1) Silicon oxide has a typical surface potential in an aqueous medium of $\varphi_{\Delta,0} = 70\ \text{mV}$ in 50 mM NaCl at pH 9. Which concentration of cations do you roughly expect close to the surface? What is the average distance between two adjacent cations? What is the local pH at the surface?

Solution

The bulk concentration c_i^0 of the Na$^+$ and Cl$^-$ ions will be:

$$C^0_{Na^+} = C^0_{cl^-} = 50\ mM$$

The H$^+$ concentration in the bulk at PH=9 is given by:

$$PH = -\log\left[a_{H^+}\right] = 9 \quad \Rightarrow C^0_{H^+} = 10^{-9}\,M$$

The Boltzmann for ions in the electrolyte at potential $\varphi_{\Delta,0}$ will determine the concentration at x=0

$$C_i(x) = \frac{n_i(x)}{N_A} = \frac{n_i^0}{N_A}\exp\left(-\frac{z_i F\varphi_\Delta(x)}{RT}\right) = C_i^0 \exp\left(-\frac{z_i F\varphi_\Delta(x)}{RT}\right)$$

$$At \quad x = 0 \quad \varphi_\Delta(x) = \varphi_{\Delta,0} = 70\ mV$$

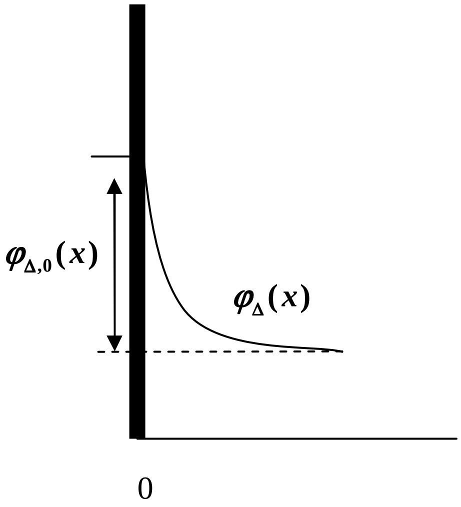
$$C_i\,(0) = C_i^0 \exp\left(-\frac{z_i F\varphi_{\Delta,0}}{RT}\right)$$

For Na$^+$: $C_{Na^+}(0) = C^0_{Na^+}\exp\left(-\frac{F\varphi_{\Delta,0}}{RT}\right) = 3.27\ mM$

For H$^+$: $C_{H^+}(0) = C^0_{H^+}\exp\left(-\frac{F\varphi_{\Delta,0}}{RT}\right) = 6.55\ .10^{-11}\ mM$

too small

$$\Rightarrow \quad C_{cations}(0) \simeq C_{Na^+}(0)$$



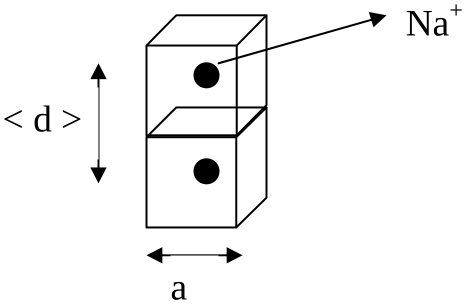
The average distance <d> can be found by calculating the volume that each of the ions occupies at a concentration $c_{Na^+}(0)$

$$V_{unit} = \left[N_A C_{Na^+}(0)\right]^{-1}$$

$$< d >= a = \left[V_{unit}\right]^{\frac{1}{3}}$$

$$< d >= \left[N_A C_{Na^+}(0)\right]^{-1/3}$$

$$= 7.97\, nm$$



Compare with $r_{Na^+} = 9.5.10^{-11} m = 0.09\, nm$ the average distance <d> shows that the distance between Na$^+$ is much larger than Na$^+$ ions. This can be a test for your calculations.

The local PH at x=0

$$PH_0 = -\log\left(a_{H^+}(0)\right) = -\log\left(6.55.10^{-11}\right) = 10.184$$

2) Supporting electrolyte:

Adsorption of ions from the electrolyte solution is important in studying adsorption phenomena on metal electrodes. Suppose we want to study specific adsorption of an anionic species A^-. The concentration of the salt AB in the bulk of the solution is 0.01 M. In addition to that, there is a supporting electrolyte CD of concentration 5M. The surface charge of the metal electrode is $\sigma^M = 0.3\ C/m^2$. We will use the Gouy-Chapman theory to study the role of the supporting electrolyte. Unfortunately, this theory can only be used directly for a situation with only one (z-z) electrolyte. Therefore, we have to proceed in several steps.

a) Consider the situation when the supporting electrolyte is absent. Calculate the surface potential $\varphi_{\Delta,0}$. Calculate the concentration of A^- at the surface. What is the ratio between surface concentration and bulk concentration?

b) Now consider the situation when only the supporting electrolyte is present. Perform the same calculation as in a). What is the surface potential $\varphi_{\Delta,0}$ in this case?

c) What is the effect of the potential distribution calculated for the situation in b) on the distribution of A^-? Discuss how the supporting electrolyte works.

Solution

In absent of supporting electrolyte:

$$\sigma^M = \sqrt{8RT\varepsilon\varepsilon_0 C^0}\,\sinh\left(\frac{F\varphi_{\Delta,0}}{2RT}\right) \quad (*)$$

For our electrolyte: A^-, B^+ in water with $C^0 = 0.01M = 0.01\frac{mol}{Lit}$, $\varepsilon = 78$

and $\sigma = 0.3\frac{C}{m^2}$:

$$0.3\frac{C}{m^2}=\sqrt{8(8.31\frac{J}{K.mol})(300K)(8.854.10^{-12}\frac{C^2}{Nm^2})(78)(0.01\frac{mol}{Lit})(10^3\frac{Lit}{m^3})}\sinh\left(\frac{96500\frac{C}{mol}}{2(8.31\frac{J}{K.mol})(300K)}\varphi_{\Delta,0}\right)$$

$$\varphi_{\Delta,0}=0.203\,V$$

The corresponding surface concentration of A^- is given by the Boltzmann law:

$$C_{A^-}(0)=C^0_{A^-}\exp\left(\frac{F\varphi_{\Delta,0}}{RT}\right)=26.14\ M \quad (**)$$

The ratio $\frac{C_{A^-}(0)}{C^0_{A^-}}=\exp\left(\frac{F\varphi_{\Delta,0}}{RT}\right)=2614.38$

Positive sign in the exponent means that we consider negative charges (A$^-$).

(b) When only supporting electrolyte is presented we get:

$$0.3\frac{C}{m^2}=\sqrt{8(8.31\frac{J}{K.mol})(300K)(8.854.10^{-12}\frac{C^2}{Nm^2})(78)(5.0\frac{mol}{Lit})(10^3\frac{Lit}{m^3})}\sinh\left(\frac{96500\frac{C}{mol}}{2(8.31\frac{J}{K.mol})(300K)}\varphi_{\Delta,0}\right)$$

$$\varphi_{\Delta,0}=0.051\ V;\quad C^{\sup}_{C^-}(0)=C^{\sup}_{C^-}\exp\left(\frac{F\varphi_{\Delta,0}}{RT}\right)=35.419\ M$$

$$\frac{C_{C^-}(0)}{C^0_{C^-}}=7.083$$

(c) Adding supporting electrolyte (i.e. ions in high concentrations which

do NOT undergo reactions with the electrode metal or electrolyte, hence remain inert) will result in a much smaller $\varphi_{\Delta,0}$ and that is, the concentration of the reactant A^- in more uniform throughout the electrolyte.

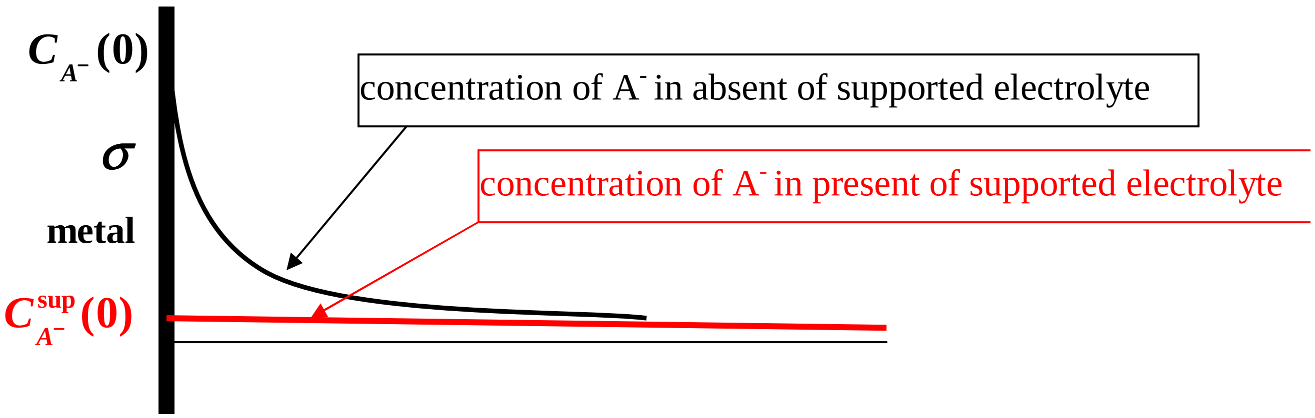
Adding of supporting CD at 5M will lead to a surface concentration of A^- of

$$C_{A^-}^{\sup}(0) = 0.01M\left(\exp\left(\frac{F\varphi_{\Delta,0}}{RT}\right)\right)$$

$$= 0.01M\left(\exp\left(\frac{96500\frac{C}{mol}}{(8.31\frac{J}{K.mol})(300K)}0.050V\right)\right) = 0.071\ M$$

$$\frac{C_{A^-}(0)}{C_{A^-}^{0}} = 7.084$$

instead of 2614!!



3) From a Tafel plot, we can estimate the exchange current density j_0 as well as the transfer coefficient α. At T=25C, the following current densities were measured for a $Pt|H_2|H^+$ electrode in diluted H_2SO_4, as a function of the applied overpotential η.

η [mV]	50	100	150	200	250
j [mA/cm2]	2.66	8.91	29.9	100	335

a) Calculate the exchange current density and the transfer coefficient.

b) How many electrons are transferred per second and per cm^2 of catalyst through the metal|solution interface at equilibrium potential.

Solution

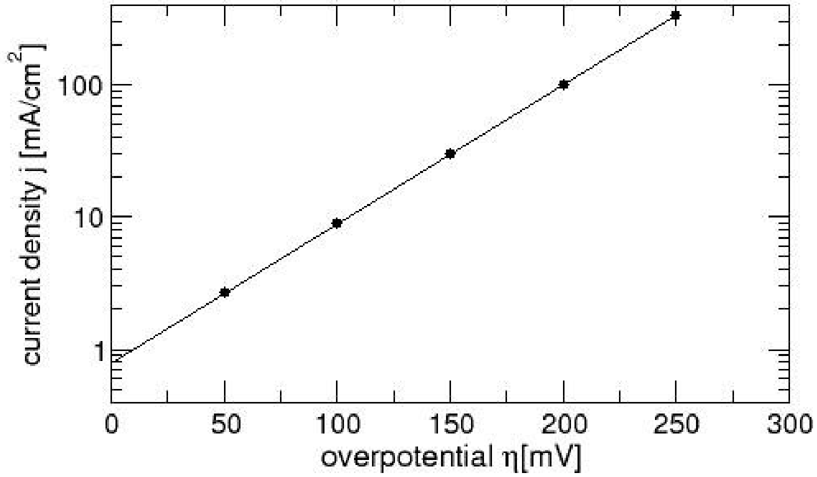
(a) Using Tafel approximation

$$\log(j) = \log(j_0) + \frac{\alpha F}{2.303RT}\eta$$

We can calculate:

α from the slop of the log(current)-voltage plot
exchange current density from y-axis intercept.

Conclusively, the exchange current density and transfer coefficient are found to be



$$\log\left(j_0\right)=0.9mA \quad \Rightarrow j_0=10^{0.9}=7.94\ mA/cm^2$$

$$\frac{\alpha F}{2.303RT}=10.5009 \quad \Rightarrow \quad \alpha=10.5009\frac{2.303RT}{F}=0.62$$

(b) At equilibrium potential, both the oxidation and reduction reaction at a equal rate of j_0. Thus the total charge transfer across the interface will be $2j_0$ The total number of electrons crossing the interface per second, n_e is:

$$n_e=\frac{2j_0}{e_0}=9.92.10^{16}\ electron/s$$