TODAY: Ⅰ Donnan Equil. ⇒ partitioning of charged molecules into charged Tissues/ gels 10/25

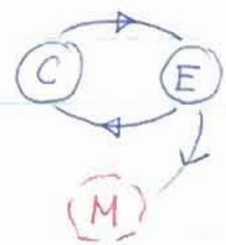
Ⅱ Ionization & Titration of Biomolecules
(cell surfaces; tissues; proteins; DNA...)

Ⅲ Non-equil. X-port in Charged Media:
case study: swelling (edema) of connective tissues

Electrochem. Coupling + X-port

(1) $\underline{N}_i = -D_i \nabla c_i + \frac{z_i}{|z_i|} u_i c_i \underline{E}$

(2) $\frac{\partial c_i}{\partial t} = -\nabla \cdot \underline{N} + R_i$



(3) $\nabla \cdot \epsilon \underline{E} = \rho_e = \sum_i z_i F c_i$

(4) $\bar{E} = -\nabla \Phi$

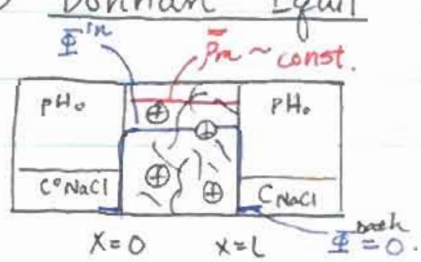
(5) $\nabla \cdot \underline{J} = -\frac{\partial \rho_e}{\partial t}$

(6) $\underline{J} = \sigma \underline{E} + (\ \ ) \nabla c_i$

sidenote: · tendon is very strong, w/ high modulus due to triple helix structure of collagen.

· $\rho_{net} \approx 0$ under physiological conditions: pulling H^+ out, $COOH \rightleftharpoons COO^- + H^+$, add H^+ in, $NH_3^+ \rightleftharpoons NH_3 + H^+$

Ⅰ "Donnan" Equil



Ⓐ Given: $\bar{\rho}_m$ "in" (fixed), C_{NaCl}, C
C^+ C^- – mobile ions.

Find: $\bar{c}_i$; $(\Phi_{in} - \Phi_{bath}) = \Delta\Phi_{Don}$.

Boltzmann $\begin{cases} \bar{c}_i = c_0 e^{-zF\Phi(x)/RT} \\ (\Phi^{in} - \Phi^{bath}) = \frac{-RT}{z_i F} \ln\left(\frac{\bar{c}_i}{c_{in}^{bath}}\right) \end{cases}$

Ⓑ Given: c_{i0}, K_a's ⇐ $\underline{N}_i \equiv 0$ in Equil.
Find: $\bar{\rho}_m$, $\bar{c}_i$

Unknowns: C_{Na^+}, C_H, C_{Cl}, C_{OH}, ρ_m p.5.2.

· Don't know potential in the beginning

· since ρ_m is constant throughout membrane, Φ is same, ∴ $E = 0$. on macro scale.

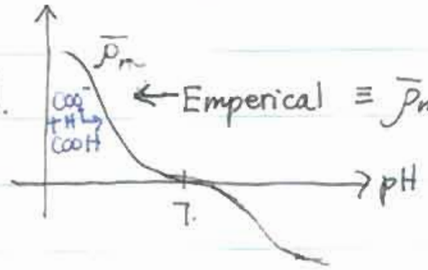
Solve Ⓑ: (macro-neutrality) for $L \gg 1/k$

From ③ $\nabla \cdot \varepsilon E = \rho_e = \bar{\rho}_m + F(\bar{C}_{Na^+} + \bar{C}_{H^+} - \bar{C}_{Cl^-} - \bar{C}_{OH^-}) \simeq 0$ [a]

[b] [c] $\left(\frac{\bar{C}_{Na^+}}{C^o_{Na}}\right) = \left(\frac{\bar{C}_{H^+}}{C^{bath}_{H^+}}\right)$ because $\ln\left(\frac{C_i}{C_{in}^{bath}}\right)^{1/z_i}$ = constant. Since $\underbrace{\Phi^{in} - \Phi^{bath}}_{\text{constant}}$

$\frac{RT}{F}$ - constant

[d] $= \left(\frac{C^o_{Cl}}{\bar{C}_{Cl}}\right) = \left(\frac{C^o_{OH}}{\bar{C}_{OH}}\right)$

[e]. 

← Emperical $\equiv \bar{\rho}_m(\bar{C}_{Na}, \bar{C}_{Cl}, \bar{C}_H, \bar{C}_{OH})$ or analytical model.

Find "Isotherm" $\bar{\rho}_m(\bar{C}_{Na}, \bar{C}_H, \bar{C}_{Cl}, \bar{C}_{OH})$ for simplicity look @ pH ≤ 9

$COOH \underset{K_{on}}{\overset{K_{off}}{\rightleftharpoons}} COO^- + H^+$

$$\boxed{\frac{[COO^-][H^+]}{[COOH]} = \frac{k_{off}}{k_{on}} \equiv k_{dissociation}}$$

Source of fix charge: backbone of tissue.

→ dilute solution.

$$-\log\frac{[COO^-]}{[COOH]} - \log[H^+] = -\log k_d$$

$$\boxed{pH = pK_d + \log\frac{[COO^-]}{[COOH]}}$$

Henderson Hasselbach

Let $n = [COOH] + [COO^-] \equiv$ Conc. of binding sites for H^+ ions.

↳ measure (biochem) ✓.

$$[\overline{COO^-}][\overline{H^+}] = K_d(\overbrace{n - [COO^-]}^{[COOH]})$$

$$[\overline{COO^-}](\bar{C}_H + K_d) = nK_d.$$

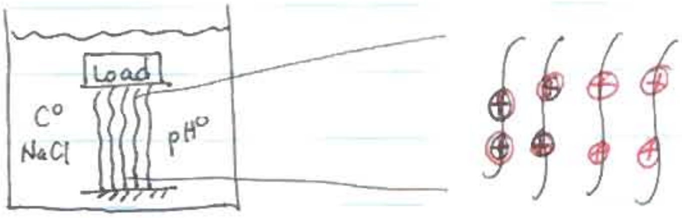
$$[\overline{COO^-}] = \left(\frac{nK_d}{K_d + \bar{C}_H}\right)$$

don't know

("Langmuir Isotherm")

$\bar{\rho}_m = \bar{\rho} - F([COO^-])$ [e']

↑ amino group.



int

fixed length.

Change in pH give rise to more charge, repel each other, causing swelling

repulsion of surrounding charges.