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ChE 385M

The Effect of Electrostatic Surface Charges on Photoresist Dissolution

Introduction/Motivation

It would be very useful and economical to have a fundamental model for the microlithographic process. While some aspects of lithography can be accurately modeled (the aerial image, exposure kinetics) other aspects are still not well understood (dissolution, post exposure bake). Many models exist for the dissolution of photoresists, but most fail to capture many experimentally observed trends. One dissolution model, termed the critical ionization (CI) model, has been developed recently by Tsiartis and Flanagan¹. The basic postulate of this model is that a critical fraction of hydroxyl groups on a given polymer (resist) chain must be deprotonated by aqueous base before that chain can dissolve. This model successfully describes several experimentally observed trends in bulk dissolution rate including molecular weight dependence, the effect of added salts into developer, and residual casting solvent effects. However, this model does not quantitatively explain the phenomenon of surface inhibition, in which the top of the photoresist film dissolves slower than the bulk of the resist.

Figure 1. shows a typical thickness verse time plot for the dissolution of a resist which exhibits surface inhibition, and the subsequent rate verse thickness plot is shown in Figure 2. The initial rate of development is nearly zero, and after a characteristic inhibition length δ , the resist reaches a steady state bulk dissolution rate. Simulations show that this effect is actually quite beneficial to the lithographic process, as it increases the sidewall angle of the resist and reduces top loss in unexposed regions of the resist (Figure 3). It has been postulated that surface inhibition is caused by a concentration gradient in resist components throughout the thickness of resist. However, recent attempts to measure the concentration gradient of residual casting solvent, photoactive

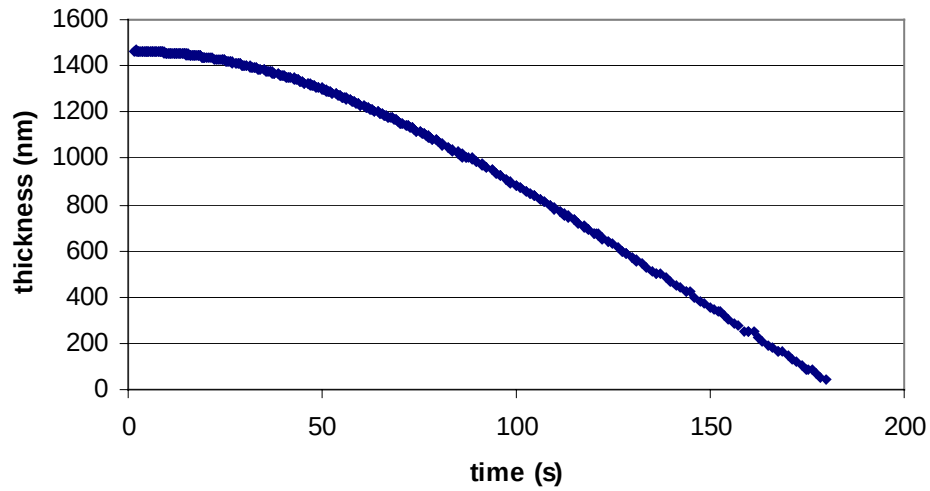


Figure 1. Thickness verse time for a novolac resist which shows typical surface inhibition

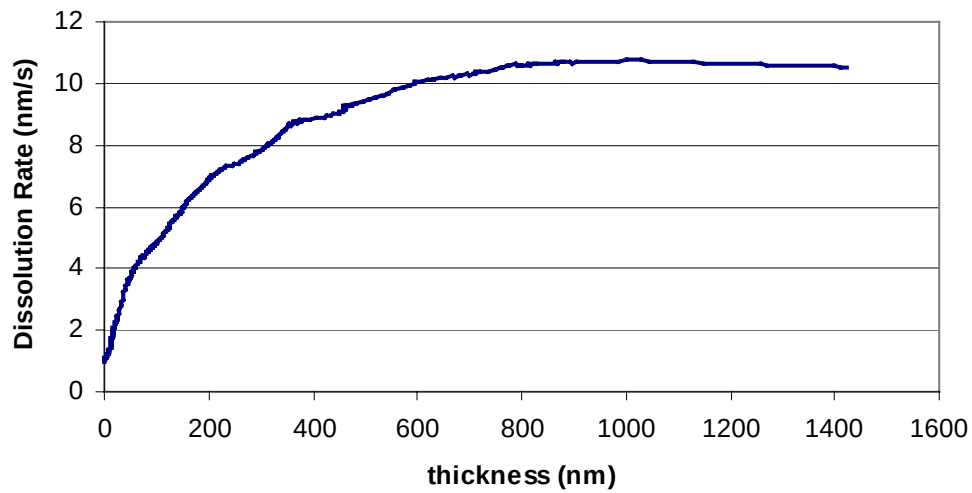


Figure 2. Dissolution rate verse thickness for the same data shown in Figure 1.

compound, low molecular weight species, and overall resist density have indicated that the resist film is homogeneous throughout thickness². Nearly all of the hypotheses presented in the literature for surface inhibition have been refuted. The origin(s) of surface inhibition remain unknown.

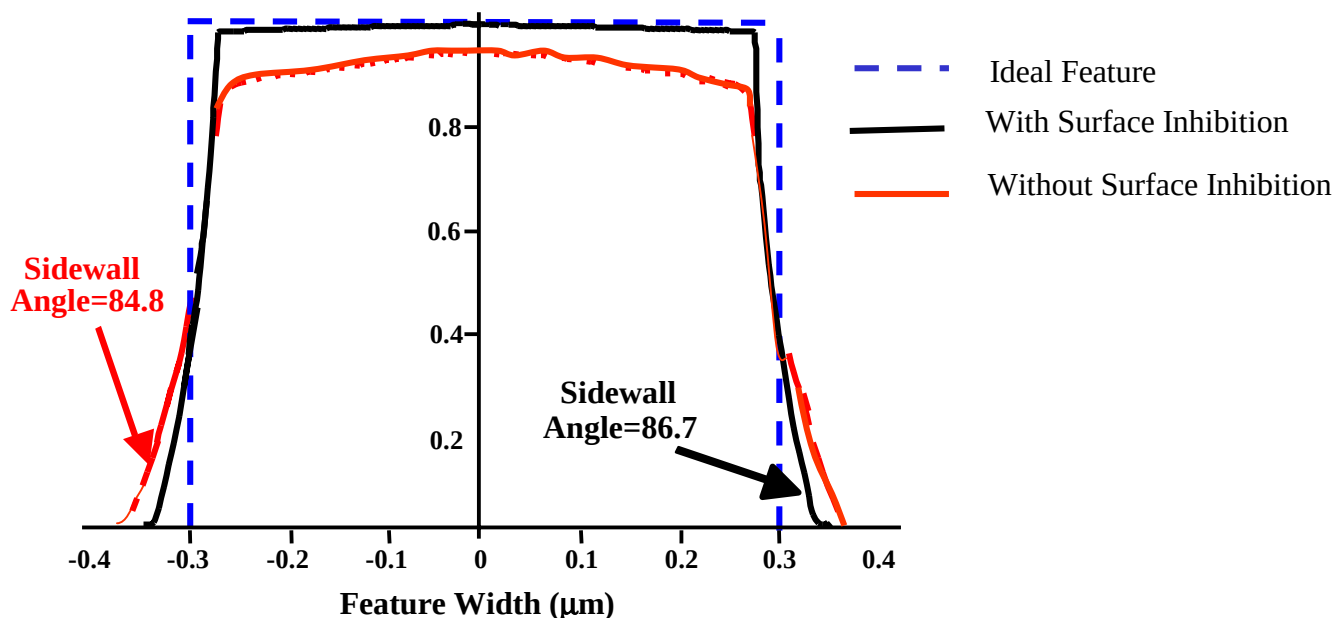


Figure 3. Prolith simulation with and without surface inhibition. The presence of surface inhibition improves the sidewall angle and resist loss from the top.

An additional motivation is that the critical ionization model is not entirely complete. The molecular level simulations which use this model require as an input parameter α , the fraction of ionized surface sites. This parameter cannot be measured. It is related to the pH and pKa of the system, but if only the bulk effects are considered, the calculated value of α is unreasonably high. Currently, a reasonable guess for α is provided to the simulation algorithm. If electrostatic effects are considered, it may be possible to calculate a more reasonable value for α , and more importantly to relate this value to the system parameters which are measureable (pH, polymer MW).

Project Description/Goals

The critical ionization model for dissolution involves the ionization (deprotonation) of hydroxyl groups on the surface of the developing resist. After a critical fraction of hydroxyl sites on a chain is deprotonated, the chain will dissolve. This critical fraction (f) has been estimated to be ~ 0.4 - 0.5 . However, before this fraction is reached the resist surface may be covered with chains with many sites which are deprotonated, each having an O^- ion contributing to the overall surface charge. The developer solution is an aqueous base (electrolyte solution) with hydroxide (OH^-) ions as well as a corresponding cation such as Na^+ , K^+ , or tetramethylammonium (TMA^+). The

negative surface charge on the resist will result in a concentration profile very close to the resist surface in which there exists a high concentration of cations and a low concentration of hydroxide ions (OH^-).

At the beginning of dissolution, no deprotonation reactions have occurred, and the surface charge on the resist is zero. As the deprotonation reactions start to occur, the surface charge increases, and the resulting ion concentration gradients increase. Since the hydroxide ions are reactants in the deprotonation reaction (which leads to dissolution), any change in their concentration should lead to a dramatic change in the dissolution rate.

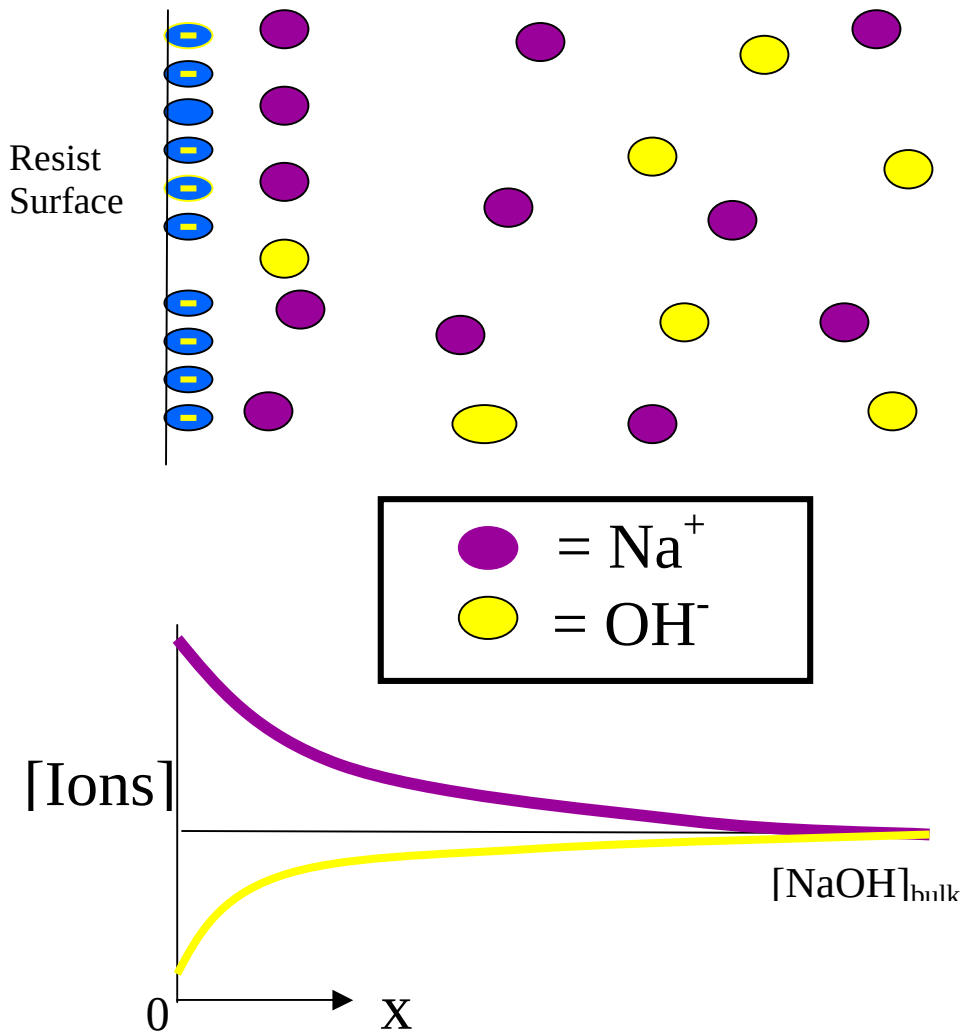


Illustration 1. Build up of Negative Charge on Resist Surface, and the Corresponding Concentration Profile of Developer Ions.

Eventually the system will reach a steady state, in which the surface concentration of hydroxide ions is balanced with the surface charge caused by the deprotonation reaction. The equations which govern the system of a flat, charged surface in an electrolyte medium have been well established. However, (to the knowledge of the author) they have not been applied to studying the dissolution of photoresists.

The goals of this project are:

- 1) Determine the surface charge, σ , surface potential, ϕ_o , and surface ion concentration as a function of developer concentration [TMAH], and fraction of deprotonated sites (α).
- 2) Calculate the Debye length (K^{-1}) for a typical photoresist as a function of developer concentration. Determine the concentration profile near the resist surface of cations, anions, and potential.
- 3) Determine the steady state values of surface charge and surface hydroxide concentration that are consistent with the critical ionization model.
- 4) Estimate the time scale to reach a steady state dissolution rate. (i.e. Does this analysis give any insight into surface inhibition?)

Determining σ , ψ_o , $[Na^+]_o$, and $[OH]_o$

Note: An overview of the relevant equations is presented here. The intermediate derivations can be found in Appendix A.

First, the surface charge, σ , is related to the fraction of ionized surface sites, α . For on-lattice simulations, the volume of a monomer unit is approximated by a cube which is .7 nm per side¹. The corresponding area for an ionizable site is therefore .49 nm², with one electronic charge possible per site. The appropriate conversion is 1C-m⁻² which corresponds to one electronic charge per 0.16 nm². For a fully ionized resist

surface, σ is equal to $0.326 \text{ C}\cdot\text{m}^{-2}$. Therefore the relationship between surface charge and the fraction of ionized sites, α , is

$$\sigma = .326 \times \alpha \quad [=] \text{ C/m}^2 \quad (1)$$

Sodium hydroxide (NaOH) will be used as the aqueous base developer for this analysis. From the Boltzmann distribution, the concentration of ions away from the surface is

$$[Na^+](x) = [Na^+]_{\infty} e^{-\frac{e\phi(x)}{kT}} \quad (2)$$

$$[OH^-](x) = [OH^-]_{\infty} e^{-\frac{e\phi(x)}{kT}} \quad (3)$$

where $\phi(x)$ is the potential change with distance, e is the charge on an electron, k is Boltzmann's constant, T is the temperature (which is taken to be 298 K) and x is defined as the distance away from the resist surface where $x=0$ at the surface. The total concentration of surface ions is

$$[Na^+]_o + [OH^-]_o = \frac{\sigma^2 A_N * 10^3}{2\epsilon\epsilon_o kT} + 2[NaOH]_{\infty} \quad (4)$$

where ϵ is the dielectric constant of the medium (in this case $\epsilon = 80$ for water), ϵ_o is the permittivity of free space, and the subscript "o" indicates a value at $x=0$ (at the surface). A_N is Avogadro's number, which is used to convert from number density to concentration in mol/L.

By combining equation (4) with equations (2) and (3), the surface potential ϕ_o can be related to the surface charge σ :

$$\phi_o = \frac{2kT}{e} \left[\sinh^{-1} \left(\frac{\sigma^2}{8\epsilon\epsilon_o kT [NaOH]_{\infty}} \right) + 1 \right] \quad (5)$$

Equations (2) and (3) can now be used in conjunction with ϕ_o to determine the surface concentration of both the sodium and hydroxide ions:

$$[Na^+]_o = [Na^+]_\infty e^{-\frac{e\phi_o}{kT}} \quad (6)$$

$$[OH^-]_o = [OH^-]_\infty e^{-\frac{e\phi_o}{kT}} \quad (7)$$

From the above relationships, it is possible to determine the effect that the fraction of ionized sites (α), and the bulk developer concentration $[NaOH]_{bulk}$ will have on the surface concentration of both cations and anions. Figure 4 shows the change in ion surface concentration with bulk developer concentration. (The surface charge is assumed to be 0.1 C/m^2 , which corresponds to $\alpha = 0.3$). As the developer concentration increases, so does the surface concentration of both ions. Figure 5 shows the change in ion surface concentration with α . (The developer concentration is held constant at 0.26 M , a typical value.) As the fraction of ionized sites increases, the surface charge becomes more negative, resulting in a larger concentration of Na^+ ions at the surface and a decreasing concentration of OH^- ions. This effect is very important as dissolution of the resist begins. Initially, there are no ionized sites ($\alpha=0$), and the surface concentration of OH^- ions is equal to the bulk concentration, 0.26 M . As dissolution proceeds, the fraction of ionized sites increases dramatically, and the surface concentration of OH^- ions decreases. For 50% of all sites ionized, the surface concentration of OH^- is about 0.01 M , an order of magnitude lower than the bulk concentration. The decrease in surface concentration of OH^- ions should decrease the rate of the surface deprotonation reactions, which may change the polymer dissolution rate.

Determining the Debye Length, K^{-1} , and the Concentration Profile of Ions

From the class notes (3/28/00), the Debye parameter is

$$K = \sum \left(\frac{z_i^2 e^2 n_o}{\epsilon \epsilon_o kT} \right)^{1/2} \quad (8)$$

The characteristic length over which the electrostatic potential acts is the Debye length, which is K^{-1} . From equation 8, it is clear that the Debye length is only a function of

dielectric constant of the medium and the concentration of electrolytes in developer. It is not dependent on the surface charge or other properties of the solid. For the 1:1 electrolyte being considered for this analysis, the Debye length is

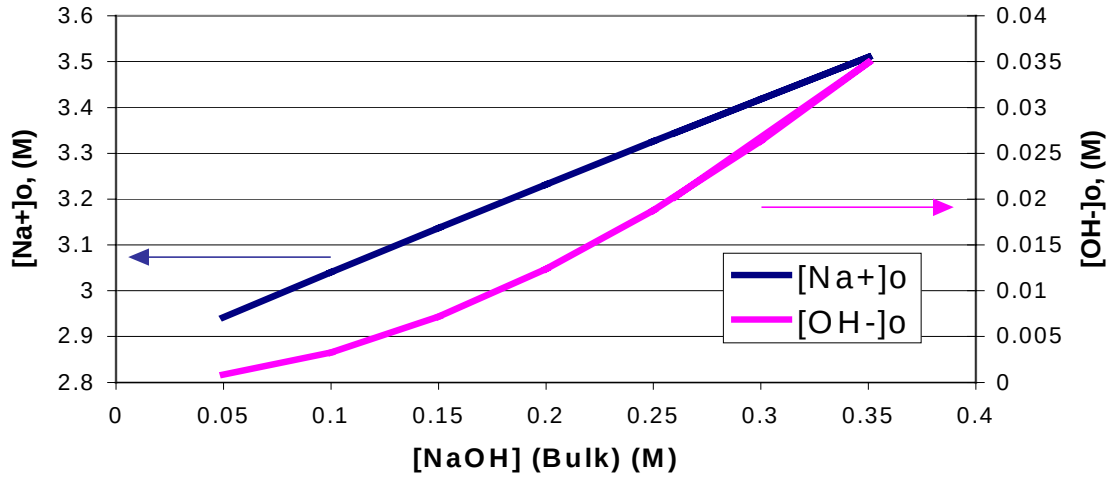


Figure 4. Surface Concentration of sodium and hydroxide ions verse bulk developer concentration

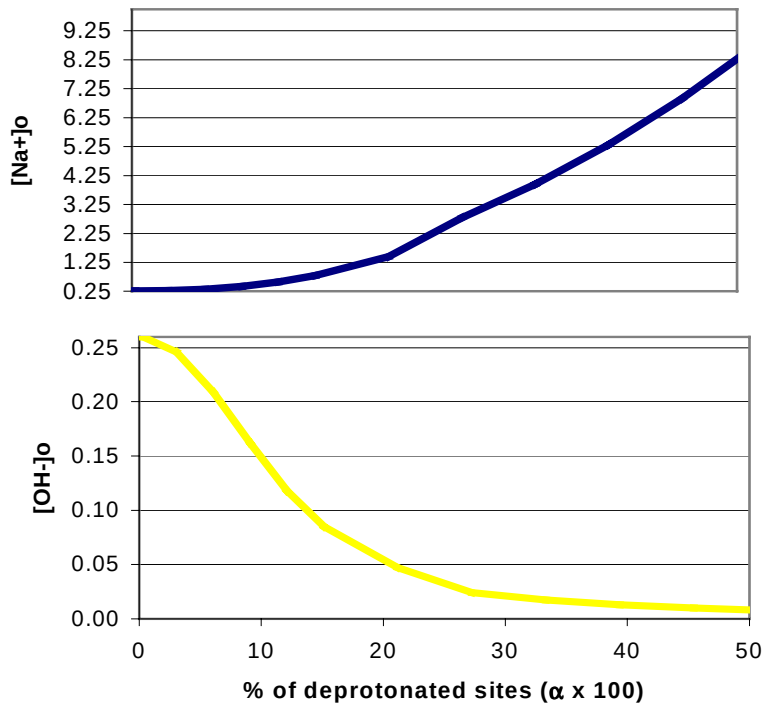


Figure 5. Surface Concentration of sodium and hydroxide ions verse the fraction of deprotonated sites, α .

$$K^{-1} = 0.430/[\text{NaOH}]^{1/2} \quad [=] \text{ nm} \quad (9)$$

Figure 6 shows the plot of Debye length verse developer concentration. For a typical developer concentration (~ 0.26 M), the Debye length is about 1nm.

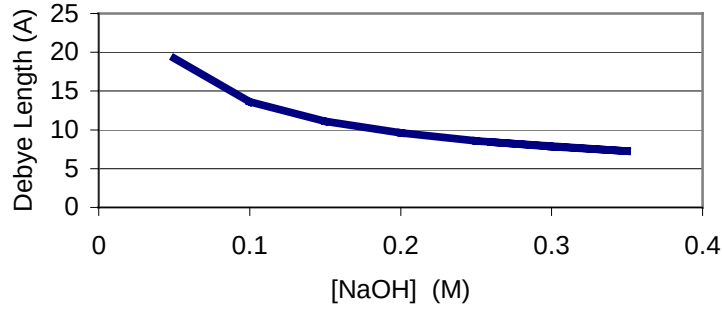


Figure 6. Debye length (K^{-1}) verse Bulk Developer Concentration.

The potential as a function of distance from the surface is

$$\phi(x) = \frac{2kT}{e} \text{LN} \left[\frac{(1 + \gamma e^{-Kx})}{(1 - \gamma e^{-Kx})} \right] \quad (10)$$

where

$$\gamma = \tanh \left(\frac{e\phi_o}{4kT} \right) \quad (11)$$

This equation is derived in Appendix A and by Israelachvili³. The concentration gradient of ions away from the surface is found by inserting $\phi(x)$ into equations (2) and (3). Figure 7 shows the potential gradient and ion gradient for a developer concentration of 0.26 M and a fraction of ionized sites of 0.3. Figure 8 shows the concentration gradient of ions for varying fraction of ionized sites. The distance over which the concentration gradients exist is small ($\sim 5\text{nm}$). It is on the order of the roughness of the resist. However, the distance over which the electrostatic forces act is not a large concern (unless it is so small that the Poisson-Boltzmann equation is no longer valid.) The most important parameters are the surface concentration of ions, which will affect the dissolution rate of the resist.

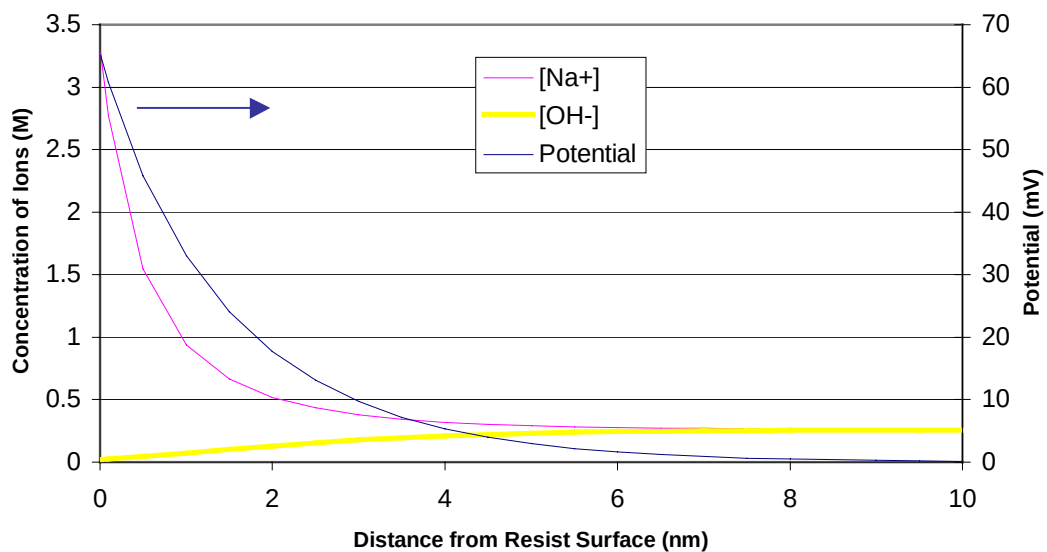


Figure 7. Potential and ion concentration gradient for $\alpha=0.3$. Developer concentration is 0.26 N.

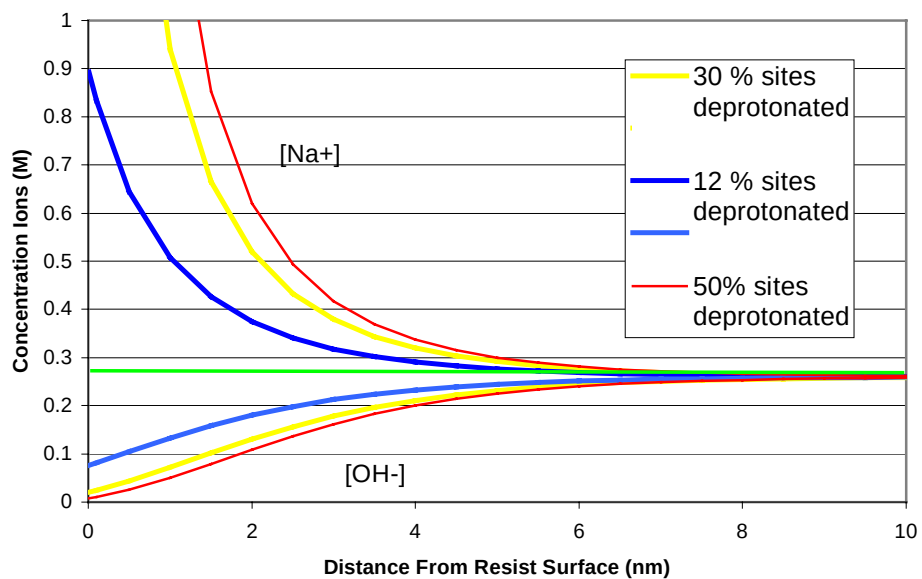
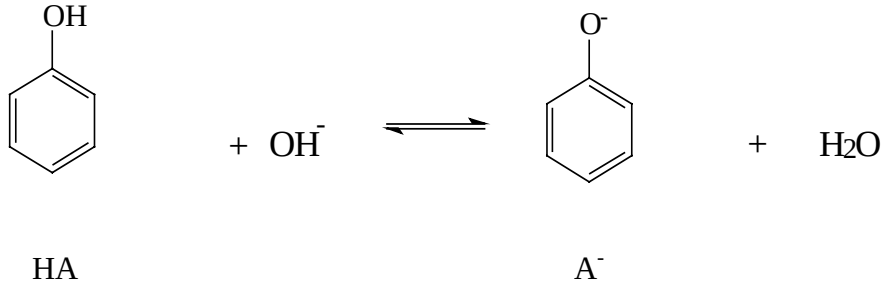


Figure 8. Ion concentration gradient for varying α . Developer concentration is 0.26 N.

Determining the Steady State Value of σ , $[\text{OH}^-]_o$, and pK_a

Next, we consider the equilibrium of the deprotonation reaction. In class, we considered an acidic surface, in which protons dissociated from the surface spontaneously. In this case, we consider the deprotonation reaction caused by OH^- ions in the developer, and we are interested in relating the surface charge of the resist to the surface and bulk concentration of OH^- ions. Considering each site separately, the reaction is:



for which the equilibrium constant is

$$K = \frac{[\text{A}^-]}{[\text{HA}][\text{OH}^-]} \quad (12)$$

For this analysis, the activity coefficients are taken to be unity, although it is noted that this is a bad assumption for a strong electrolyte solution. The value $[\text{A}^-]$ can be replaced by the number of sites ionized per area, N_s . The value $[\text{HA}]$ can be replaced by the number of total sites minus the number of ionized sites, $N_o - N_s$. And $[\text{OH}^-]$ is equal to the surface concentration, $[\text{OH}^-]_o$. Recognizing that $\alpha = N_s/N_o$, and rearranging equation (12),

$$\alpha = \frac{K[\text{OH}^-]}{1 + K[\text{OH}^-]} \quad (13)$$

While K is not necessarily known, Flanagan has established a relationship between α , the pH of the solution, and the pK_a of the polymer:¹

$$\alpha = \frac{10^{pH - pK_a}}{1 + 10^{pH - pK_a}} \quad (14)$$

This equation is a restatement of equation (13), but Flanagan's analysis was more rigorous. He considered the sequential equilibrium reactions on a polymer chain. More importantly he discusses ways to estimate the polymer pK_a (which provides an estimate for the unknown K). The polymer pK_a is a function of the number of ionized sites on a polymer chain, but for the time being a range of pK_a from 11-13 will be considered. It should also be noted that the pH in equation (14) is not the pH of the bulk solution. Rather, it is related to the surface concentration of OH^- ions. A relationship now exists between the fraction of ionized sites and the surface concentration of hydroxide ions based on the equilibrium of the deprotonation reaction.

By combining equations (1), (5), and (7), we have another direct relationship between the surface concentration of OH^- ions and the fraction of ionized sites based on electrostatic arguments. Solving both equations simultaneously yields one value of the surface concentration of OH^- ions and a corresponding value of α . This set of equations is tricky to solve analytically, but it is trivial to solve graphically. Figure 9 shows the $[OH^-]_o$ dependence on α for both the electrostatic influence and the reaction equilibrium constraint. The pK_a has been allowed to vary from 11-13. This was done in order to determine how sensitive the steady state conditions were on polymer pK_a . For a pK_a of 12, the condition at which both equations is satisfied is for $\alpha = 0.5$, and $[OH^-]_o = 0.01$ M.

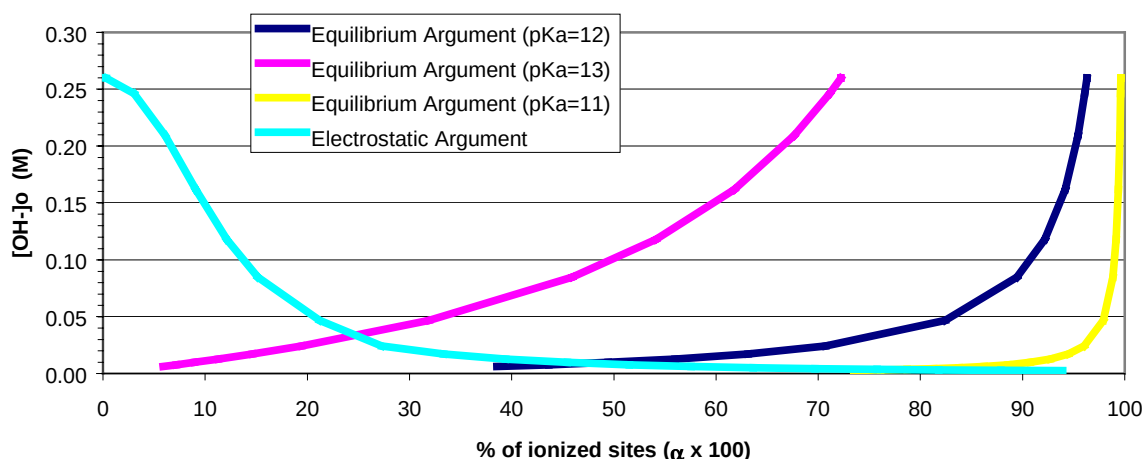


Figure 9. Surface concentration of hydroxide ions based on electrostatic constraints and on reaction equilibrium constraints (for pKa from 11-13)

Flanagin was able to estimate a relationship between α and pKa for common photoresist polymers¹. Figure 10 is a reproduction of his analysis for both novolac and polyhydroxystyrene (PHOST) resists. With a pKa dependence on α , the last degree of freedom vanishes and it is possible to determine the steady state pKa, α , and $[\text{OH}^-]_0$. For novolac, it is evident that the pKa is equal to ~ 12 when $\alpha=0.5$ and $[\text{OH}^-]_0 = 0.01$ M.

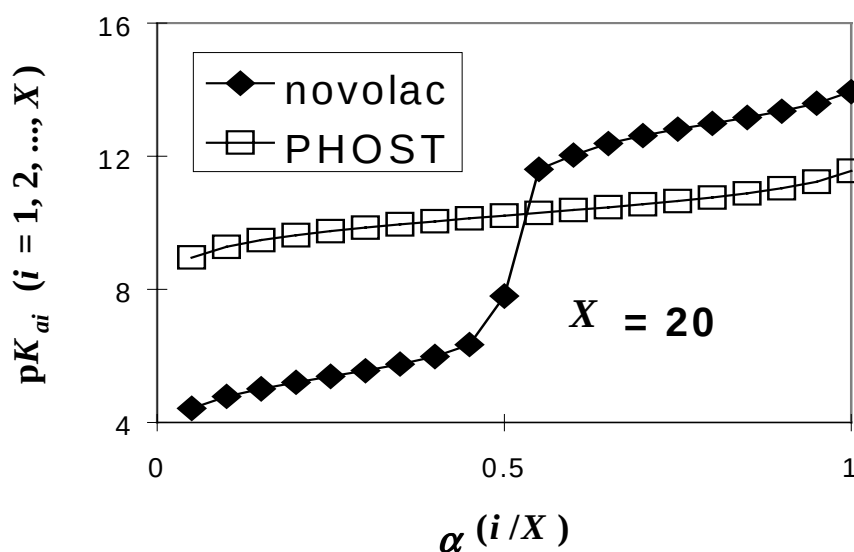


Figure 10. Relationship between fraction of ionized sites (α) and pKa for novolac and polyhydroxystyrene polymers¹. This calculation is for polymers with 20 monomer units.

Considering electrostatic charge effects, it has been determined that the steady state fraction of ionized sites is $\sim 50\%$ for a novolac polymer chain which is 20 monomer units long and using a 0.26 N developer solution. In order to determine the importance of the electrostatic effects, we consider the same case assuming there is no surface charge ($\sigma = 0$), in which case the surface concentration of hydroxide ions is equal to the bulk hydroxide concentration. In this case, the value of α is determined only by equation (14) and the function that is represented in Figure 10. Solving both equations, $\alpha \sim 0.8$. The electrostatic effects considerably change the steady state value of the fraction of ionized sites, and have a large effect on the dissolution algorithm developed by Flanagan. (Coincidentally, Flanagan uses $\alpha = 0.5$ in most of his lattice simulations.) If we consider that α should be somewhat close to the critical ionization fraction (f) for a randomly oriented polymer lattice at a steady state dissolution rate, 0.5 is a more reasonable value for α than 0.8. It has already been estimated that $f \sim 0.4-0.5$, so a value of $\alpha = 0.5$ is more reasonable.

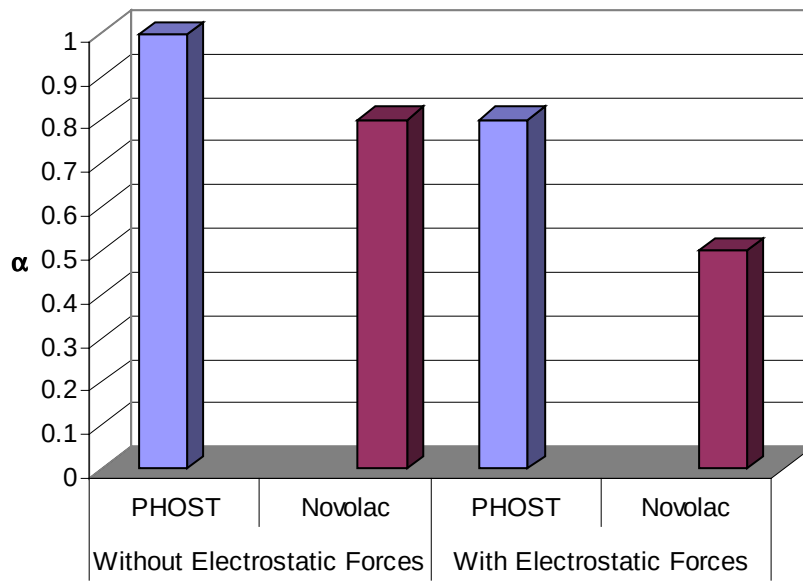


Figure 11. Calculated Value of Fraction of Ionized Surface Sites (α) Without Electrostatic Forces, and Considering Electrostatic Forces. ($[\text{NaOH}] = 0.26 \text{ N}$, polymer chain length = 20).

Figure 11 shows the change in α by considering electrostatic effects for novolac and PHOST. For novolac, the change in α is very reasonable. For PHOST, the change in

α from 1.0 to 0.8 is in the right direction, but the value is still high. However, the importance of considering electrostatic forces in calculating α has been demonstrated. It may now be possible to use a rigorously calculated, reasonable value of α in the critical ionization model simulations that is dependent only on the polymer material, the molecular weight of the polymer, and the developer concentration.

Future Work

Thus far, only steady state dissolution has been considered. The simplest way to consider a non-steady state case is to add an electrostatic contribution to Flanagan's dissolution algorithm. Considering electrostatic effects could potentially give some insight into surface inhibition. However, the deprotonation reaction and ion concentration gradient probably occur very quickly. It is unlikely that non-linear dissolution rates are a result of electrostatic charge effects. However, electrostatic charge effects are still very important in modeling bulk dissolution.

References

1. Flangin, L. *PhD Dissertation*. University of Texas at Austin, 1999
2. Gardiner, A. *et al.* *J Vac Sci Tech*. Submitted for publication, 2000
3. Israelachvili, Jacob. *Intermolecular and Surface Forces*, 2nd Ed. Harcourt Brace & Company, London. 1992, Ch 12.

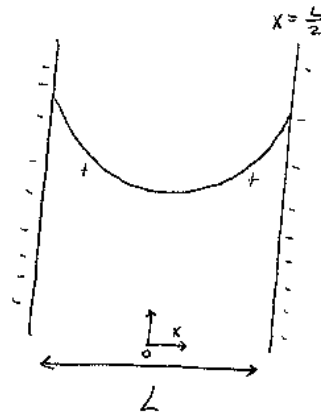
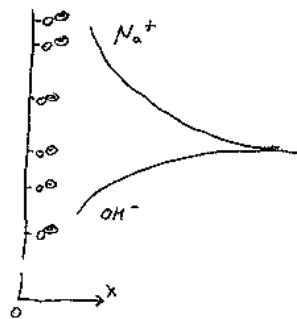
Appendix A

Derivation of Equation (4) (THIS DERIVATION IS ALSO FOUND IN REF 3)

Start with Poisson-Boltzmann Equation and Poisson Equation

$$\nabla^2 \phi = -\left(\frac{ze\rho_0}{\epsilon\epsilon_0}\right) e^{-\frac{ze\phi}{kT}} \quad zep = -\epsilon\epsilon_0 (\nabla^2 \phi)$$

We want to consider an isolated, charged surface surrounded by an electrolyte solution. First, we will consider two charged plates a distance L apart, with no added electrolyte (only counterions present). Then we will allow $L \rightarrow \infty$.



BOUNDARY CONDITIONS FOR 2 PLATES

① FROM SYMMETRY $E_0 = \left(\frac{\partial \phi}{\partial x}\right)\bigg|_{x=0} = 0$

② CHARGE NEUTRALITY. THE TOTAL CHARGE OF COUNTERIONS IN THE GAP MUST EQUAL THE CHARGE ON THE SURFACES. FROM THE POISSON EQUATION

$$\sigma = -\int_0^{L/2} zep dx = \epsilon\epsilon_0 \int_0^{L/2} \left(\frac{\partial^2 \phi}{\partial x^2}\right) dx$$

$$\sigma = \epsilon\epsilon_0 \left(\frac{\partial \phi}{\partial x}\right)\bigg|_{L/2} = \epsilon\epsilon_0 E\bigg|_{L/2} \quad \text{where } E = \frac{\partial \phi}{\partial x} \text{ is the electric field}$$

$$E_{\text{surface}} = \frac{\sigma}{\epsilon\epsilon_0}$$

(CONT)

DIFFERENTIATE THE BOLTZMANN DISTRIBUTION

$$\frac{\partial p}{\partial x} = -\frac{ze}{kT} p_0 e^{-\frac{ze\phi(x)}{kT}} \frac{\partial \phi(x)}{\partial x}$$

INSERT THE POISSON-BOLTZMANN EQUATION

$$\frac{\partial p}{\partial x} = \frac{\epsilon \epsilon_0}{kT} \left(\frac{\partial \phi}{\partial x} \right) \left(\frac{\partial^2 \phi}{\partial x^2} \right)$$

RECOGNIZING THAT

$$\frac{\partial}{\partial x} \left(\frac{\partial \phi}{\partial x} \right)^2 = 2 \left(\frac{\partial \phi}{\partial x} \right) \left(\frac{\partial^2 \phi}{\partial x^2} \right)$$

$$\frac{\partial p}{\partial x} = \frac{\epsilon \epsilon_0}{kT} \frac{\partial}{\partial x} \left(\frac{\partial \phi}{\partial x} \right)^2$$

INTEGRATING

$$p(x) - p_0 = \int_0^x \frac{\partial p}{\partial x} = \frac{\epsilon \epsilon_0}{2kT} \int_0^x \frac{\partial}{\partial x} \left(\frac{\partial \phi}{\partial x} \right)^2 = \frac{\epsilon \epsilon_0}{2kT} \left(\frac{\partial \phi}{\partial x} \right)^2 \Big|_x$$

$$p(x) = p_0 + \frac{\epsilon \epsilon_0}{2kT} \left(\frac{\partial \phi}{\partial x} \right)^2 \Big|_x \quad p_0 = \# \text{ concentration at the midplane}$$

AT THE SURFACE

$$x = \frac{L}{2} \quad \left(\frac{\partial \phi}{\partial x} \right)^2 = E_{\text{surface}}^2 = \frac{\sigma^2}{\epsilon \epsilon_0}$$

$$p_{\text{surface}} = p_0 + \frac{\sigma^2}{2\epsilon \epsilon_0 kT}$$

THIS EQUATION IS DERIVED FOR NO ADDED ELECTROLYTE - IF WE CONSIDER AN ISOLATED SURFACE, $p_0 \rightarrow 0$. WITH AN ADDED ELECTROLYTE,

$$p_0 \rightarrow p_{\text{bulk}}$$

(CONT)

SO, FOR AN ISOLATED SURFACE WITH ADDED ELECTROLYTE

$$P_s = P_\infty + \frac{\sigma^2}{2\epsilon\epsilon_0 kT}$$

THIS IS TRUE OF EVERY ION, SO

$$P_{Si} = P_{\infty i} + \frac{\sigma^2}{2\epsilon\epsilon_0 kT}$$

NOW THAT WE ARE CONSIDERING AN ISOLATED SURFACE, $x=0$ AT THE SURFACE SO WE WILL USE "0" INSTEAD OF "S"

THE TOTAL SURFACE CONCENTRATION OF IONS IS

$$\sum_i P_{0i} = \sum_i P_{\infty i} + \frac{\sigma^2}{2\epsilon\epsilon_0 kT} \quad [=] \quad \frac{\#}{m^2}$$

TO CONVERT TO MOLARITY, MULTIPLY BY $6.022 \times 10^{26} = A_N \times 10^3$

WHERE A_N = AVOGADRO'S # ("Na" IS LEFT FOR SODIUM)

$$[Na^+]_0 + [OH^-]_0 = [Na^+]_\infty + [OH^-]_\infty + \frac{\sigma^2}{2\epsilon\epsilon_0 kT} \times A_N \times 10^3$$

$$\text{SINCE } [Na^+]_\infty = [OH^-]_\infty = [NaOH]_{\text{BULK}}$$

$$[Na^+] + [OH^-]_0 = 2[NaOH]_{\text{BULK}} + \frac{\sigma^2}{2\epsilon\epsilon_0 kT} \times A_N \times 10^3 \quad \text{Eq (4)}$$

Derivation of Equations (5), (6), & (7)

EQUATIONS (6) & (7) ARE EQUATIONS (2) & (3) EVALUATED
AT THE SURFACE ($x=0$)

$$[Na^+]_0 = [Na^+]_{bulk} \exp(-e\phi_0/kT) \quad \text{Eq 6}$$

$$[OH^-]_0 = [OH^-]_{bulk} \exp(+e\phi_0/kT) \quad \text{Eq 7}$$

RECALL

$$\frac{\sigma^2}{2\epsilon\epsilon_0 kT} = \sum_i \rho_{oi} - \sum_i \rho_{oi}$$

$$\sigma^2 = 2\epsilon\epsilon_0 kT \left(\sum_i \rho_{oi} - \sum_i \rho_{oi} \right)$$

$$\rho_{oi} = \rho_{oi} e^{-e\phi_0/kT}$$

$$\sigma^2 = 2\epsilon\epsilon_0 kT \left\{ [Na^+]_{bulk} e^{-e\phi_0/kT} + [OH^-]_{bulk} e^{+e\phi_0/kT} - [Na^+]_{bulk} - [OH^-]_{bulk} \right\}$$

$$[Na^+]_{bulk} = [OH^-]_{bulk} = [NaOH]_{bulk}$$

$$\sigma^2 = 2\epsilon\epsilon_0 kT [NaOH]_{bulk} \left\{ e^{-\frac{e\phi_0}{kT}} + e^{\frac{e\phi_0}{kT}} - 2 \right\}$$

RECOGNIZING THAT

$$\sinh^2 x = \left(\frac{e^{+x} - e^{-x}}{2} \right)^2 = \frac{e^{+2x} + e^{-2x} - 2(e^{-x+x})}{4}$$

$$\sinh^2 x = \frac{e^{+2x} + e^{-2x} - 2}{4}$$

(CONT)

$$\sigma^2 = 8 \epsilon \epsilon_0 kT [N_{AON}] \sinh^2 \left(\frac{e \phi_0}{2kT} \right)$$

REARRANGING FOR ϕ_0

$$\phi_0 = \frac{2kT}{e} \sinh^{-1} \left(\frac{\sigma^2}{\epsilon \epsilon_0 kT [N_{AON}] x_{AN} \times 10^3} \right)^{1/2} \quad E_2 (5)$$

Derivation of Equations (8) & (9)

Equation 8 was derived in the class notes

$$K = \left(\frac{\sum z_i^2 e^2 n_o}{\epsilon \epsilon_o k T} \right)^{1/2}$$

$$K^{-1} = \left[\frac{(1.602 \times 10^{-19} \text{ C})^2 [NaOH]_{\infty} (6.022 \times 10^{26} \frac{\text{molecules}}{\text{mol}}) (\frac{\text{mol}}{\text{L}}) (\frac{\text{L}}{\text{m}^3})}{(8.85 \times 10^{-12} \frac{\text{C}^2}{\text{J} \cdot \text{m}}) (\frac{80}{9.205}) (1.38 \times 10^{-23}) (298 \text{ K})} \right]^{-1/2}$$

$$K^{-1} = \frac{0.430}{\sqrt{[NaOH]_{\infty}}} \quad [=] \quad \text{nm} \quad \text{Equation 9}$$

Derivation of Equations (10), (11)

Start with

$$\sum_i p_{xi} = \sum_i p_{oi} + \frac{\epsilon \epsilon_0}{2kT} \left(\frac{d\phi}{dx} \right)^2$$

$$\left(\frac{d\phi}{dx} \right)^2 = \frac{2kT}{\epsilon \epsilon_0} \left(\sum_i p_{xi} - \sum_i p_{oi} \right) = \frac{2kT}{\epsilon \epsilon_0} [NaOH]_{\infty} \left(e^{-\frac{e\phi}{kT}} + e^{\frac{e\phi}{kT}} - 2 \right)$$

$$\frac{d\phi}{dx} = \left(\frac{8kT}{\epsilon \epsilon_0} [NaOH]_{\infty} \sinh^2 \frac{e\phi}{2kT} \right)^{1/2}$$

$$\frac{d\phi}{dx} = \sqrt{\frac{8kT[NaOH]_{\infty}}{\epsilon \epsilon_0}} \sinh \frac{e\phi}{2kT}$$

$$\int_{\phi=\phi_0}^{\phi(x)} \operatorname{csch} \left(\frac{e\phi}{2kT} \right) d\phi = \sqrt{\frac{8kT[NaOH]_{\infty}}{\epsilon \epsilon_0}} \int_0^x dx$$

$$\int \operatorname{csch} x dx = \ln \tanh \frac{x}{2}$$

$$\int_{\phi_0}^{\phi(x)} \operatorname{csch} \left(\frac{e\phi}{2kT} \right) d\phi = \frac{2kT}{e} \ln \tanh \frac{e\phi}{2kT} \bigg|_{\phi_0}^{\phi(x)} = \frac{2kT}{e} \ln \left[\frac{\tanh \frac{e\phi(x)}{2kT}}{\tanh \frac{e\phi_0}{2kT}} \right]$$

$$\frac{\tanh \frac{e\phi(x)}{4kT}}{\tanh \frac{e\phi_0}{4kT}} = \exp \left(\underbrace{\frac{e}{2kT} \sqrt{\frac{8kT[NaOH]_{\infty}}{\epsilon \epsilon_0}}}_K \right) x$$

Define $\chi = \tanh \frac{e\phi_0}{4kT}$

For now, define $\frac{e\phi(x)}{4kT} = \chi$

(cont)

$$\tanh u = \gamma e^{-kx}$$

$$\tanh u = \frac{e^u - e^{-u}}{e^u + e^{-u}} = \gamma e^{-kx}$$

$$e^u - e^{-u} = (e^u + e^{-u}) \gamma e^{-kx}$$

$$0 = e^u \gamma e^{-kx} - e^{-u} + e^{-u} \gamma e^{-kx} + e^{-u}$$

$$0 = e^u (\gamma e^{-kx} - 1) + e^{-u} (\gamma e^{-kx} + 1)$$

$$\frac{e^u}{e^{-u}} = \frac{-(\gamma e^{-kx} + 1)}{(\gamma e^{-kx} - 1)} = e^{2u} = \frac{1 + \gamma e^{-kx}}{1 - \gamma e^{-kx}}$$

$$u = \frac{1}{2} \ln \frac{1 + \gamma e^{-kx}}{1 - \gamma e^{-kx}}$$

$$\phi(x) = \frac{2k\epsilon}{e} \ln \left[\frac{1 + \gamma e^{-kx}}{1 - \gamma e^{-kx}} \right] \quad \text{Eq (10)}$$

where

$$\gamma = \tanh \left(\frac{e \phi_0}{4k\epsilon} \right) \quad \text{Eq (11)}$$

