501.

In the case that $\phi = 0, d\phi/dz = 0$ at $z \rightarrow -\infty$, we take "plus" term in Eq.(32) and the integrals are changed from z to z_{OHP} .

$$\frac{d\phi}{dz} = \sqrt{\frac{8000k_B T N_{Ac}^*}{\epsilon_0 \epsilon_{GC}}} \sinh \left(\frac{Ze\phi}{2k_B T} \right) \quad (46)$$

$$\int_{\phi}^{\phi_{\text{OHP}}} d\phi \dots = +\sqrt{\dots/\dots} \int_z^{z_{\text{OHP}}} \quad (47)$$

$$\frac{\tanh(Ze\phi/(4k_B T))}{\tanh(Ze\phi_{\text{OHP}}/(4k_B T))} = \exp[\kappa(z - z_{\text{OHP}})], \quad \kappa = \sqrt{\frac{2Z^2 e^2 n^o}{\epsilon_0 \epsilon_{GC} k_B T}} \quad (48)$$

4.2 In the case of no specific adsorption

Let's consider case (I): no specific adsorption. In this case $\sigma_{\text{IHP}} = 0$, then

$$\sigma_M = -\epsilon_0 \epsilon_{\text{inner}} \left. \frac{d\phi}{dz} \right|_{M+} \quad (49)$$

$$\epsilon_0 \epsilon_{\text{inner}} \left. \frac{d\phi}{dz} \right|_{\text{IHP}-} - \epsilon_0 \epsilon_{\text{inner}} \left. \frac{d\phi}{dz} \right|_{\text{IHP}+} = \sigma_{\text{IHP}} = 0 \quad (50)$$

$$\epsilon_0 \epsilon_{\text{inner}} \left. \frac{d\phi}{dz} \right|_{\text{OHP}-} - \epsilon_0 \epsilon_{\text{GC}} \left. \frac{d\phi}{dz} \right|_{\text{OHP}+} = \sigma_{\text{OHP}} = 0 \quad (51)$$

$$\sigma_{\text{GC}} = -(\sigma_M + \sigma_{\text{IHP}}) = -\sigma_M = \epsilon_0 \epsilon_{\text{GC}} \left. \frac{d\phi}{dz} \right|_{\text{OHP}+} \quad (52)$$

There is no charge in the Stern(inner) layer and if we assume $\epsilon_{\text{inner}} = \epsilon_{\text{GC}} (= \epsilon_W)$,

$$\left. \frac{d\phi}{dz} \right|_{M+} = \left. \frac{d\phi}{dz} \right|_{\text{OHP}+} \quad (53)$$

$$\begin{aligned} \sigma_M &= -\epsilon_0 \epsilon_W \left. \frac{d\phi}{dz} \right|_{M+} = -\epsilon_0 \epsilon_W \left. \frac{d\phi}{dz} \right|_{\text{OHP}+} = \epsilon_0 \epsilon_W \sqrt{\frac{8k_B T n^o}{\epsilon_0 \epsilon_W}} \sinh\left(\frac{Ze\phi_{\text{OHP}}}{2k_B T}\right) \\ &= \sqrt{8k_B T \epsilon_0 \epsilon_W n^o} \sinh\left(\frac{Ze\phi_{\text{OHP}}}{2k_B T}\right) \end{aligned} \quad (54)$$

In the last equation we assume that the electrolyte is symmetric ($Z : Z$ electrolyte), i.e. $Z_+ = -Z_- = Z$. The number density n^o/m^{-3} is given by $n^o = 1000 N_A c^*$ where the concentration of electrolyte in bulk is given by $c^*/\text{mol dm}^{-3}$, Avogadro constant N_A/mol^{-1} .

$$\sigma_M = \sqrt{8000 k_B T N_A \epsilon_0 \epsilon_W c^*} \sinh\left(\frac{Ze\phi_{\text{OHP}}}{2k_B T}\right) \quad (55)$$

$$\phi_{\text{OHP}} = \frac{2k_B T}{Ze} \operatorname{arcsinh}\left(\frac{\sigma_M}{\sqrt{8000 N_A k_B T \epsilon_0 \epsilon_W c^*}}\right) \quad (56)$$

If we know the surface charge density σ_M we can get ϕ_{OHP} .

$$\phi_{\text{OHP}} = \frac{2k_B T}{Ze} \ln(X + \sqrt{X^2 + 1}) \quad (57)$$

$$X \equiv \frac{\sigma_M}{\sqrt{8000 N_A k_B T \epsilon_0 \epsilon_W c^*}} \quad (58)$$

2

4.3 concentration dependence of the electric double layer effect

If $Z = 1$, $\sigma_M < 0$, and $|Ze\phi_{\text{OHP}}| > 2k_B T$ ($\phi_{\text{OHP}} < -52$ mV at 300 K, $\sinh x \simeq -e^{-x}/2$), then

$$\exp\left(-\frac{e\phi_{\text{OHP}}}{2k_B T}\right) \simeq -2c^{*-1/2} \frac{\sigma_M}{\sqrt{8000 N_A k_B T \epsilon_0 \epsilon_W}}$$

2

$$\sinh x = \frac{e^x - e^{-x}}{2} \equiv X, \quad \operatorname{arcsinh} x = \ln(x + \sqrt{x^2 + 1}) \quad (59)$$

$$X^2 = \frac{e^{2x} + e^{-2x} - 2}{4}, \quad X^2 + 1 = \frac{e^{2x} + e^{-2x} + 2}{4}, \quad \sqrt{X^2 + 1} = \frac{e^x + e^{-x}}{2}, \quad X + \sqrt{X^2 + 1} = e^x$$

$$\ln(X + \sqrt{X^2 + 1}) = x = \operatorname{arcsinh} \sinh x = \operatorname{arcsinh} X, \quad \operatorname{arcsinh} X = \ln(X + \sqrt{X^2 + 1})$$

$$\tanh x = \frac{\sinh x}{\cosh x} = \frac{e^x - e^{-x}}{e^x + e^{-x}} = \frac{e^{2x} - 1}{e^{2x} + 1} \equiv X$$

$$e^{2x} - 1 = X(e^{2x} + 1), \quad e^{2x}(1 - X) = X + 1, \quad e^{2x} = \frac{1 - X}{1 + X}, \quad x = \frac{1}{2} \ln \left| \frac{1 - X}{1 + X} \right|$$

$$\operatorname{arctanh}(\tanh x) = \operatorname{arctanh} X = x = \frac{1}{2} \ln \left| \frac{1 - X}{1 + X} \right|, \quad \operatorname{arctanh} X = \frac{1}{2} \ln \left| \frac{1 - X}{1 + X} \right| \quad (60)$$

$$\begin{aligned}
\phi_{\text{OHP}} &= -\frac{2k_B T}{e} \ln \left(-2c^{*-1/2} \frac{\sigma_M}{\sqrt{8000N_A k_B T \epsilon_0 \epsilon_W}} \right) \\
&= -\frac{2k_B T}{e} \left(-\frac{1}{2} \ln c^* + \ln \left(-2 \frac{\sigma_M}{\sqrt{8000N_A k_B T \epsilon_0 \epsilon_W}} \right) \right) \quad (61)
\end{aligned}$$

The concentration dependence of the redox reaction rate can be calculated when we assume $\phi_2 = \phi_{\text{OHP}}$

$$\ln k_{\text{app}} = \ln k^0 + \frac{(\alpha n - z)e\phi_2}{k_B T} = \ln k^0 + \frac{(\alpha n - z)e\phi_{\text{OHP}}}{k_B T} \quad (62)$$

$$\begin{aligned}
&= \ln k^0 + \frac{(\alpha n - z)e}{k_B T} \left(-\frac{2k_B T}{e} \right) \left(-\frac{1}{2} \ln c^* + \ln \left(-2 \frac{\sigma_M}{\sqrt{8000N_A k_B T \epsilon_0 \epsilon_W}} \right) \right) \\
&= \ln k^0 - 2(\alpha n - z) \left(-\frac{1}{2} \ln c^* + \ln \left(-2 \frac{\sigma_M}{\sqrt{8000N_A k_B T \epsilon_0 \epsilon_W}} \right) \right) \quad (63)
\end{aligned}$$

$$\log_{10} k_{\text{app}} = (\log_{10} e) \ln k_{\text{app}} \quad (64)$$

³ If $Z = 1$, $\sigma_M > 0$, and $|Ze\phi_{\text{OHP}}| > 2k_B T$ ($\phi_{\text{OHP}} > 52$ mV at 300 K, $\sinh x \simeq e^x/2$), then

$$\begin{aligned}
\exp \left(\frac{e\phi_{\text{OHP}}}{2k_B T} \right) &\simeq 2c^{*-1/2} \frac{\sigma_M}{\sqrt{8000N_A k_B T \epsilon_0 \epsilon_W}} \\
\phi_{\text{OHP}} &= \frac{2k_B T}{e} \ln \left(2c^{*-1/2} \frac{\sigma_M}{\sqrt{8000N_A k_B T \epsilon_0 \epsilon_W}} \right) \\
&= \frac{2k_B T}{e} \left(-\frac{1}{2} \ln c^* + \ln \left(2 \frac{\sigma_M}{\sqrt{8000N_A k_B T \epsilon_0 \epsilon_W}} \right) \right) \quad (65)
\end{aligned}$$

The concentration dependence of the redox reaction rate can be calculated when we assume $\phi_2 = \phi_{\text{OHP}}$

$$\begin{aligned}
\ln k_{\text{app}} &= \ln k^0 + \frac{(\alpha n - z)e}{k_B T} \left(\frac{2k_B T}{e} \right) \left(-\frac{1}{2} \ln c^* + \ln \left(2 \frac{\sigma_M}{\sqrt{8000N_A k_B T \epsilon_0 \epsilon_W}} \right) \right) \\
&= \ln k^0 + 2(\alpha n - z) \left(-\frac{1}{2} \ln c^* + \ln \left(2 \frac{\sigma_M}{\sqrt{8000N_A k_B T \epsilon_0 \epsilon_W}} \right) \right) \quad (66)
\end{aligned}$$

3

$$\begin{aligned}
\exp(\ln x) &= x, & \ln e^x &= x, & 10^{\log_{10} x} &= x, & \log_{10} 10^x &= x \\
e^x &= y \\
\ln e^x &= x = \ln y, & \log_{10} e^x &= x \log_{10} e = \log_{10} y \\
\ln y \log_{10} e &= \log_{10} y, & \ln y &= \frac{\log_{10} y}{\log_{10} e} \\
\log_{10} e &= 0.4342944818, & \frac{1}{\log_{10} e} &= 2.302585094
\end{aligned}$$

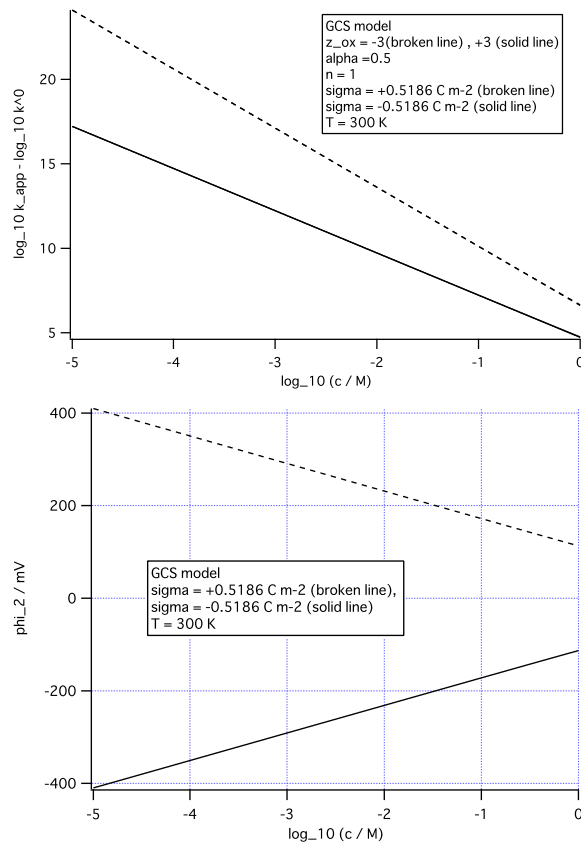


Figure 6: Dependence of the rate constant (top) and ϕ_2 (bottom) on the electrolyte solution. The calculation is done by GCS model and the parameters used are shown in the figures. In the top figure the calculated results by Eq.(44) and (45) are shown and they give the almost the same results, because the condition $|Ze\phi_{\text{OHP}}| > 2k_B T$ ($\phi_{\text{OHP}} < -52$ mV at 300 K) is satisfied. The difference of the slope of the top figure is due to $(\alpha n - z)e/(k_B T)$.

5 Appendix

電気化学を専門としている学生諸氏の間で電気二重層がよくわからないという声を良く聞く。電気二重層の理論は、電磁気学と統計・熱力学に基礎を置く。化学系の学生は、電磁気学（より正確にはガウスの法則）を理解していないことが、よくわからない原因であるようだ。以下それを解説した。

5.1 発散, divergence, Gauss の定理

今、場所に依存したベクトル場を考えよう。例えば、場所 \mathbf{r} における物質の流速（単位時間、単位面積当たりの物質の移動速度ベクトル）を $\mathbf{J}(\mathbf{r})$ と置く。今、下図 (a) のように \mathbf{r} における立方体の微少体積 $dV = dx dy dz$ を考える。ベクトル \mathbf{J} を各成分に分けて考える（図 (b)）。

$$\mathbf{J} = J_x \mathbf{i} + J_y \mathbf{j} + J_z \mathbf{k} \quad (67)$$

微少体積に出入りする物質量は（流速×面積）の差になり、その合計が微少体積内での物質量（密度×体積）になるので

$$\frac{\partial \rho}{\partial t} dx dy dz = [J_x(x+dx) - J_x(x)] dy dz + [J_y(y+dy) - J_y(y)] dx dz + [J_z(z+dz) - J_z(z)] dx dy \quad (68)$$

$$= \left[\frac{\partial J_x}{\partial x} dx \right] dy dz + \left[\frac{\partial J_y}{\partial y} dy \right] dx dz + \left[\frac{\partial J_z}{\partial z} dz \right] dx dy \quad (69)$$

$$\frac{\partial \rho}{\partial t} = \frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} + \frac{\partial J_z}{\partial z} \left(\mathbf{i} \frac{\partial}{\partial x} + \mathbf{j} \frac{\partial}{\partial y} + \mathbf{k} \frac{\partial}{\partial z} \right) \cdot (J_x \mathbf{i} + J_y \mathbf{j} + J_z \mathbf{k}) = \nabla \cdot \mathbf{J} = \text{div} \mathbf{J} \quad (70)$$

となる。すなわち、 \mathbf{J} の発散は微少体積に出入りする量を表す。また Eq.(68) は図 (c) において立方体の各面での法線単位ベクトル \mathbf{n} (面の外向きに方向をとる。) と \mathbf{J} との内積の和になる。すなわち、

$$\begin{aligned}
 & [J_x(x+dx) - J_x(x)]dydz + [J_y(y+dy) - J_y(y)]dxdz + [J_z(z+dz) - J_z(z)]dxdy \\
 = & \sum_{\text{six surfaces}} \mathbf{J} \cdot \mathbf{n}dS = \text{div}\mathbf{J}dxdydz \quad (71)
 \end{aligned}$$

図 (d) にあるような一般の形状をしているものを、微少体積に分割し全ての和をとると、立方体で接している面では、 $\mathbf{J} \cdot \mathbf{n}dS$ は打ち消し合い、最外表面だけが残る。(Gauss の定理)

$$\sum_{\text{all } dV} \text{div}\mathbf{J}dV = \sum_{\text{exterior surface}} \mathbf{J} \cdot \mathbf{n}dS \quad (72)$$

$$\int dV \text{div}\mathbf{J} = \int dS \mathbf{J} \cdot \mathbf{n} \quad (73)$$

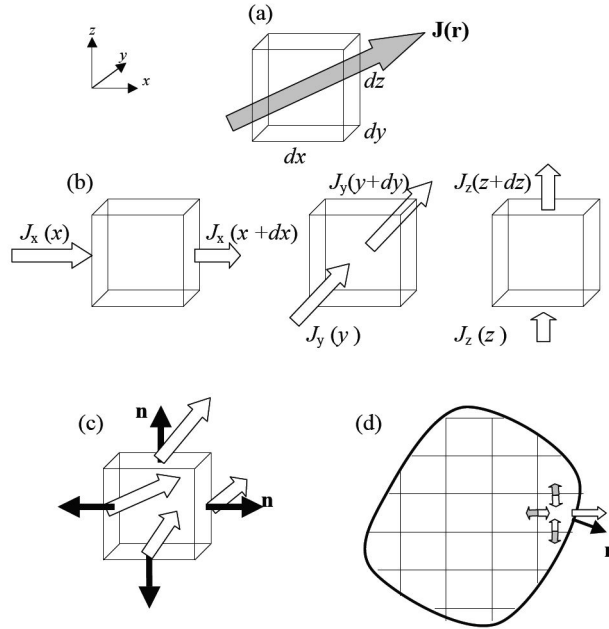


Figure 7:

5.2 Coulomb の法則, 電場, ガウスの法則

ϵ の比誘電率をもつ媒体を考える。原点にある電荷 q_0 と \mathbf{r} にある電荷 q の間に働く Coulomb 力 \mathbf{F} は、

$$\mathbf{F} = \frac{1}{4\pi\epsilon\epsilon_0} \frac{q_0 q \mathbf{r}}{r^2 r} \quad (74)$$

で与えられる。 q_0 が作る電場 \mathbf{E} は、

$$\mathbf{F} = q\mathbf{E} \quad (75)$$

で与えられるので、

$$\mathbf{E} = \frac{1}{4\pi\epsilon\epsilon_0} \frac{q_0 \mathbf{r}}{r^2 r} \quad (76)$$

である。この電場ベクトルにガウスの定理を適用すると

$$\int dS \mathbf{E} \cdot \mathbf{n} = \int dV \text{div}\mathbf{E} \quad (77)$$

電場ベクトルは球対称なので以下の図のような球面を考え、この球面上の面積分を考える。面積要素 dS の法線ベクトルは、 $\mathbf{n} = \mathbf{r}/r$ となるので

$$\int dS \mathbf{E} \cdot \mathbf{n} = \int dS \frac{1}{4\pi\epsilon\epsilon_0} \frac{q_0}{r^2} \underbrace{\left(\frac{\mathbf{r}}{r} \cdot \frac{\mathbf{r}}{r} \right)}_{=1} = \frac{1}{4\pi\epsilon\epsilon_0} \frac{q_0}{r^2} \int dS = \frac{1}{4\pi\epsilon\epsilon_0} \frac{q_0}{r^2} 4\pi r^2 = \frac{q_0}{\epsilon\epsilon_0} \quad (78)$$

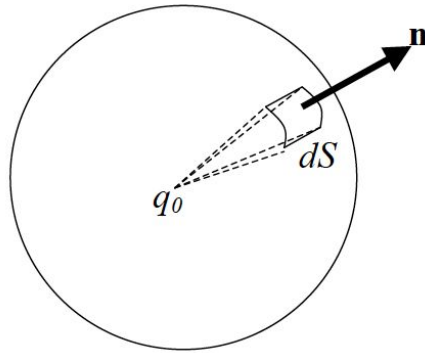


Figure 8:

q_0 は球体内にある電荷密度の積分量と見なせるので

$$\frac{q_0}{\epsilon\epsilon_0} = \frac{1}{\epsilon\epsilon_0} \int dV \rho(\mathbf{r}) = \int dV \operatorname{div} \mathbf{E} \quad (79)$$

となる。従って、

$$\operatorname{div} \mathbf{E} = \frac{\rho(\mathbf{r})}{\epsilon\epsilon_0} \quad (80)$$

$$\operatorname{div} \mathbf{D} = \rho(\mathbf{r}) \quad (81)$$

が得られる。

5.3 EDL は電気化学者にはどのように考えられているのか？

垣内隆, 第4回基礎電気化学フォーラム(2005年1月14日)の案内文(*Rev. Polarography* 2005, 51, 260. より抜粋して引用)

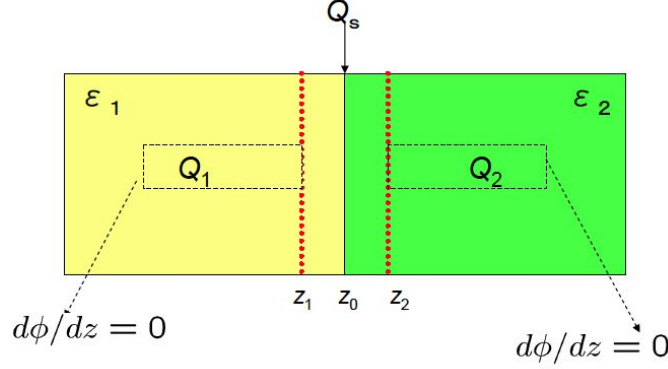
“電気二重層というのは、ボルタンメトリーで物質の分析や電子移動速度を測定するうえで、われわれを困らせる厄介者です。電流-電圧曲線の形の本質には関係がないようなので、ないとありがたいのだが、それが無い電極はおよそあり得ないから、無視するわけにもいかない。それで、電気二重層に関する勉強はどうしてもあとまわしになるし、やるとしてもさらっと済ませておこう、ということが多いのではないのでしょうか。しかし、もちろん、「つきあわなければならないから仕方なく」、という以上に、電気二重層は科学の対象としてますます興味深いし、スーパーキャパシタなどの応用を見てもわかるように、この古くから知られたせいぜい数ナノメートルの薄層の理解は今日的にも重要であることはいまでもありません。以下略”

5.4 Electric double layer at liquid-liquid interface with Gouy-Chapman-Stern model with specific adsorption at the interface

The EDL at the liquid/liquid (oil/water and room-temperature-molten-salt/water) interface can be calculated by the extension of the theory of EDL for the solid/liquid interface. The dielectric constant of DCE (and RTMS) is $\epsilon_1 = 10.42$ and that of water is $\epsilon_2 = 78.5$. The inner layer thickness of water and DCE (and RTMS) is 2.125 \AA . The inner layer thickness of water and DCE (and RTMS) is 2.125 \AA . The potential difference between the two phase is defined as

$$\Delta_o^w \phi = \phi^w - \phi^o \quad (82)$$

In the following we consider the specific adsorption at L|L interface, but if there is no specific adsorption please set $Q_s = 0$.



断面積 S のGauss Box1およびGauss Box2内の電荷 Q_1, Q_2 とし、界面に特異吸着した分子の電荷を Q_s とする。

$$\text{電気的中性の条件: } Q_1 + Q_s + Q_2 = 0$$

Figure 9: EDL at Oil (left)|Water (right) interface

Before going to the numerical calculation, we should reformulate the equations. **In the Gauss box 2** $\phi = 0, d\phi/dz = 0$ at $z \rightarrow +\infty$, we can get

$$\left. \frac{d\phi}{dz} \right|_{z_2^+} = \frac{1}{\epsilon_0 \epsilon_2} \frac{Q_2}{S} \quad (83)$$

$$\left. \frac{d\phi}{dz} \right|_{z_2^+} = -\sqrt{\frac{8000k_B T N_A c_2^*}{\epsilon_0 \epsilon_2}} \sinh\left(\frac{Ze\phi(z_2^+)}{2k_B T}\right) \quad (84)$$

$$\frac{1}{\epsilon_0 \epsilon_2} \frac{Q_2}{S} = -\sqrt{\frac{8000k_B T N_A c_2^*}{\epsilon_0 \epsilon_2}} \sinh\left(\frac{Ze\phi(z_2^+)}{2k_B T}\right) \quad (85)$$

$$-\frac{1}{\sqrt{8000\epsilon_0 \epsilon_2 k_B T N_A c_2^*}} \frac{Q_2}{S} = \sinh\left(\frac{Ze\phi(z_2^+)}{2k_B T}\right) \quad (86)$$

$$\phi(z_2^+) = \frac{2k_B T}{Ze} \ln(X + \sqrt{X^2 + 1}) \quad (87)$$

$$X = -\frac{1}{\sqrt{8000\epsilon_0 \epsilon_2 k_B T N_A c_2^*}} \frac{Q_2}{S} \quad (88)$$

The potential profile can be calculated by

$$\tanh(Ze\phi/(4k_B T)) = \tanh[Ze\phi(z_2^+)/(4k_B T)] \exp[-\kappa(z - z_2)], \quad (89)$$

$$\kappa = \sqrt{2Z^2 e^2 n^o / (\epsilon_0 \epsilon_2 k_B T)} = \sqrt{2000Z^2 e^2 N_A c_2^* / (\epsilon_0 \epsilon_2 k_B T)} \quad (90)$$

$$X = \tanh[Ze\phi(z_2^+)/(4k_B T)] \exp[-\kappa(z - z_2)] \quad (91)$$

$$\phi(z) = \frac{2k_B T}{Ze} \ln \left| \frac{1 - X}{1 + X} \right| \quad (92)$$

At the OHP $z = z_2$,

$$\left. \frac{d\phi}{dz} \right|_{z_2^-} = \left. \frac{d\phi}{dz} \right|_{z_2^+} \quad (93)$$

Between z_0 and z_2 there is no charge, then

$$\frac{d\phi}{dz} = \text{constant} \quad (94)$$

At the interface $z = z_0$,

$$\frac{Q_s}{S} = \epsilon_0 \epsilon_1 \left. \frac{d\phi}{dz} \right|_{z_0^-} - \epsilon_0 \epsilon_2 \left. \frac{d\phi}{dz} \right|_{z_0^+} = -\frac{Q_1}{S} - \frac{Q_2}{S} \quad (95)$$

In the Gauss box 1 $\phi = \phi^o$, $d\phi/dz = 0$ at $z \rightarrow -\infty$. In this case $\rho(z) = e \sum_i Z_i n_i^0 \exp[-Z_i e \phi / (k_B T)]$ is not converged to zero at $z \rightarrow -\infty$. If we use the new definition of "biased-potnetial" $\varphi = \phi - \phi^o$ ⁴,

$$\lim_{z \rightarrow -\infty} \rho(z) = \lim_{z \rightarrow -\infty} e \sum_i Z_i n_i^0 \exp[-Z_i e \varphi(z) / (k_B T)] = 0 \quad (98)$$

We take "plus" term of Eq.(32) and then we can get

$$\left. \frac{d\varphi}{dz} \right|_{z_1^-} = -\frac{1}{\epsilon_0 \epsilon_1} \frac{Q_1}{S} \quad (99)$$

$$\left. \frac{d\varphi}{dz} \right|_{z_1^-} = \sqrt{\frac{8000 k_B T N_A c_1^*}{\epsilon_0 \epsilon_1}} \sinh\left(\frac{Z e \varphi(z_1^-)}{2 k_B T}\right) \quad (100)$$

$$-\frac{1}{\epsilon_0 \epsilon_1} \frac{Q_1}{S} = \sqrt{\frac{8000 k_B T N_A c_1^*}{\epsilon_0 \epsilon_1}} \sinh\left(\frac{Z e \varphi(z_1^-)}{2 k_B T}\right) \quad (101)$$

$$-\frac{1}{\sqrt{8000 \epsilon_0 \epsilon_1 k_B T N_A c_1^*}} \frac{Q_1}{S} = \sinh\left(\frac{Z e \varphi(z_1^-)}{2 k_B T}\right) \quad (102)$$

$$\varphi(z_1^-) = \frac{2 k_B T}{Z e} \ln(X + \sqrt{X^2 + 1}) \quad (103)$$

$$X = -\frac{1}{\sqrt{8000 \epsilon_0 \epsilon_1 k_B T N_A c_1^*}} \frac{Q_1}{S} \quad (104)$$

In the Gauss box 1 we should use Eq.(48). The potential profile can be calculated by

$$\tanh(Z e \varphi / (4 k_B T)) = \tanh[Z e \varphi(z_2^+) / (4 k_B T)] \exp[\kappa(z - z_2)], \quad (105)$$

$$\kappa = \sqrt{2 Z^2 e^2 n^o / (\epsilon_0 \epsilon_2 k_B T)} = \sqrt{2000 Z^2 e^2 N_A c_2^* / (\epsilon_0 \epsilon_2 k_B T)} \quad (106)$$

$$X = \tanh[Z e \varphi(z_2^+) / (4 k_B T)] \exp[\kappa(z - z_2)] \quad (107)$$

$$\varphi(z) = \frac{2 k_B T}{Z e} \ln \left| \frac{1 - X}{1 + X} \right| \quad (108)$$

5.4.1 Algorithm

1. If there is no specific adsorption, just set $Q_s = 0$.
2. $\epsilon_1, z_1, c_1^*, \epsilon_2, z_2, c_2^*$ are given. 1:1 electrolyte solution is assumed and the bulk concentrations of oil and water phase are given by c_1^* and c_2^* respectively.
3. the potential difference $\Delta_o^w \phi = \phi^w - \phi^o$ between the water and oil phase is given.
4. In the beginning we use the reference $\phi^w(z = +\infty) = 0$.

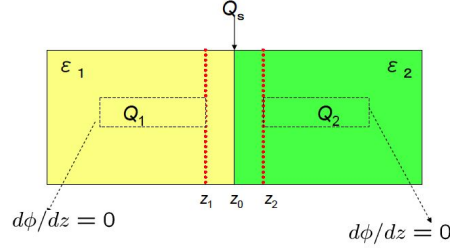
⁴If we consider the i ion distribution between oil and water phase, the electrochemical potentials between the two phase are the same.

$$\mu_i^{\ominus, o} + k_B T \ln a_i^o + z_i e \phi^o = \mu_i^{\ominus, w} + k_B T \ln a_i^w + z_i e \phi^w \quad (96)$$

$$\frac{a_i^w}{a_i^o} = \exp\left[-\frac{\mu_i^{\ominus, w} - \mu_i^{\ominus, o}}{k_B T}\right] \exp\left[-\frac{z_i e (\phi^w - \phi^o)}{k_B T}\right] \quad (97)$$

I can not understand this relation for i ion and the electrolyte distribution defined above is consistent or not.

5. We take some value for Q_s . This may be potential-dependent $Q_s(\Delta_0^w \phi)$. Q_s may be determined from some experiments and/or theoretical model.
6. We set a value to Q_2 . The calculation loop start here.
7. $Q_1 = -Q_s - Q_2$
8. We can determine $\phi(z_2^+)$ from $\phi(z_2^+) = (2k_B T / Ze) \ln(X + \sqrt{X^2 + 1})$,
 $X = -(Q_2 / S) / \sqrt{8000 N_A k_B T \epsilon_0 \epsilon_2 c_2^*}$.
9. From the relation at z_2 , $d\phi(z_2^+) / dz = Q_2 / (\epsilon_0 \epsilon_2 S) = d\phi(z_2^-) / dz$, we can determine the potential from z_0^+ to z_2^- . $\phi(z) = \phi(z_2^+) + (z - z_2) d\phi(z_2^+) / dz$
10. Using the equation $\phi(z) = (2k_B T) / (Ze) \ln |(1 - X) / (1 + X)|$,
 $X = \tanh[Ze\phi(z_2^+) / (4k_B T)] \exp[-\kappa(z - z_2)]$, we can get the potential profile.
11. In the oil phase ($z \leq 0$), the new potential $\varphi = \phi - \phi^o$ should be used.
12. From the following relation we can determine $d\phi(z_0^-) / dz = d\varphi(z_0^-) / dz$, $\epsilon_0 \epsilon_1 d\phi(z_0^-) / dz = -\epsilon_0 \epsilon_2 d\phi(z_0^+) / dz - Q_s / S$
13. From $\phi(z_0^+)$ and $d\phi(z_0^+) / dz$, we can determine the potential between z_0^+ and z_1^- .
 $\phi(z) = \phi(z_0^+) + z [d\phi(z_0^+) / dz]$, $\varphi(z) = \phi(z) - \phi^o$.
14. The potential slope $d\phi(z_1^-) / dz$ should be the same as the slope obtained by $\epsilon_0 \epsilon_1 d\phi(z_1^-) / dz = -Q_1 / S$.
15. The potential slope $d\varphi(z_1^-) / dz$ should be the same as $\sqrt{(8000 k_B T N_A c_1^*) / (\epsilon_0 \epsilon_1)} \sinh[(Ze\varphi(z_1^-)) / (2k_B T)]$.
 If not back to process 6.
16. Using the equation $\tanh(Ze\phi / (4k_B T)) / \tanh(Ze\phi(z_2^+) / (4k_B T)) = \exp[\kappa(z - z_2^+)]$, $\kappa = \sqrt{(2Z^2 e^2 n_2^*) / (\epsilon_0 \epsilon_2 k_B T)}$, we can get the potential profile for $z < z_2$.
17. Now we can check $\lim_{z \rightarrow -\infty} \varphi(z) = 0$. If not go back to process (6).
18. If the numerical solution is consistent, the calculation is finished. We replot the potential in the new definition $\varphi(z) = \phi(z) - \phi^o$ in the water phase.



断面積SのGauss Box1およびGauss Box2内の電荷 Q_1, Q_2 とし、界面に特異吸着した分子の電荷を Q_s とする。

$$\text{電氣的中性の条件: } Q_1 + Q_s + Q_2 = 0$$

Figure 10: EDL at Oil (left)|Water (right) interface

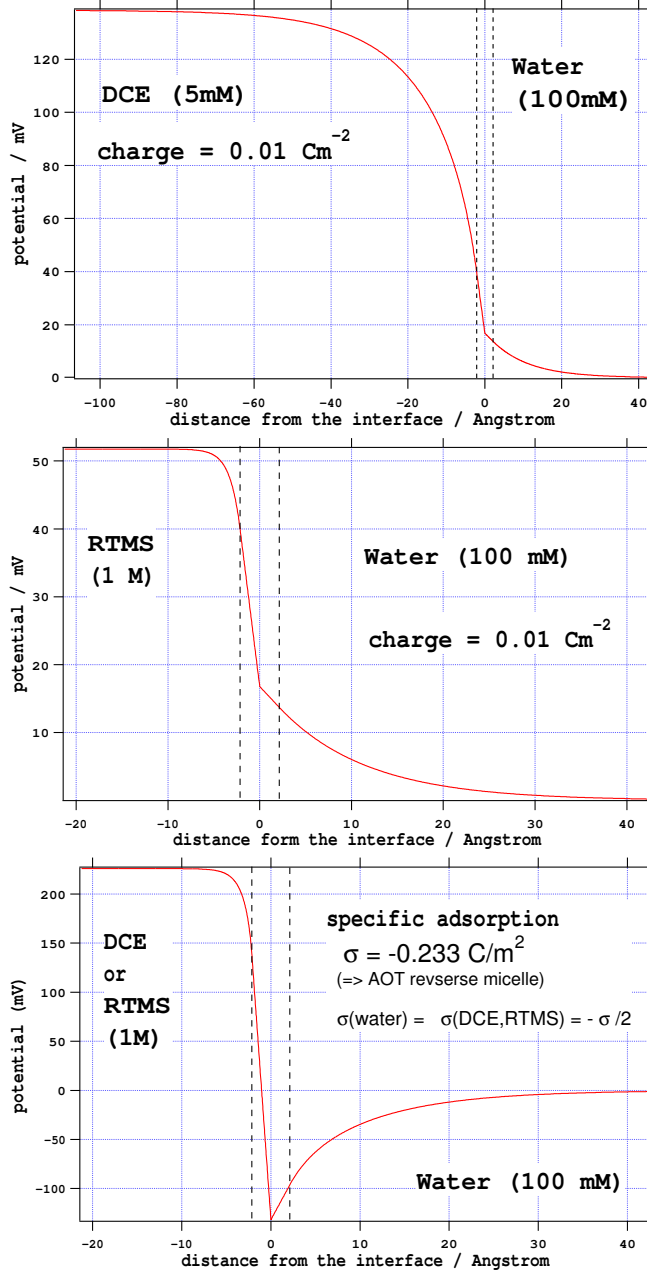


Figure 11:

6 Numerical solution of 1D Nonlinear Poisson-Boltzmann Equation

If you do not like the solution above, we have another solution. By numerically solve the Nonlinear Poisson-Boltzmann equation, we can get the potential and density.

$$-\epsilon_0 \nabla \cdot (\epsilon(\mathbf{r}) \nabla \phi(\mathbf{r})) = e \sum_i Z_i n_i^0 \exp\left(\frac{-Z_i e \phi(\mathbf{r})}{k_B T}\right), \quad (3D \text{ case}) \quad (109)$$

$$-\epsilon_0 \frac{d}{dz} \left[\epsilon(z) \frac{d}{dz} \phi(z) \right] = e \sum_i Z_i n_i^0 \exp\left(\frac{-Z_i e \phi(z)}{k_B T}\right), \quad (1D \text{ case}) \quad (110)$$

The detail of the 3D numerical solution was given by Soda et al. and will be described soon.

6.1 EDL from second harmonic generation(SHG) spectroscopy

From the potential dependence of the SHG signal the EDL at metal/electrolyte interface can be detected by optically!!. If the surface electron is free electron like, the cubic nonlinear

susceptibility become dominant. The SHG signal can be written as

$$S \propto \left| F(\chi_b^{(2)} + \chi_s^{(2)} + \chi_{\text{eff}}^{(3)} \Delta\Phi) \right|^2 \quad (111)$$

Here F is the Fresnel factor, and $\chi_b^{(2)}, \chi_s^{(2)}, \chi_{\text{eff}}^{(3)}$ is the bulk, surface, and effective cubic susceptibility, respectively. $\Delta\Phi$ is the potential drop at the metal electrode.

GUYOTSIIONNEST and TADJEDDINE reported the potential dependence of the SHG signal of Ag(111) and Au(111). (*J. Chem. Phys.* **1990**, *92*, 734-738.)

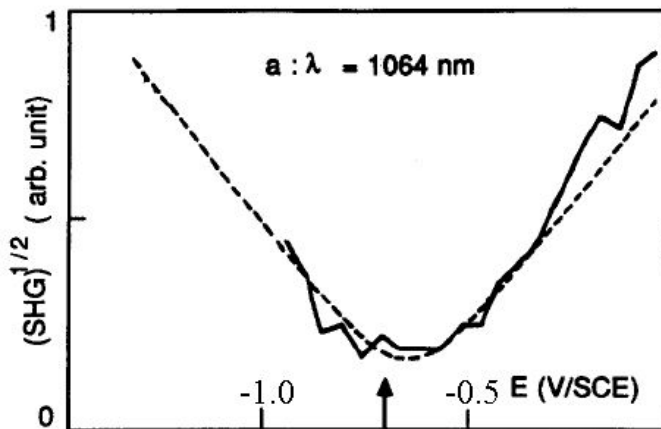


Figure 12: Square root of the nonlinear signal as a function of the potential for Ag(111) in 0.1 M KClO_4 . Scan rate 10 mV /s. pzc(shown as arrow) and the minimum of the parabola of the SHG signal is in good agreement.

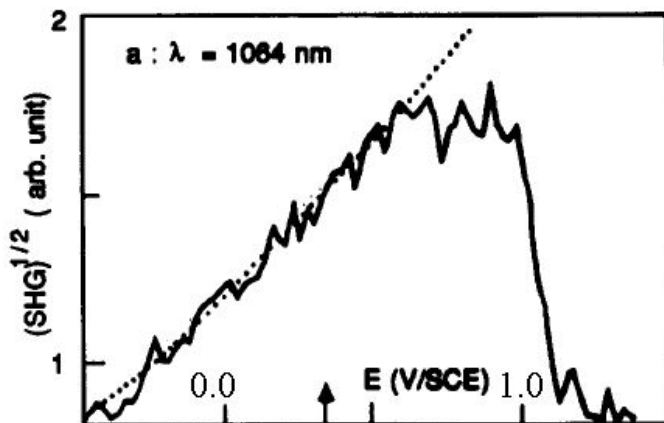


Figure 13: Square root of the nonlinear signal as a function of the potential for Au(111) in 0.1 M HClO_4 . Scan rate 10 mV /s. There is no minimum of the SHG signal and pzc(shown as arrow) can not be determined. The inter-band transition and plasmon resonance at 2ω may enhance the $\chi_b^{(2)} + \chi_s^{(2)}$ contribution and the relative contribution from cubic nonlinearity become smaller.

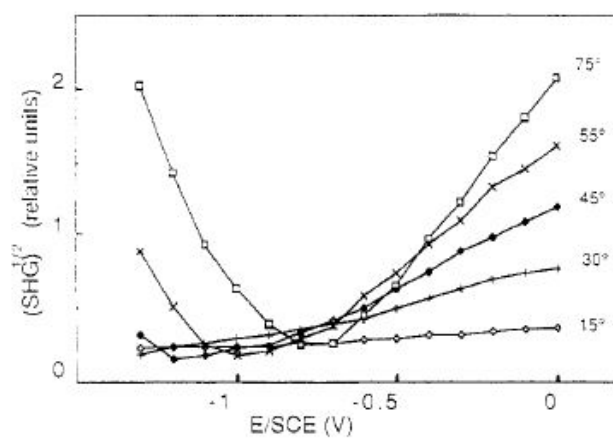


Figure 14: Square root of SHG as a function of the potential at 1064 nm at various angles of incidence for Ag(111) in 0.1 M KClO_4 . The SHG signal strongly depends on the incident angle. This is due to the Fresnel factor dependence of the incident angle. (A. TADJEDDINE, P. GUYOTSIIONNEST, *J. Phys. Chem.* **1990**, *94*, 5191-5196.)