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CBE 521

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Homework 1

1. Calculate the average linear velocity and the bulk flow rate of water at 293^oK for cylindrical nanocapillary with diameter 500 nm and length 1 cm. The applied pressure is 5 atm. (The viscosity of water is $9.93 \times 10^{-4}\ Pa \cdot s$)

Beginning with the continuity and momentum equations as well as pressure differential,

$$\frac{\partial v_z}{\partial z} = 0$$

$$\eta \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial v_z}{\partial r}\right) = \frac{\partial p}{\partial z}$$

$$-\frac{\partial p}{\partial z} = \frac{p_{in} - p_{out}}{L}$$

Integrating twice,

$$\partial\left(r\frac{\partial v_z}{\partial r}\right) = \frac{1}{\eta}\frac{\partial p}{\partial z} r\partial r$$

$$r\frac{\partial v_z}{\partial r} = \frac{1}{2\eta}\frac{\partial p}{\partial z}r^2 + c_1$$

$$v_z = \frac{1}{4\eta}\frac{\partial p}{\partial z}r^2 + c_1 + c_2$$

Applying the boundary conditions,

$$at\ r = 0 \quad \frac{\partial v_z}{\partial r} = 0 \quad c_1 = 0$$

$$at\ r = R \quad v_z = 0 \quad c_2 = -\frac{1}{4\eta}\frac{\partial p}{\partial z}R^2$$

The equation becomes,

$$v_z = \frac{1}{4\eta}\frac{\partial p}{\partial z}(r^2 - R^2)$$

$$v_z = \frac{1}{4\eta}\frac{p_{in} - p_{out}}{L}(R^2 - r^2)$$

Applying the equations with the following parameters,

$$R = \frac{500\ nm}{2} = 250\ nm = 0.000000250\ m$$

$$L = 1\ cm = 0.010\ m$$

$$p_{in} - p_{out} = 5\ atm = 506625\ Pa$$

$$\eta = 9.93 \times 10^{-4}\ Pa \cdot s$$

The average velocity is,

$$\langle v_z \rangle = \frac{\int_0^{2\pi}\int_0^R v_z r dr\, d\theta}{\int_0^{2\pi}\int_0^R r dr\, d\theta} = \frac{p_{in} - p_{out}}{8\eta L}R^2$$

$$\langle v_z \rangle = \frac{506625\ Pa}{8(9.93 \times 10^{-4}\ Pa \cdot s)(0.010\ m)}(0.000000250\ m)^2$$

$$\boxed{\langle v_z \rangle = 3.9859 \times 10^{-4}\ \frac{m}{s}}$$

The bulk flow rate is,

$$Q = \int_0^{2\pi}\int_0^R v_z r dr\, d\theta = \pi R^2 \frac{p_{in} - p_{out}}{8\eta L}R^2 = \pi R^2 \langle v_z \rangle$$

$$Q = \pi(0.000000250\ m)^2\left(3.9859 \times 10^{-4}\ \frac{m}{s}\right)$$

$$\boxed{Q = 7.8263 \times 10^{-17}\ \frac{m^3}{s}}$$

2. Washburn equation for a horizontal capillary can be written in the form

$$\langle v \rangle = \frac{dL}{dt} = \frac{\gamma R}{4\mu L}$$

Derive expression for the time dependencies of the length of travel $L(T)$ and the average velocity of capillary driven fluid motion $\langle v \quad t \rangle$.

Starting with the equation derived for a perfectly wetting capillary from problem 1 where the pressure is dictated by capillary forces in a horizontal capillary ($\theta = 0$),

$$v_z = \frac{1}{4\mu} \frac{p_c}{L} (R^2 - r^2)$$

$$p_c = \frac{2\gamma}{r} \cos(\theta)$$

To obtain the average velocity,

$$\langle v_z \rangle = \frac{\int_0^{2\pi} \int_0^R v_z r dr \, d\theta}{\int_0^{2\pi} \int_0^R r dr \, d\theta} = \frac{p_c}{8\mu L} R^2$$

$$\boxed{\langle v_z \rangle = \frac{\gamma R}{4\mu L}}$$

Integrating over time,

$$\frac{dL}{dt} = \frac{\gamma R}{4\mu L}$$

$$L dL = \frac{\gamma R}{4\mu} dt$$

$$\frac{L^2}{2} = \frac{\gamma R}{4\mu} t + c_1$$

Applying boundary condition,

$$at \; t = 0 \quad L = 0 \quad c_1 = 0$$

Equation becomes,

$$\boxed{L(t) = \sqrt{\frac{\gamma R}{2\mu} t}}$$

3. The surface tension of pure water at room temperature is equal to 72 mN/m. Calculate the pressure drop at the water surface in a capillary with radius 0.5 mm. Assume perfect wetting of the walls.

Pressure drop for a perfectly wetting capillary is just the pressure of the capillary forces,

$$p_c = \frac{2\gamma}{R}$$

$$p_c = \frac{2\left(72\ \frac{mN}{m}\right)\left|\frac{1\ N}{1000\ mN}\right|}{0.5\ mm\ \left|\frac{1\ m}{1000\ mm}\right|}$$

$$\boxed{p_c = 288\frac{N}{m^2}}$$

4. Using the correct expression for the potential distributions (and low potential approximations), derive relationships for the surface charges at the solid liquid interface for

The electrokinetic phenomena are described by Poisson's and Boltzmann's equations,

$$\nabla \cdot \varepsilon \nabla \Psi = -\frac{\rho_e}{\varepsilon_0}$$

$$\nabla^2 \Psi = -\frac{\rho_e}{\varepsilon \varepsilon_0}$$

$$\rho_e = e \sum_i z_i n_i$$

$$n_i = n_i^0 \exp\left(-\frac{z_i e \Psi}{kT}\right)$$

$$\nabla^2 \Psi = -\frac{e}{\varepsilon \varepsilon_0} \sum_i z_i n_i^0 \exp\left(-\frac{z_i e \Psi}{kT}\right)$$

Applying the low potential approximation yields the electrostatic potential ODE,

$$\frac{z_i e \Psi}{kT} \ll 1 \quad where\ \frac{kT}{e} = 25.9\ mV\ at\ T = 298^o K$$

$$\nabla^2 \Psi = \kappa^2 \Psi \quad where\ \kappa = \sqrt{\frac{e^2 \sum_i z_i^2 n_i^0}{\varepsilon \varepsilon_0 K_B T}}$$

For each case, below, there is a specific solution for the electrostatic potential that is used to derive the charge potential equation, below, at the solid-liquid interface,

$$\sigma = -\varepsilon \varepsilon_0 \nabla \Psi|_{at\ interface}$$

a. Single double layer

$$\Psi = \Psi_0 \exp -\kappa x$$

$$\left.\frac{d\Psi}{dx}\right|_{x=0} = -\Psi_0 \kappa \exp -\kappa x = -\Psi \kappa$$

$$\boxed{\sigma = \varepsilon \varepsilon_0 \Psi_0 \kappa}$$

b. Spherical double layer

$$\Psi = \Psi_0 \frac{\exp -\kappa(r - R)}{r}$$

$$\left.\frac{d\Psi}{dr}\right|_{r=R} = -\Psi_0\kappa\frac{\exp -\kappa(r-R)}{r} = -\frac{\Psi\kappa}{\mathrm{R}}$$

$$\boxed{\sigma = \frac{\varepsilon\varepsilon_0\Psi\kappa}{R}}$$

c. Single cylindrical double layer (Hint: $\frac{dK_0x}{dx} = -K_1x$ – modified K Bessel function of first order)

$$\Psi = \Psi_0\frac{K_0(\kappa r)}{K_0(\kappa R)}$$

$$\left.\frac{d\Psi}{dr}\right|_{r=R} = -\frac{\Psi_0\kappa}{K_0(\kappa R)}K_1(\kappa r) = -\Psi_0\kappa\frac{K_1(\kappa R)}{K_0(\kappa R)}$$

$$\boxed{\sigma = \varepsilon\varepsilon_0\Psi_0\kappa\frac{K_1(\kappa R)}{K_0(\kappa R)}}$$

d. Slit shaped channel

$$\Psi = \Psi_0\frac{\cosh\kappa\left(\frac{h}{2}-x\right)}{\cosh\kappa\left(\frac{h}{2}\right)}$$

$$\left.\frac{d\Psi}{dx}\right|_{x=0} = -\frac{\Psi_0\kappa}{\cosh\kappa\left(\frac{h}{2}\right)}\sinh\kappa\left(\frac{h}{2}-x\right) = -\Psi_0\kappa\frac{\sinh\kappa\left(\frac{h}{2}\right)}{\cosh\kappa\left(\frac{h}{2}\right)}$$

$$\boxed{\sigma = \varepsilon\varepsilon_0\Psi_0\kappa\frac{\sinh\kappa\left(\frac{h}{2}\right)}{\cosh\kappa\left(\frac{h}{2}\right)}}$$

e. Cylindrical capillary (Hint: $\frac{dI_0x}{dx} = -I_1x$ – modified I Bessel function of first order)

$$\Psi = \Psi_0\frac{I_0(\kappa r)}{I_0(\kappa R)}$$

$$\left.\frac{d\Psi}{dx}\right|_{r=0} = -\frac{\Psi_0\kappa}{I_0(\kappa R)}I_1(\kappa r) = -\Psi_0\kappa\frac{I_1(\kappa R)}{I_0(\kappa R)}$$

$$\boxed{\sigma = \varepsilon\varepsilon_0\Psi_0\kappa\frac{I_1(\kappa R)}{I_0(\kappa R)}}$$

5. A particle is suspended in KCL solution with ionic strength equal to 0.001 M. When subjected to electric field with strength of 2000 V/m the particle moves with a velocity of 130 $\mu m/s$. Calculate the ζ-potential at room temperature ($T = 298^o K$) if the particle radius is

The parameters used are the following,

$$\varepsilon = 78.25 \qquad \varepsilon_0 = 8.854 \times 10^{-12} \frac{C^2}{J \cdot m} \qquad \eta = 0.001\ Pa \cdot s \qquad T = 298^o\ K$$

$$I = 0.001\ M \qquad \vec{E} = 2000\ \frac{V}{m} \qquad v_{ep} = 130\ \frac{\mu m}{s}$$

The Debye length is first calculated to dictate which electrophoresis relationship to use,

$$\kappa^{-1} = \frac{0.304}{\sqrt{I}} \Rightarrow \frac{0.304}{\sqrt{0.001}} = 9.613\ nm$$

Then the characteristic size parameter is calculated,

$$\kappa R$$

And then the electrophoretic mobility equation is solved for ζ.

a. 500 nm

Checking characteristic size parameter,

$$\kappa R = \frac{500\ nm}{9.613\ nm} = 52.013 \gg 1$$

Fits the case of Smoluchowski where $\kappa R \gg 1$,

$$v_{ep} = \frac{\varepsilon \varepsilon_0 \zeta}{\eta} \vec{E}$$

Solving for ζ,

$$\zeta = \frac{v_{ep}\eta}{\varepsilon \varepsilon_0 \vec{E}}$$

$$\zeta = \frac{\left(130\ \frac{\mu m}{s}\right)(0.001\ Pa \cdot s)\left|\frac{1\ m}{1000000\ \mu m}\right|\left|\frac{1\frac{N}{m^2}}{1\ Pa}\right|}{(78.25)\left(8.854 \times 10^{-12} \frac{C^2}{J \cdot m}\right)\left(2000\ \frac{V}{m}\right)\left|\frac{1\frac{J}{C}}{1\ V}\right|}$$

$$\boxed{\zeta = 93.819\ mV}$$

b. $1\ nm$

Checking characteristic size parameter,

$$\kappa R = \frac{1\ nm}{9.613\ nm} = 0.104 < 1$$

Fits the case of Debye-Huckel where $\kappa R \ll 1$,

$$v_{ep} = \frac{2}{3}\frac{\varepsilon\varepsilon_0\zeta}{\eta}(1+\kappa R)\vec{E}$$

Solving for ζ,

$$\zeta = \frac{3}{2}\frac{v_{ep}\eta}{\varepsilon\varepsilon_0(1+\kappa R)\vec{E}}$$

$$\zeta = \frac{3}{2}\frac{\left(130\ \frac{\mu m}{s}\right)(0.001\ Pa\cdot s)\left|\frac{1\ m}{1000000\ \mu m}\right|\left|\frac{1\frac{N}{m^2}}{1\ Pa}\right|}{(78.25)\left(8.854\times 10^{-12}\frac{C^2}{J\cdot m}\right)(1+0.104)\left(2000\ \frac{V}{m}\right)\left|\frac{1\frac{J}{C}}{1\ V}\right|}$$

$\boxed{\zeta = 127.471\ mV}$

c. $10\ nm$

Checking characteristic size parameter,

$$\kappa R = \frac{10\ nm}{9.613\ nm} = 1.040 \sim 1$$

Fits the case of Henry where $\kappa R \sim 1$,

$$\frac{v_{ep}}{\vec{E}} = \frac{2}{3}\frac{\varepsilon\varepsilon_0\zeta}{\eta}\left\{1+\frac{1}{2}\left\{1+\left[\frac{5}{2\kappa R}(1+2e^{-\kappa R})\right]\right\}^3\right\}$$

Solving for ζ,

$$\zeta = \frac{3}{2}\frac{v_{ep}\eta}{\varepsilon\varepsilon_0\vec{E}\left\{1+\frac{1}{2}\left\{1+\left[\frac{5}{2\kappa R}(1+2e^{-\kappa R})\right]\right\}^3\right\}}$$

$$\zeta = \frac{3}{2}\frac{\left(130\ \frac{\mu m}{s}\right)(0.001\ Pa\cdot s)\left|\frac{1\ m}{1000000\ \mu m}\right|\left|\frac{1\frac{N}{m^2}}{1\ Pa}\right|}{(78.25)\left(8.854\times 10^{-12}\frac{C^2}{J\cdot m}\right)\left(2000\ \frac{V}{m}\right)\left\{1+\frac{1}{2}\left\{1+\left[\frac{5}{2(1.040)}(1+2e^{-1.040})\right]\right\}^3\right\}\left|\frac{1\frac{J}{C}}{1\ V}\right|}$$

$\boxed{\zeta = 2.087\ mV}$

6. A cylindrical capillary filled with 0.01 M NaCl solution and has ζ-potential equal to 80 mV. The length of the capillary is 1 m and its diameter is 1 mm.

   a. Check the validity of the Smoluchowski model for this dimensions and ionic strength.

   The Debye length is first calculated,

$$\kappa^{-1} = \frac{0.304\ nm}{\sqrt{I}} \Rightarrow \frac{0.304\ nm}{\sqrt{0.01\ M}} = 3.04\ nm$$

   Then the characteristic size parameter is calculated,

$$\kappa R = \frac{500{,}000\ nm}{3.04\ nm} = 164473.684$$

   Which is valid for the Smoluchowski case where $\kappa R \gg 1$.

   b. Calculate the electroosmotic linear and volumetric flow rates if a potential difference of 1000 V is applied at both ends.

   The fluid velocity is the following,

$$v_{eo} = -\frac{\varepsilon\varepsilon_0\zeta}{\eta}\frac{E}{l}$$

$$v_{eo} = -\frac{(78.25)\left(8.854\times 10^{-12}\frac{C^2}{J\cdot m}\right)(80\ mV)\left|\frac{1\ V}{1000\ mV}\right|\left|\frac{1\frac{J}{C}}{1\ V}\right|}{(0.001\ Pa\cdot s)\left|\frac{1\frac{N}{m^2}}{1\ Pa}\right|}\left(\frac{1000\ V}{1\ m}\right)\left|\frac{1\frac{N\cdot m}{C}}{1\ V}\right|$$

$$\boxed{v_{eo} = -5.543\times 10^{-11}\ \frac{m}{s}}$$

   The volumetric flow rate is then the following,

$$V = \pi R^2 v_{eo}$$

$$V = \pi(5\times 10^{-4}\ m)^2\left(-5.543\times 10^{-11}\ \frac{m}{s}\right)$$

$$\boxed{V = -4.353\times 10^{-17}\ \frac{m^3}{s}}$$