Chem. Engr. 06-607 Physical Chemistry of Colloids and Surfaces

Homework #5 **3-5-02**

Due: 3-14-02, beginning of class.

1. Problem 3.2, Evans.

2. Problem 3.7, Evans.

3. Problem 3.11, Evans.

4. Plot the following quantities as a function of the distance (x) from a surface having a surface charge density (s) of –0.003 C/m^2 in 1 mM NaCl and 10 mM NaCl (T = 298K). Neglect the counterions released from the charged surface, and plot the functions from x = 10 nm to x = 100 nm using data calculated in 10 nm intervals.

   a) The electrostatic potential (F) in mV vs. x in nm.
   b) The concentration of cations (c_{Na+}*) in mM vs. x in nm.
   c) The concentration of anions (c_{Cl-}*) in mM vs. x in nm.

5. Consider a surface with one negative surface charge per 2000 Å^2 of surface area. It is exposed to pH 7, de-gassed water that contains 0.1 mM NaCl (T=298K).

   a) What is the surface charge density in C/m^2?
   b) Estimate the pH in the water immediately adjacent to the surface.

You may find the following information useful:

Grahame equation (symmetric electrolyte):

$$s = \sqrt{8kTc_{\infty}^{*} e_r e_o}\left(exp\left(\frac{zeF_o}{2kT}\right) - exp\left(\frac{zeF_o}{2kT}\right)\right) = \sqrt{8kTc_{\infty}^{*} e_r e_o}\, sinh\left(\frac{zeF_o}{2kT}\right)$$

Gouy-Chapman expression (symmetric electrolyte):

$$F(x) = \frac{2kT}{ze} ln\left\{\frac{1 + G_o\, exp(-kx)}{1 - G_o\, exp(-kx)}\right\}$$; where

$$G_o = \frac{exp(\frac{zeF_o}{2kT}) - 1}{exp(\frac{zeF_o}{2kT}) + 1} = tanh\left(\frac{zeF_o}{4kT}\right)$$; and $$\frac{1}{k} = \sqrt{\frac{e_r e_o kT}{\sum_i (z_i e)^2 c_{i\infty}^{*}}}$$

Boltzmann distribution for ionic species:

$$c_i^{*}(x) = c_{i\infty}^{*}\, exp\left(\frac{-z_i eF(x)}{kT}\right)$$

Physical constants:

kT (298K) = 4.114 x 10^{-21} J
ε_o = 8.854 x 10^{-12} C^2/J*m
ε_r (water, 298 K) = 78
e = 1.602 x 10^{-19} C

Variables (mks units):

$F(x) =$ electrostatic potential, units of volts (J/C)
$F_o =$ surface electrostatic potential, units of volts (J/C)
$s =$ surface charge density, units of (C/m^2)
$\frac{1}{k} =$ Debye length, units of (m)
$c_i^{*} =$ local concentration of ion i, units of (ions/m^3)
$c_{i\infty}^{*}$ bulk concentration of ion i, units of (ions/m^3)
c_{∞}^{*} bulk concentration of symmetric electrolyte, units of (molecules electrolyte added/m^3)
$z_i =$ valency of ion i
$z =$ valency of symmetric electrolyte (always positive)