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Novel Separation Process

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Dialysis :- Driving force \rightarrow Concentration grad.

Batch Dialyses :- 

Transport mechanism :- Diffusion of solute

$$N_i = \frac{\text{mass flux of } i\text{th species}}{\text{area}} = D_{im} \frac{dC_{im}}{dx} = D_{im} \frac{\Delta C_{im}}{L}$$

D_{im} = Diffusivity of i th solute through the membrane
 L = membrane thickness

$$N_i = \frac{D_{im}}{L} (C_{if} - C_{id})$$

$$m_i = \frac{C_{im}^f}{C_{if}} = \frac{C_{im}^d}{C_{id}} \Rightarrow \text{Partition factor}$$

$$N_i = \frac{D_{im} m_i}{L} (C_{if} - C_{id})$$

for Phenol :- $m_i = 0.01$ (P & memb. material)
 $m_i = 0.5$ for urea soln & sepn cellulose

$$D_{im} = 10^{-11} \text{ m}^2/\text{s} \quad (\text{Diffusivity in bulk})$$

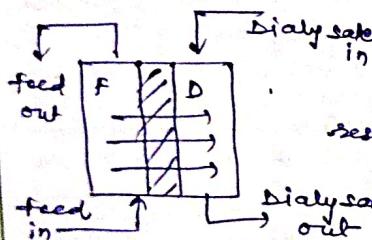
$$D_{im} = D_{ib} \in \text{Forag}$$

Tortuosity \rightarrow memb. porosity

\rightarrow diffusivity of i th species in the bulk

$$f_{\text{drag}} = 1 - 2.1 \left(\frac{r_i}{r_s} \right)^3 + 2.09 \left(\frac{r_i}{r_s} \right)^5 - 0.95 \left(\frac{r_i}{r_s} \right)^5$$

r_i = solute rad.
 r_s = pore rad.



resistive films:

R_F = liq. film resistance in feed side
 R_d = liq. film resistance at the dialysate side

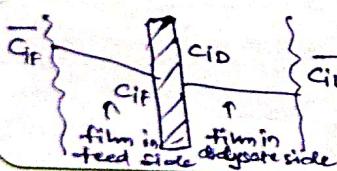
R_m = memb. resistance

N = solute flux

$$N_i = \frac{C_{if} - C_{id}}{R_F} \quad (\text{across liq. film in feed side})$$

$$N_i = \frac{D_{im}}{L} \frac{(C_{if} - C_{id})}{R_m} \quad (\text{across the memb.})$$

$$N_i = \frac{C_{id} - C_{if}}{R_d} \quad (\text{across liq. film in dialysate side})$$



$$= \frac{1}{MTC}$$

$$N_i = \frac{C_{if} - C_{id}}{R_o} \quad (\text{across liq. film in dialysate side})$$

$$(1/K_{\text{eq}}) R_o = R_F + L/D_m + R_d = 1/k_F + L/D_m + 1/k_D$$

Calc. the net mass flux across the membrane in a dialysate unit :-

$$dm = \text{mass flow rate across } dA = k_o A \Delta C A$$

$$V_F = \text{volumetric feed flow rate}$$

$$V_D = \text{volumetric dialysate flow rate}$$

$$dm = -V_F dC_F = V_D dC_D$$

$$\text{rearrangement} \rightarrow dC_F = -\frac{dm}{V_F} \quad dC_D = \frac{dm}{V_D}$$

$$dC = C_F - C_D \quad d(C) = dC_F - dC_D$$

$$d(C) = -\left(\frac{1}{V_F} + \frac{1}{V_D}\right) dm \quad dm = k_o A \Delta C dA$$

$$d(C) = -\left(\frac{1}{V_F} + \frac{1}{V_D}\right) k_o A \Delta C dA$$

$$\int_0^A d(C) = -\left(\frac{1}{V_F} + \frac{1}{V_D}\right) \int_0^A k_o A \Delta C dA$$

$$\ln\left(\frac{C_{lo}}{C_{hi}}\right) = -\left(\frac{1}{V_F} + \frac{1}{V_D}\right) \int_0^A dm$$

$$C_{lo} - C_{hi} = -\left(\frac{1}{V_F} + \frac{1}{V_D}\right) m$$

$$m \text{ (kg/s)} = k_o A = \frac{(C_{lo}) - (C_{hi})}{\ln\left(\frac{C_{lo}}{C_{hi}}\right)}$$

Batch Dialyses :-

$$\frac{d(C_{id} V_D)}{dt} = \frac{A m D_{im} (C_{if} - C_{id})}{L}$$

$$\frac{d(C_{if} V_F)}{dt} = -\frac{A m D_{im} (C_{if} - C_{id})}{L}$$

initial condn :- at $t=0$, $C_{if} = C_{if}^0$; $C_{id}^0 = 0$
applying Laplace transform :-

$$s C_{id} D = \frac{A m D_{im} (C_{if}^0 - C_{id})}{L V_D}$$

$$s C_{if} - C_{if}^0 = -\frac{A m D_{im} (C_{if}^0 - C_{id})}{L V_F}$$

$$\frac{A m D_{im}}{L} = K$$

$$s C_{id} = \frac{K}{V_D} (C_{if}^0 - C_{id}) \quad \leftrightarrow \quad C_{id} = \left(\frac{K}{V_D}\right) C_{if}^0$$

$$s C_{if} - C_{if}^0 = -\frac{K}{V_F} (C_{if}^0 - C_{id}) \quad \leftrightarrow \quad C_{if} = \left(\frac{K}{V_F} + \frac{1}{V_D}\right) C_{if}^0$$

$$\text{Defining } \alpha = K \left(\frac{1}{V_F} + \frac{1}{V_D}\right)$$

$$K = A m D_{im}$$

$$C_{id} = \left(\frac{K}{V_D}\right) C_{if}^0 \left(\frac{1}{s} - \frac{1}{s+\alpha}\right)$$

$$\text{Taking inverse Laplace} : C_{id}(+) = C_{if}^0 \left(\frac{V_F}{V_F + V_D}\right) [1 - e^{-\alpha t}]$$

$$C_D(t) = b \left(1 - e^{-kDt} \right)$$

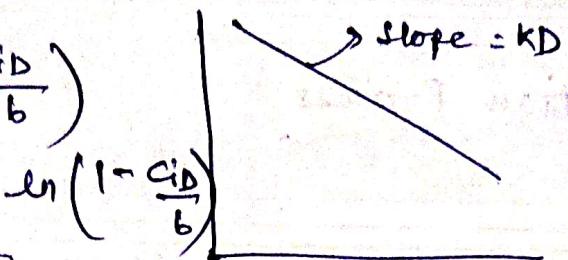
$$\frac{C_D}{b} = 1 - e^{-kDt}$$

$$e^{-kDt} = 1 - \frac{C_D}{b}$$

$$\Rightarrow -kDt = \ln \left(1 - \frac{C_D}{b} \right)$$

$$\frac{\text{Aim Dim}}{L} = \frac{\text{Slope}}{D}$$

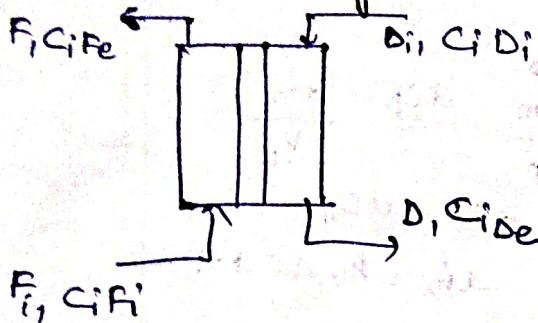
$$D = \frac{1}{V_F} + \frac{1}{V_D}$$



$$\frac{\Delta \text{dim}}{\Delta t} = \frac{\text{slope} \times L}{D}$$

less comp. to bulk value

Continuous Dialyzer :-



Assumpn :- (1) const feed and Dialyse flow rate

(2.) Dialyser perf. dep. on the value of film & membrane resistance

(3.) film thickness solely depends on the geometry and vel. profile in the channel.

$$m_i = k_o A_m (\Delta C_i)_{\text{lim TD}} \rightarrow (AC)_i - (AC)_o$$

$$= V_F (C_i F_i - C_i F_e) \quad \ln \left[\frac{(AC)_i}{(AC)_o} \right]$$

$$= V_D (C_i D_e - C_i D_i)$$

$$\eta = \frac{\text{Efficiency} \rightarrow \text{actual amt. of solute depleted in feed}}{\text{max amt. seepn possible}} = \frac{V_F (C_i F_i - C_i F_e)}{V_F C_i F_i - V_D C_i D_i}$$

$C_i D_i \approx 0$ bcoz CO_2 free in a dialyzer

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Electric field enhanced UF

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- Electrokinetic Effects - if a charged surf. has set. net. past a second surf./Node \Rightarrow then no. of phenomena occurs which are grouped as electrokinetic effect.

→ origin: - + + + + Phase 1
- - - - - Phase 2

(i) If we have a truly charged surf. placed in an electrolytic solⁿ (NaCl, 1:1 electrolyte) the true charges will accumulate on the surf. The conc. of -ve charges will be max. at the interface, and reduces as moved away from the surf.

(ii) Bulk: @ Electro neutrality is maintained
① for 1:1 electrolyte conc. of both ionic species becomes equal.

In bulk \rightarrow electrostatic potential is zero. Location of the bulk is typically 5 to 100 nm from the charged surf. (This distance is influenced by the conc. of electrolyte solⁿ)

Electric Double Layer: — arrangement and distribution of the charges from the interface to the bulk.

Categories of Electrokinetic effect:

Electrophoresis \rightarrow in one phase is liq. (orgas) in which the 2nd phase is suspended as solid (or liq.), then particles can be induced to move by applying an ext. electric field. Vel. of particles can be measured under various electric strength \rightarrow electrophoretic velocity \rightarrow gives information abt. the particle or potential on its surf.

Electroosmosis \rightarrow In this case, the solid surf. is stationary and the liq. moves under the influence of an ext. electric field. It occurs when a capillary or porous plug is filled up with an electrolytic solⁿ.

electrolytic solⁿ

$E_d = V$
true charges of electrolyte solⁿ move and drag liqs along with them. \rightarrow one can find charged liqs along with them. \rightarrow one can find charged liqs along with them.
Streaming potential \rightarrow electrolyte solⁿ fills up the solid capillary \rightarrow apply a p.s. gradient \rightarrow Transport of excess charges near the wall by liq. movement

leads to acc. of charges in the downstream of the channel / capillary tube \rightarrow develop an electric field that drives the electric current against the flow dirn.

at SS is reached \rightarrow pot. diff. is defined as streaming potential (across capillary) (gives info. abt. surf. potential / wall charge density of charged wall).

Sedimentation potential \rightarrow When charged colloidal particles are allowed to settle through a fluid under gravity or centrifugal field \rightarrow A potential is gen. gives info. about charged density or surf. potential of fluid.

Surf. of shear \rightarrow Imaginary surf. close to which charged particles move in colⁿ under ext. E during electrophoresis.

\rightarrow viscosity is infinity

\rightarrow surf. of shear

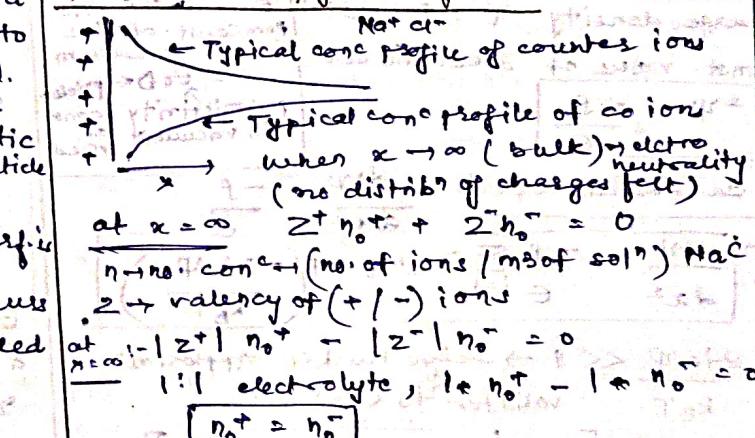
Stear layers \rightarrow When a charged particle moves in the electrolytic solⁿ under the influence of external E an envelope of fluid particles move along with it. The potential on outside particles is known as zeta Potential (gen. consists of counter ions)

Electrophoretic mobility = $\frac{\text{electrophoretic vel. } (\text{m.m})}{\text{electric field strength } (\text{V.V}^{-1})}$

$= (\text{m}^2 \text{s}^{-1} \text{V}^{-1})$

Zeta pot. gives info. about stability of colloids solⁿ.

Conc. of profiles of ions in electrolytic solⁿ in presence of charged surfaces:



2:1 electrolyte: CaCl₂: Ca²⁺ Cl⁻

$$2n_0^+ = n_0^-$$

pot. energy of anion in an E at a dist. x from the surface. $\Phi(x) = Ze\psi(x)$

Net ion flux = $J(n_0/m^2)$ P.R.E.
2 components \rightarrow diffusive flux (due to conc grad.)
 \rightarrow Electric pot. grad. flux

$$J = - \left[D \frac{dn}{dx} + n \frac{d\psi}{dx} \right]$$

at \$x=0\$

$$\frac{dn}{dx} = \frac{1}{k_B T} \int_0^{\infty} d\psi$$

gradual variation factor grad

$$\int_{n_0}^{n(x)} \frac{dn}{n} = \frac{1}{k_B T} \int_0^{\infty} d\psi$$

$$\Rightarrow n(x) = n_0 \exp \left[-\frac{\psi(x)}{k_B T} \right]$$

Boltzmann Distribn

$$\frac{d\psi}{dx} = \frac{D}{n} \frac{dn}{dx}$$

Stokes Einstein

$$D = \frac{k_B T}{\eta}$$

Boltzmann const. diffusivity

If Debye length very small \rightarrow thin double layer

$$\frac{d^2\psi}{dx^2} \approx K^2 \psi$$

Under Debye Hückel App

$$\text{at } x \rightarrow \infty, \psi = 0$$

$$\text{at } x = 0, 2\psi = \psi_0$$

More generalized sol'n of Pot. Distribn for 2:2 e in flat plate geometry:-

$$\frac{d^2\psi}{dx^2} = \frac{-1}{e} \Sigma z_i n_i \exp \left(-\frac{2ie\psi}{k_B T} \right)$$

Multiply both sides by $\frac{2d\psi}{dx}$ and integrate:

$$\int \frac{2d\psi}{dx} \frac{d^2\psi}{dx^2} = - \int \frac{1}{e} (\Sigma) \frac{2}{e} \frac{d\psi}{dx}$$

$$\Rightarrow \left(\frac{d\psi}{dx} \right)^2 = - \frac{2}{e} \Sigma n_i z_i e \int_0^\psi \exp \left(-\frac{2ie\psi}{k_B T} \right)$$

$$\Rightarrow \left(\frac{d\psi}{dx} \right)^2 = \frac{2k_B T}{e} \Sigma n_i \left[\exp \left(-\frac{2ie\psi}{k_B T} \right) - 1 \right]$$

for symmetric electrolyte, $\Sigma z_+ = \Sigma z_-$

$$\left(\frac{d\psi}{dx} \right)^2 = \frac{2k_B T n_0}{e} \left[\exp \left(\frac{2ie\psi}{k_B T} \right) + \exp \left(-\frac{2ie\psi}{k_B T} \right) - 2 \right]$$

$$\Rightarrow \frac{d\psi}{dx} = -2K k_B T \sinh \left(\frac{2ie\psi}{2k_B T} \right)$$

$$\tanh \left(\frac{2e\psi}{\pi} \right) = \tanh \left(\frac{2\psi_0}{\pi} \right) \exp \left(-Kz \right) \quad (\psi_0 =$$

boils down to $\psi = \psi_0 \exp(-Kz)$
if $\psi_0 < 25 \text{ mV}$

Double Layer Analysis around the charged sphere

Poisson Eqn in spherical polar coordinates \rightarrow Boltzmann \rightarrow Debye Hückel App

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi}{dr} \right) = K^2 \psi \quad r \rightarrow \text{dist}$$

BC: $\psi \rightarrow 0$ as $r \rightarrow \infty$

$\psi \rightarrow \psi_0$ at $r = a$ substitute $\psi = \psi_0 / r$

$$\frac{d^2\psi}{dr^2} = \frac{-1}{r^2} \left[\frac{1}{r^2} \sum z_i n_i \exp \left(-\frac{2ie\psi}{k_B T} \right) \right]$$

$$\Rightarrow A = 0$$

$$\psi_0 = B \frac{e^{-ka}}{a}$$

$$\Rightarrow B = a \psi_0 e^{ka}$$

$$\Rightarrow \psi = \psi_0 a e^{-K(a-r)}$$

Estimation of charge on sphere from Potential

a charged sphere in an electrolytic soln

$$\Psi(r) = \frac{1}{r} \psi_0 a \exp(-K(r-a))$$

Making a charge balance:-

$$Q(\text{charge residing in}) + (4\pi r^2 \rho dr) (\text{charge due to double layer})$$

\uparrow the particle \downarrow a \rightarrow to double layer

charge on the surface \rightarrow charge in EDL

$$\rightarrow Q = - \int_a^\infty 4\pi r^2 \rho dr$$

$$\rightarrow Q = - \int_a^\infty 4\pi r^2 dr \Sigma n_i z_i \exp \left(-\frac{2ie\psi}{k_B T} \right)$$

Using Debye Hückel Approx. ($\psi < 25 \text{ mV}$)

1D cartesian coord. $\rightarrow \frac{d^2\psi}{dx^2} = -\frac{p}{e}$

Poisson-Helmholtz Eqn $\rightarrow \frac{d^2\psi}{dx^2} = -\frac{p}{e} \sum z_i n_i \exp \left(-\frac{2ie\psi}{k_B T} \right)$

for $\frac{2ie\psi}{k_B T} \ll 1 \rightarrow$ Debye Hückel Approx.

valid for $\psi_0 < 25 \text{ mV}$

$$\frac{d^2\psi}{dx^2} = -\frac{1}{e} \left[\Sigma z_i n_i \exp \left(-\frac{2ie\psi}{k_B T} \right) \right]$$

electroneutrality condn

$$\Rightarrow \frac{d^2\psi}{dx^2} = \frac{1}{e K_B T} \sum z_i^2 n_i \psi = K^2 \psi$$

only term to differ (+/-)

$$\therefore K^2 = \sqrt{\frac{e^2 \sum z_i^2 n_i}{e K_B T}} \quad (\text{length}^{-1})(\text{m}^{-1})$$

(as $K=1 \rightarrow [\text{m}] \rightarrow$ Debye length)

\hookrightarrow \rightarrow (conc. of electrolyte, nature of electrolyte environment (E), Temp.)

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$$= - \int_{-\infty}^{\infty} 4\pi r^2 dr \sum_{i=1}^{\infty} n_i z_i e \left(1 - \frac{z_i e \psi}{k_B T} \right)$$

$$\mu V = \epsilon E E_s$$

$$V_e = \frac{\epsilon E E_s}{\mu}$$

$$U_e = \frac{V_e}{E}$$

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$$\begin{aligned} \Psi &= \int_a^{\infty} \epsilon r^2 dr \sum_{i=1}^{\infty} n_i z_i e^2 \frac{n_i \psi}{k_B T} \\ &= \epsilon k_B T \int_a^{\infty} n^2 \psi(r) dr \\ &= 4\pi k_B T \int_a^{\infty} \Psi_0 a \exp(-k(z-a)) r dr \\ &= 4\pi \epsilon a (1 + K_a) \Psi_0 \end{aligned}$$

$$\Psi_0 = \frac{\Psi}{4\pi \epsilon a (1 + K_a)}$$

Effect of electric double layers

→ if stokes layer thickness can be neglected
 $\Psi_0 \approx \psi_e$ (zeta potential)

$$\Psi_0 \approx 4\pi \epsilon a (1 + K_a)^{\frac{1}{2}}$$

Electrophoresis:-

Case 1 :- $K_a \ll 1$ for electrostatic force applied on the particle due to ext. electric field. field strength $\propto 1/a$. $K \rightarrow$ Debye length $\propto \sqrt{K_a}$

Electric force on the particle $\propto 1/a$
 Viscous force $\propto a$ → Stokes region

$$F_{vis} = 6\pi \mu R V$$

$$SS \rightarrow F_{vis} = F_e \rightarrow 6\pi \mu R V = q E$$

$$\rightarrow V_e = \frac{q E}{6\pi \mu R}$$

$$\text{Electrophoretic mobility} = u = \frac{V_e}{E} = \frac{q}{6\pi \mu R}$$

$$u = \frac{q}{3 \pi \mu a} \times \frac{1}{\sqrt{1 + K_a}}$$

$$u = \frac{2 \epsilon E}{3 \mu} \quad V_e = \frac{2 \epsilon E E_s}{3 \mu}$$

Case 2 :- $K_a \gg 1$ $K_a > 1$

$K^{-1} \ll a \rightarrow$ compact double layer
 curvature effect of spherical particle is lost. (stand very close to it it will look flat)
 consider the charges in a continuum. Use H-S eqn. (Neglect pressure gradient &

$$\frac{d^2 V}{dx^2} = -E \frac{d^2 \psi}{dx^2} \Rightarrow \text{After integration}$$

$$k_B = \frac{\epsilon S}{\mu} \quad \text{Helmholtz Smoluchowski eqn}$$

Coupling with Ultrafiltration system:-

Case 1 :- gel layer controlling UF

Gor. Eqn :- At SS.

$$(V_w - V_e) C + \frac{dC}{dy} = 0$$

Net convective flux towards the membrane

$$\rightarrow (V_w - V_e) C + \frac{dC}{dy} = 0$$

$$BC : \text{at } y=0, C = C_0 \quad \text{at } y=a, C = C_g$$

$$K = \frac{D}{S}$$

$$\Rightarrow V_w = K \ln \left(\frac{C_g}{C_0} \right) + V_e \quad \text{electrophoretic vel} \quad V_e = \frac{\epsilon S}{\mu} \quad \text{for } K_a \gg 1$$

Case 2 :- osmotic pressure controlled

$$\text{Osmotic pressure} \rightarrow \frac{dP}{dy} = -(V_w - V_e) \frac{dC}{dy} = D \frac{dC}{dy^2}$$

Species bal.

$$BC : \text{at } y=0, C = C_0$$

$$\text{at } y=\infty, C = C_0$$

$$\text{at } y=0, (V_w - V_e) C + D \frac{dC}{dy} = 0$$

Similarity soln / Appx Integral Method.

Order of magnitude of Debye length :-

NaCl soln (1:1 electrolyte) 0.01M

$$K^{-1} = 9, T = 300K$$

$$AB \rightleftharpoons A^+ + B^-$$

$$K^2 = \frac{e^2 \sum_{i=1}^{\infty} z_i^2 n_i}{6\pi \mu R} \quad K_B = 1.38 \times 10^{-23} J/K$$

$$n_i = \text{no. conc. of ions} \quad (\text{no.}/\text{m}^3)$$

$$20 = \frac{10^3 \cdot M \cdot N_A}{6.023 \times 10^{23} \cdot 10^3 \cdot 10^{-3}} \quad \text{no.}/\text{m}^3$$

$$N_A = 6.023 \times 10^{23}$$

$$e = 1.6 \times 10^{-19} C$$

$$E = \epsilon_0 D$$

$$\epsilon_0 = \text{permittivity of water} \approx 80$$

$$D = \text{dielectric const. of water} \approx 80$$

$$D = \text{permittivity in vacuum} \approx 8.85 \times 10^{-12} \text{ C}^2/\text{N} \cdot \text{m}^2$$

$$K^2 = (1.6 \times 10^{-19})^2 \cdot 1000 \cdot N_A \sum_{i=1}^{\infty} \frac{z_i^2 n_i}{6 \cdot 80 \cdot 10^{-3}}$$

$$= e^2 \cdot 1000 \cdot N_A \cdot M \cdot (z_1^2 + z_2^2)$$

$$= 2000 \cdot N_A \cdot M \cdot \frac{CK_B T}{GK_B T}$$

$$= 1.05 \times 10^{15} \quad \text{P.R.E.}$$

$$K^{-1} = 30.8 \text{ A} \quad K.T.$$

Q. A +ively charged spherical particle is placed (of mass m) at the bottom of a tall vertical tank. Tank is filled up with 10^{-4} M NaCl soln
 $r = \text{particle radius} = 100 \text{ } \mu\text{m}$

$$\rho_p = \text{density of particle} = 2000 \text{ kg/m}^3$$

$\rho_w = 10^3 \text{ kg/m}^3$ A suitable electric field is applied b/w the top and bottom of the vessel. Particle is attracted and moves towards the top plate. zeta potential is measured. 'E' mV. $E = 20 \text{ mV}$

- Find min E so that particle is lifted up.
- If $E = 2E_{\min}$ is applied, find particle vel. profile. $v(t)$
- What is the terminal vel of particle?

i) $E_{\min} \rightarrow \text{min. value of electric field strength}$

$$Q_s = \epsilon_0 \cdot 4\pi r a (1 + ka) \quad \leftarrow \text{surf. charge on the spherical particle}$$

$$\begin{array}{l} F_E \uparrow \\ F_B \downarrow \\ mg \downarrow \\ w \end{array} \quad F_E + F_B = mg$$

$$mg - F_B = F_E \quad (\text{electric field})$$

$$F_B \quad (\text{buoyant force}) = \left(\frac{m}{\rho_p} \right) \rho_w g$$

$$\Rightarrow F_E = mg - m \left(\frac{\rho_w}{\rho_p} \right) g$$

$$\Omega E_{\min} = mg \left(1 - \frac{\rho_w}{\rho_p} \right) \rightarrow E_{\min} = \frac{mg \left(1 - \frac{\rho_w}{\rho_p} \right)}{\Omega}$$

$$\Rightarrow E_{\min} = mg \left(1 - \frac{\rho_w}{\rho_p} \right) \rightarrow \text{To set particle in motion.}$$

$$\Omega E_{\min} = mg \left(1 - \frac{\rho_w}{\rho_p} \right) \rightarrow E = 2E_{\min} \rightarrow ma = F_B + F_E - mg - \text{Friction}$$

$$\cancel{ma} \frac{mdv}{dt} = \frac{m \rho_w g}{\rho_p} - mg + \Omega E \quad \begin{matrix} (\text{viscous}) \\ \cancel{(\text{drag})} \\ - \Omega \pi \mu a v \end{matrix}$$

$$\Rightarrow \frac{dv}{dt} = \left(\frac{\rho_w}{\rho_p} - 1 \right) g + \Omega E - \Omega \pi \mu a v$$

$$\Rightarrow \frac{dv}{\Omega E - \left(1 - \frac{\rho_w}{\rho_p} \right) g - \Omega \pi \mu a v} = dt$$

$$\Rightarrow \Omega E - \left(1 - \frac{\rho_w}{\rho_p} \right) g - \Omega \pi \mu a v = 2$$

$$\Rightarrow \frac{dv}{\Omega E - \left(1 - \frac{\rho_w}{\rho_p} \right) g - \Omega \pi \mu a v} = \frac{dz}{\Omega \pi \mu a}$$

$$\Rightarrow \int \frac{dz}{z} = \int -\Omega \pi \mu a dt$$

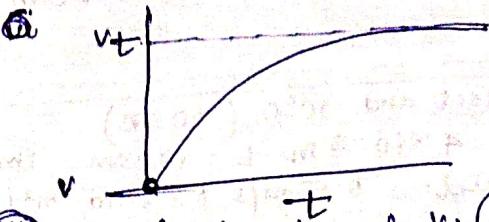
$$\Rightarrow \ln z = q_1 \exp(-\Omega \pi \mu a t)$$

$$\Rightarrow \Omega E - \left(1 - \frac{\rho_w}{\rho_p} \right) g - \Omega \pi \mu a v = q_1 \exp(-\Omega \pi \mu a t)$$

$$\Rightarrow q_1 = \Omega E - \left(1 - \frac{\rho_w}{\rho_p} \right) g$$

$$\rightarrow \Omega E - \left(1 - \frac{\rho_w}{\rho_p} \right) g - \Omega \pi \mu a v = \left\{ \Omega E - \left(1 - \frac{\rho_w}{\rho_p} \right) g \right\} \exp(-\Omega \pi \mu a t)$$

$$\rightarrow v(t) = \frac{\Omega E - \left(1 - \frac{\rho_w}{\rho_p} \right) g}{\Omega \pi \mu a} \left[1 - \exp(-\Omega \pi \mu a t) \right]$$



iii) Terminal vel. at $t \rightarrow \infty$ $\frac{dv}{dt} = 0$

$$\Rightarrow \Omega \pi \mu a v_t = \left(\frac{\rho_w}{\rho_p} - 1 \right) g + \Omega E$$

$$\Rightarrow v_t = \frac{1}{\Omega \pi \mu a} \left[\Omega E - \left(1 - \frac{\rho_w}{\rho_p} \right) g \right]$$

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Gas Separation by Membrane

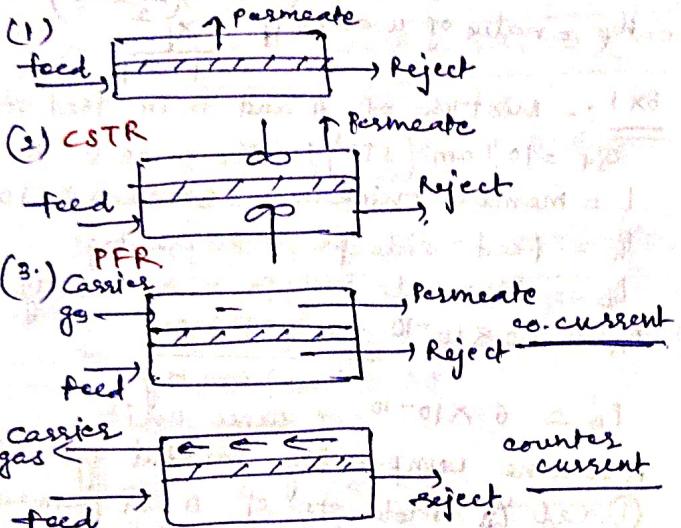
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Dense Membrane:
 feed side \rightarrow High pressure
 permeate side \rightarrow low pressure
 Gasous side \rightarrow high diffusivity \rightarrow Feed is assumed to be well mixed (There is no conc grad. of solute in feed side) (species conc is uniform)
 Gas film resistance can be neglected.

Depending on flow characteristics we have various kinds of flow configurations.

- (1) Simple cross flow
- (2) complete mixing flow: acts like a CSTR
- (3) carrier gas \rightarrow used to take away permeate

$\begin{cases} \text{co-current} \\ \text{counter current} \end{cases}$



Design of a completely mixed model:-

-Assump's involved:-

- (1) Isothermal cond'n
- (2) po drop thro' in feed & in permeate are negligible

(3) Permeability of each comp. is constant

$\frac{\text{low press}}{\text{high press}} = \frac{Q_f}{Q_p} = \frac{Q_f}{Q_f - Q_p}$ $Q_o \rightarrow \text{outlet flow rate}$
 $Q_R = (1 - \theta) Q_f$ $Q_p \rightarrow \text{permeate flow rate}$
 Q_f, X_f, X_o fraction of feed going into permeate flow rate
 (mole/s) mole fr. of comp.
 $Q_p \rightarrow \text{mole fr. in feed going out of the sys.}$

$$\text{Overall mat. bal. } 1 - Q_f = Q_p + Q_o$$

rate of diffusion / permeation of species A in a binary mixture of A & B is given as,

$$\frac{Q_A}{A_m} = \frac{Q_f Y_P}{A_m} = \left(\frac{P_A}{L_m} \right) (P_h X_A - P_L Y_A)$$

$L_m = \text{Total length of membrane}$
 $P_A = \text{Permeability coefficient}$ $\left(\frac{\text{cm}^3}{\text{cm}^2 \text{ sec} \text{ atm}} \right)$
 $P_h = \text{Partial po of feed in feed side}$
 $P_L = \text{Partial po of permeate in permeate side}$

$X_A = \text{mole fraction of A in reject}$
 $Y_A = \text{mole fraction of A in permeate}$

$$\text{Vol. flux of } J_A = \frac{Q_f Y_A}{A_m} = \frac{P_A}{L_m} (P_h X_A - P_L Y_A)$$

$$J_B = \frac{Q_B}{A_m} = \frac{Q_f (1 - Y_A)}{A_m} = \frac{Q_f Y_B}{A_m} = \frac{P_B}{L_m} (P_h X_B - P_L Y_B)$$

$$X_B = 1 - X_A \quad Y_B = 1 - Y_A \quad J_A = \alpha X_A \quad J_B = \alpha Y_B$$

$$\frac{Y_A}{X_A} = \alpha \left[X_A - \left(\frac{P_L}{P_h} \right) Y_A \right] \quad (1 - X_A) = \left(\frac{P_L}{P_h} \right) (1 - Y_A)$$

$\alpha = \frac{P_A}{P_B}$ \rightarrow i.e. ideal sep. factor.

overall component bal. for A, \rightarrow

$$Q_f X_A = Q_R X_A + Q_p Y_A \quad \theta = \frac{Q_p}{Q_f} = X_A - X_{AF}$$

$$X_{AF} = \frac{Q_R X_A}{Q_f} + \frac{Q_p Y_A}{Q_f} \quad X_A = X_{AF} - \theta Y_A$$

$$\rightarrow X_{AF} = (1 - \theta) X_A + \theta Y_A \quad Y_A = X_{AF} - X_A (1 - \theta)$$

$$Q_f = \theta Q_f \quad Q_p Y_A = \frac{P_A}{L_m} (P_h X_A - P_L Y_A)$$

$$Q_f X_A = \frac{X_{AF} - \theta Y_A}{1 - \theta} \quad A_m = \theta Q_f X_A$$

$$(P_h X_A - P_L Y_A) = (P_h X_A - P_L Y_A)$$

P.R.E.

$$\frac{P_A}{y_A} = \frac{P_A}{P_B} \frac{P_h X_A - P_L Y_A}{P_h X_B - P_L Y_B} \quad Y_A = \frac{P_L}{P_h}$$

$$\frac{dA}{1-y_A} = \alpha \frac{X_A - Y_A}{(1-X_A) - \alpha(1-Y_A)}$$

7 vars :- $X_F, X_A, Y_A, \theta, \alpha, P_L, A_m$.
Generally 4 out of 7 are ⁱⁿ independent.

Case 1 :- $X_F, X_A, \alpha, P_L/P_h$ are given.
 $\theta, A_m \rightarrow$ needs to be determined.

$$\frac{Y_A}{1-y_A} = \alpha^* \left[X_A - \left(\frac{P_L}{P_h} \right) Y_A \right] \quad \frac{dA}{1-y_A} = \frac{(1-\theta)(1-X_A)}{(1-X_A) - (P_L/P_h)(1-Y_A)}$$

$$Y_A = Y_A(\theta, \alpha^*, P_L/P_h)$$

Quadratic in $Y_A \rightarrow$ estimate values of P_A

can be, $X_A = \frac{X_{AF} - \theta Y_A}{1-\theta}$
cal'd :- $X_A = \frac{X_{AF} - \theta Y_A}{1-\theta}$

$$\rightarrow \theta(Y_A - X_A) = X_{AF} - X_A$$

$$\rightarrow \theta = \frac{X_{AF} - X_A}{X_A - X_F} \quad A_m \approx \frac{\theta \phi_F Y_A}{\frac{P_A}{P_h} X_A}$$

membrane area reqd.

Case 2 :- $X_{AF}, \theta, \alpha^*, P_L/P_h \rightarrow$ given
 $\gamma_A, X_A, A_m \rightarrow$ needs to be estimated.
min conc of reject stream \rightarrow realized when $\theta = 1$
 $\phi_P = \phi_F, X_{AF} = X_A$

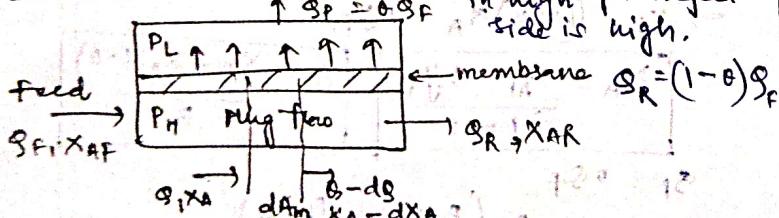
for all values of $\theta < 1$:- $Y_A > X_{AF}$

$$X_{Amin} = \min \text{ reject. comp. for } = X_{AF} \left[1 + (\alpha^* - 1) \frac{P_L}{P_h} (1 - X_{AF}) \right]$$

given X_{AF}

A feed comp. having a mole fr. of X_{AF} cannot be stripped lower than X_{Amin} even with a very large membrane area in a completely mixed system.

Cross flow configuration :- longitudinal vel.



Assumptions :- 1) feed side vel. high enough to have plug flow

2) No mixing in feed and permeate over a differential membrane area dA_m at any pt local permeation rate for comp. A :-

$$-Y_A dS = \frac{P_L}{L} [P_h X_A - P_L Y_A] dA_m \quad (1)$$

-for comp. B :-

$$-(1-Y_A) dS = \frac{P_L}{L} [P_h (1-X_A) - P_L (1-Y_A)] dA_m$$

$$\frac{Y_A}{1-Y_A} = \alpha^* \left[X_A - \left(\frac{P_L}{P_h} \right) Y_A \right] \quad (2)$$

$Y_A \& X_A \rightarrow$ are pt. fr. \rightarrow vary along the length of the membrane.

Analytical soln

Design eqn's :-

$$\frac{(1-\theta)(1-X_A)}{(1-X_A)} = \left[\frac{u_f - E/D}{u - E/D} \right]^R \left(\frac{u_f - \alpha^* + F}{4 - \alpha^* + F} \right)$$

$$\alpha^* = 1 - \theta/\phi_F ; i = 2/1-x$$

$$u = -\Delta i + \sqrt{\Delta i^2 + 2Ei + F^2}$$

$$D = 0.5 \left[(1-\alpha^*) P_h + \alpha^* \right]$$

$$E = \alpha^* - DF ; F = -0.5 \left[(1-\alpha^*) \frac{P_L}{P_h} - 1 \right]$$

$$R = 1/(2D-1) ; S = \frac{\alpha^*(D-1)+F}{(2S-1)(\frac{\alpha^*+F}{2})}$$

$$u_f = \text{value of } u \text{ at } i = 1 \text{ if } = \frac{x_f}{1-x_f}$$

Ex 1 :- Mixture of A and B in feed stream

$$\phi_F = 10^4 \text{ cm}^3 \text{ (STP)} \mu X_{AF} = 0.5 \quad X_A = 0.1$$

$$L = \text{membs. thickness} = 3 \times 10^{-3} \text{ cm}$$

$$P_h = \text{feed side ps.} = 80 \text{ cm Hg}$$

$$P_L = \text{permeate side ps.} = 20 \text{ cm Hg}$$

$$P_A' = 2.0 \times 10^{-10} \text{ cm}^3 \text{ (STP)} \cdot \text{cm}^2 \text{ cm}^2 \text{ cm Hg}$$

$$P_B' = 6 \times 10^{-10} \text{ of same unit}$$

Assume completely mixed sys. Cal.

i) Cal Y_A = mole fr. of A in permeate

ii) Start iteration (details not given)

iii) Am.

$$\text{soln} : - \phi_F = 10^4 \text{ cm}^3 \text{ (STP)} / s$$

$$X_{AF} = 0.5 \quad X_A = 0.25 \quad P_h = 80 \quad P_L = 20$$

$$\alpha^* = \frac{P_A'}{P_B'} = \frac{60 \times 10^{-10}}{6 \times 10^{-10}} = \frac{P_L}{P_h} = 10$$

$$P_L = \frac{20}{80} = 0.25 \quad \frac{P_h}{P_L} = 4$$

$$X_{AF}, X_A, \alpha^*, P_L/P_h \rightarrow \text{known}$$

$$Y_A, \theta, A_m \rightarrow \text{det.}$$

$$\frac{Y_A}{1-Y_A} = \alpha^* \left[X_A - \left(\frac{P_L}{P_h} \right) Y_A \right] \quad (1 - Y_A) \cdot \left(\frac{P_L}{P_h} \right) L^{1-Y_A}$$

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$$\text{Design Eqn: } Y_A = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$a = 1 - \alpha^*$$

$$b = \frac{P_h}{P_L} (1 - X_A) - \alpha^* \frac{P_h}{P_L} X_A + \alpha^*$$

$$c = -\alpha^* \frac{P_h}{P_L} X_A$$

$$a = 1 - 10 = -9$$

$$b = 4(1 - 0.25) - 10 \times 4 \times 0.25 + 10 \\ = 80 + 10 + 10 = 100 \\ = 22$$

$$c = -10 \times 4 \times 0.25 = -10$$

$$Y_A = \frac{-22 \pm \sqrt{(22)^2 - 4 \times (-9)(-10)}}{2 \times (-9)} \\ = \frac{-22 \pm 11.135}{-18} = 0.604$$

$$X_A = \frac{Y_A - \theta Y_A}{1 - \theta} \Rightarrow 0.25 = \frac{0.5 - 0(0.604)}{1 - \theta}$$

$$\rightarrow 0.25 - 0.25\theta = 0.5 - 0.604\theta$$

$$\rightarrow 0.354\theta = 0.25$$

$$\theta = 0.706$$

$$A_m = \frac{\theta Q_F Y_A}{\left(\frac{P_A}{L} \right) (P_h X_A - P_L Y_A)} \\ = 2.7 \times 10^{-8} \text{ cm}^2$$

Ex 2. Membrane Thickness = $3 \times 10^{-3} \text{ cm}$

Sepn of oxygen & nitrogen

$$P'_A = 300 \times 10^{-10} \text{ cm}^3 (\text{STP}) \text{ cm}$$

$$\alpha^* = \frac{P_A}{P'_A} = 10 \quad Q_F = 2 \times 10^{-6} \text{ cm}^3 (\text{STP}) \text{ s}$$

$$\theta = 0.2 \quad P_h = 200 \text{ cm Hg} \quad P_L = 20 \text{ cm Hg}$$

Assume complete mixing model

$$A_m = ? \quad Y_A = ? \quad X_A = ?$$

① $\alpha^*, \theta, P_h/P_L, Q_F \rightarrow \text{given}$

$$A_m, X_A, Y_A = ?$$

Soln: $- X_p = 0.21$ (mole fraction of oxygen in air)

$$q_1 = \theta + \frac{P_h}{P_L} - \frac{P_h}{P_h} \theta - \alpha^* \theta - \alpha^* \frac{P_h}{P_h} + \alpha^* \frac{P_h}{P_h}$$

$$= 0.2 + \frac{20}{200} - \frac{20}{200} \times 0.2 - 10 \times 0.2 - 10 \times \frac{20}{200}$$

$$+ 10 \times \frac{20}{200} \times 0.2$$

$$= 0.2 + 0.1 - 0.02 - 2 - 1 + 0.12$$

$$= -2.52$$

$$(b) = 1 - \theta - X_p - \frac{P_h}{P_h} + \frac{P_h}{P_h} \theta + \alpha^* \theta + \alpha^* \frac{P_h}{P_h}$$

$$= 1 - 0.2 - 0.21 - \frac{20}{200} + \alpha^* \times 0.21$$

$$= 5.41$$

$$c_1 = -\alpha^* X_{AP} = -10 \times 0.21 = -2.1$$

$$Y_A = \frac{-5.41 \pm \sqrt{5.41^2 - 4 \times (-2.52)(-2.1)}}{2(-2.52)}$$

$$Y_A = 0.509$$

$$Y_A = 51.1$$

$$X_A = \frac{Y_A - \theta Y_A}{1 - \theta} = \frac{0.21 - 0.2 \times 0.51}{1 - 0.2}$$

$$= 0.195 \quad = 1.21 \times 10^{-9} \text{ cm}^2$$

$$A_m = \theta Q_F Y_A$$

$$\left(\frac{P_A}{L} \right) \left(\frac{P_h X_A}{-P_L Y_A} \right)$$

DATE

Surfactant Based Separation Processes.

SHEET NO.

Cloud point extraction :- Non ionic surfactants only Temp beyond which aqueous soln of a solute separates into 2 phases - surfactant rich phase & surfactant lean phase
 (i) called dense phase / coacervate phase
 (ii) called → lean phase / dilute phase mainly constituted of the surfactant monomers mostly water lean in surfactants \rightarrow surfactant monomers conc close to CMC

CMC :- Critical Micellar Conc. \rightarrow Beyond a particular conc, surfactant monomers combine in a config with the min energy spherical config. \rightarrow Thermodynamically stable & favourable.

Hydrophobic end \rightarrow hydrophilic end

Mechanism of Phase separn:-

(1) Phase separn abt. CPE is rev.
 (a) for non ionic surfactants \rightarrow Dielectric constant of Water \downarrow as T \uparrow redⁿ in interⁿ b/w hydrophobic part of surfactant & water \rightarrow solvatesⁿ occurs on ext layers of micelles.

(b) At lower (T) (below CPE) \rightarrow intermicellar repulsive forces are dominant
 Above CPT, intermicellar forces become attractive.

mechanism of solubilisⁿ of solutes in coacervate phase:-

(1) organics get solubilised within hydrophobic core of micelles.

(2) Beyond CPT, Micelles loaded with organic solutes go to the coacervate phase.

pollutant rich coacervate phase outcome \rightarrow Pollutant rich coacervate phase Dilute phase devoid of pollutants

Triton X-100 (Isooctyl Phenyl Polyethoxy Ethanol)
 MW: 628 Da; CMC = 2.8×10^{-4} M; CPT: 64°C

Triton X-114 (Octyl Phenyl Polyethylene Glycol Ether)
 MW: 537 Da; CMC = 2.1×10^{-4} M; CPT: 37°C

Case study of removal of C.I. Solvent Blue 10 dye :-

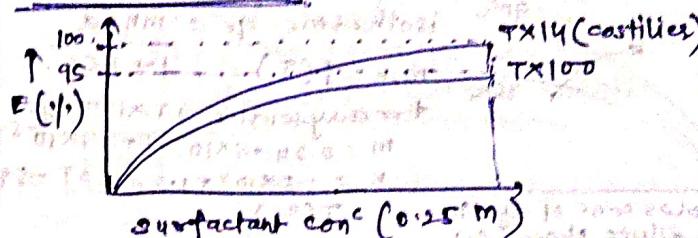
Conc of dye : 100 ppm

TX-114 and TX-100 both are use

CPT = 27°C CPT = 64°C
 70°C 70°C \leftarrow operating Temp.

Extent of $= (1 - \frac{C_f}{C_0}) \times 100\%$,
 Extraction of dye (E) $= \frac{C_f}{C_0}$, feed conc

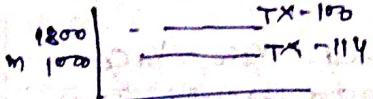
Fc = Volumetric factor = $\frac{\text{Vol. of coacervate phase}}{\text{Total Vol}}$
 Fc $\rightarrow 0.04 \sim 0.23$



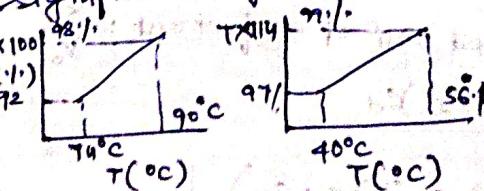
Surfactant (m) = $\frac{\text{Conc of surfactant in coacervate phase}}{\text{partition coeff}}$
 at a const. $T \sum CPT$ \rightarrow dilute phase

Phase diagram \rightarrow Conc of surfactant in dilute phase \sim CMC

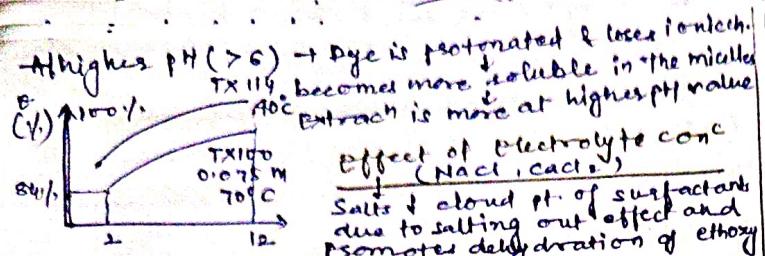
Thus to maintain the material balance Fc \uparrow as the conc of surfactant in the feed \uparrow . If surfactant conc \uparrow \rightarrow more micelles will be formed \rightarrow more solutes will be solubilized within the micelles \rightarrow \uparrow E(%)



Effect of Temp. on Extraction Effects :-
 (1) At higher T, CMC of non ionic surfactants \downarrow more micelles are formed
 (2) At high T, non ionic surfactants become hydrophobic due to dehydration of ether oxygen. Solubilisⁿ of organic pollutants in the micelles are preferred / favoured \downarrow significant \uparrow of extraction efficiency with Temp.



Effect of pH \rightarrow pk value of chrysanthene dye is ~6. operating pH $<$ pk \rightarrow dye is fully charged protonated at lower pH, solubilisⁿ of dye is less \downarrow \uparrow ionic character of micelles



At higher pH (> 6) → Dye is protonated & loses ionizability.
TX-114 becomes more soluble in the micelle at 40°C .
Extract is more at higher pH value.

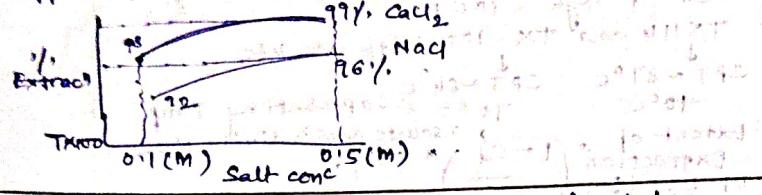
Effect of Electrolyte conc (NaCl, CaCl₂)

Salts ↓ cloud pt. of surfactants due to salting out effect and promotes dehydration of ethoxy group on the outer surface of micelles.

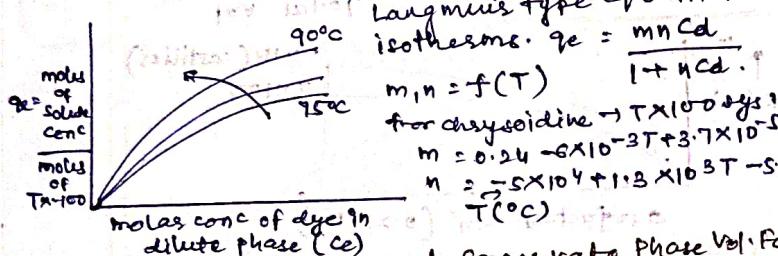
Extent of solubilization in the micelle favoured at high conc.

Addition of salt + CPT of surfactant
 $\text{TX-100} \rightarrow \text{CPT} = 64^\circ\text{C} \rightarrow$ on addn of 0.05M NaCl → CPT $\approx 50^\circ\text{C}$

Effect of divalent salt is stronger than monovalent salt.



Solubilization isotherm → presents moles of solute solubilized per mole of surfactant.



Variation of fractional coacervate Phase Vol Fc

$$F_c = aC_s b \quad a = P + ST \quad b = R + ST$$

$P, Q, R, S \rightarrow f(C_d)$ feed conc of surfactant
of feed.

$a, b \rightarrow f(T)$ for TX-100 - chrysoidine sys.

$Q = 5.9 - 200C_d - 1.9 \times 10^{-3} T$
 $R = 0.418 + 6.9 \times 10^{-3} T$
 $S = 0.09 C_d^2 + 4 \times 10^{-9} T$

Design of cloud pt. Extractor! —

Solubilization isotherm $q_e = \frac{\text{moles of solute solubilized}}{\text{moles of solute fed}}$

$$q_e = \frac{A}{x}$$

$$A = \text{moles of dye solubilized} = V_0 C_d - V_d C_d$$

$$V_0 \rightarrow \text{initial vol. of extractor solution in dil. phase}$$

$$C_d \rightarrow \text{feed conc of dye}$$

$$A = V_0 \left[C_d - \frac{V_d}{V_0} C_d \right]$$

$$F_c = \text{vol. of coacervate phase} \rightarrow \frac{V_d}{V_c} = 1 - F_c$$

$$\text{Total vol.} = V_0 + V_c$$

$$A = V_0 \left[C_d - (1 - F_c) C_d \right] = V_0 \left[C_d - (1 - aC_s b) C_d \right]$$

$$x = \frac{A}{q_e} = \frac{V_0}{q_e} \left[C_d - (1 - aC_s b) C_d \right]$$

$$\text{moles of surfactant used in feed} \quad q_e = \frac{x}{V_0}$$

$$C_s = \frac{C_d - (1 - aC_s b) C_d}{q_e}$$

$$C_s = \frac{\left[C_d - (1 - aC_s b) C_d \right]}{m n C_d}$$

Ext. dye is extracted using TX-100 at 70°C , to be reduced from $4 \times 10^{-4} \text{ M}$ to $3.8 \times 10^{-6} \text{ M}$.

$C_s = ?$

Given data: $q_e = m n C_d$

$$m = 2.4 \times 10^{-1} - 5.9 \times 10^{-3} T + 3.7 \times 10^{-5} T^2 \quad T = 70^\circ\text{C}$$

$$n = -6 \times 10^{-4} + 1.3 \times 10^{-3} T - 5.9 T^2$$

$$P = a C_s b \quad a = P + ST \quad b = R + ST$$

$$P = 5.9 - 200 C_d - 1.9 \times 10^{-3} C_d^2$$

$$R = 0.418 + 6.9 \times 10^{-3} C_d + 4 \times 10^{-9} C_d^2$$

$$S = -0.05 \quad C_d = \text{molar conc of surfactant}$$

$$so \quad C_s = \text{conc of surfactant reqd.}$$

$$so \quad C_s = [C_d - (1 - aC_s b) C_d] / [1 + n C_d]$$

$$so \quad C_s = \frac{m n C_d}{1 + n C_d}$$

$$so \quad C_s = \frac{m n C_d}{1 + 1.21 \times 10^{-4} \times 3.8 \times 10^{-6}}$$

$$so \quad C_s = \frac{8.3 \times 10^{-3} \times 1.21 \times 10^{-4} \times 3.8 \times 10^{-6}}{1 + 1.21 \times 10^{-4} \times 3.8 \times 10^{-6}}$$

$$so \quad C_s = 1.085 \text{ M}$$

$$NR \quad C_s = 1.085 \text{ M}$$

$$Ex 2. A dye is removed from $3 \times 10^{-4} \text{ M}$$$

$$\text{Cloud pt. extract with } 0.05 \text{ M TX-114}$$

$$\text{at } 40^\circ\text{C}: \text{find out the dye conc in the dil.}$$

$$so \quad C_s = [C_d - (1 - aC_s b) C_d] / [1 + n C_d]$$

$$given: - \quad m n C_d$$

$$m = 0.47 - 0.19 \times 10^{-2} T + 2.1 \times 10^{-4} T^2$$

$$n = -1.6 \times 10^{-4} + 5.9 \times 10^{-3} T - 37.4 T^2$$

$$a = 4.9 - 0.11 T \quad b = R + 0.09 T$$

$$P = 5.9 + 8 \times 10^{-2} C_d + 1.8 \times 10^{-8} / C_d^2$$

$$R = 4.2 \times 10^{-1} - 2.4 \times 10^{-3} C_d + 2.2 \times 10^{-6}$$

$$S = 7.8 \quad R = -0.276$$

$$at \quad T = 40^\circ\text{C}; \quad m = 0.046; \quad n = 96160$$

$$C_s = 3 \times 10^{-4} \quad a = 7.2 - 0.11 \times 40 = 2.8$$

$$b = -0.276 + 0.09 \times 40$$

$$C_s = 0.05 \text{ M} = 5 \times 10^{-2} \text{ M}$$

$$5 \times 10^{-2} = [3 \times 10^{-4} - (1 - 2.8 \times (5 \times 10^{-2})) C_d]$$

$$0.046 \times 16160 \times 6 = 33.32 C_d - 3 \times 10^{-4}$$

$$\rightarrow 16160 C_d^2 + 33.32 C_d - 3 \times 10^{-4} = 0$$

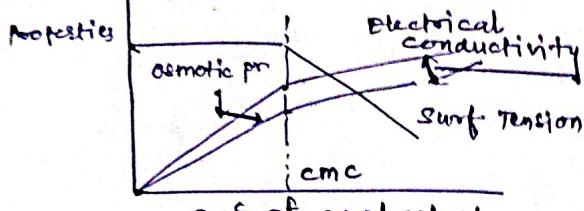
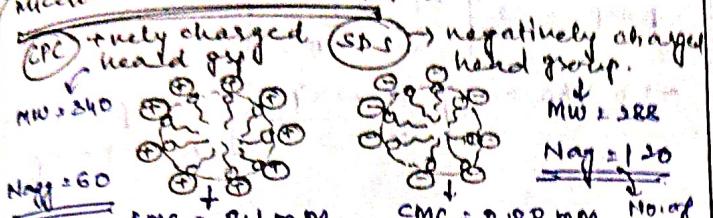
$$C_d = 8.96 \times 10^{-6} \text{ M}$$

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Micellar Enhanced UP :-



Quantification of MBUP :-

1) Extent of solubilization of the solutes within the micelles

$$\text{S} = \frac{\text{Solubility coeff}}{\text{Conc of surfactant}} = \frac{C_0 - C_p}{C_0^s - \text{CMC}}$$

= Amt. of solute solubilized in micelles / Conc of micelles in terms of monomers

C_0 → feed conc of solute

C_p → permeate / unsolubilized conc of solute

C_0^s → feed conc of surfactant

CMC → Critical micelle conc

for single component solute system :-

$$S = \frac{C_0 - C_p}{C_0^s - \text{CMC}} = \frac{g_1 b_1 C_p}{1 + b_1 C_p} \quad S$$

g_1, b_1 → isotherm constants

for multicomponent solute sys. :-

These will be competitive absorption
Extended Langmuir Isotherm type eqn

$$S_1 = \frac{C_{01} - C_{p1}}{C_0^s - \text{CMC}} = \frac{g_1 b_1 C_{p1}}{1 + b_1 C_{p1} + b_2 C_{p2}}$$

$$S_2 = \frac{C_{02} - C_{p2}}{C_0^s - \text{CMC}} = \frac{g_2 b_2 C_{p2}}{1 + b_1 C_{p1} + b_2 C_{p2}}$$

$$V_w = K \ln \left(\frac{C_p}{C_0^s} \right) \quad C_0^s \rightarrow \text{feed conc of surfactants}$$

gel layer conc of micelles (c_0) :-

micelles → 366 kg/m^3
 $\rightarrow 210 \text{ kg/m}^3$

Permeate flux :-

Micelles form a gel type of layer on the membrane stuff.

$$V_w = K \ln \left(\frac{C_p}{C_0^s} \right) \quad \text{feed conc of surfactants}$$

$$\text{pure CPC soln} \rightarrow C_p = 366 \text{ kg/m}^3$$

$$\text{SDS} \rightarrow C_p = 210 \text{ kg/m}^3$$

Inorganic pollutants → $\text{Pb}^{2+}, \text{Cd}^{2+}, \text{As}^{3+}, \text{Hg}^{2+}, \text{Sn}^{2+}, \text{Cu}^{2+}$

Anionic pollutants → $\text{ClO}_4^-, \text{MnO}_4^-, \text{Cr}_2\text{O}_7^{2-}$

CPC. In presence of inorganic pollutants, some phenomena occur:-

1) CMC of surfactants is reduced.

2) In presence of cations repulsion decreases

3) Inter-surfactant facilitates micelle formation

- repulsive force

In presence of these actions / counterions

CMC of surfactants ↓

More micelles will form at a fixed conc of feed surfactant ↓

More solubilisation of counter ions ↓

Enhanced separation / efficiency

2) Effect on gel layer conc

(a) : bridging effect b/10
 - micelles → form a bridge at early conc
 C_p is a ↓ to of counter ion conc in bulk

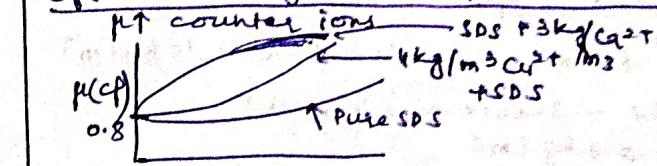
$$\text{ss flux} \quad C_p = 366(1 - 0.21 C_a)^{1/4} \quad C_a < 1 \text{ kg/m}^3$$

$$\text{for } \text{Ca}^{2+} \text{ sys.} \quad C_p = 366(1 - 0.14 C_a)^{1/4} \quad C_a < 1 \text{ kg/m}^3$$

Effect of binary mixture on gel layer conc

Reduction of gel layer conc is a% of compn of counter ions.

Effect of charge in κ in presence of counterions



SDS conc needs to be included in mass-to-coeff. Counterion bonding on micellar surface

$$\mu_i = K_i C_i e^{-\frac{z_i \psi}{k_B T}} \quad \text{B} = \text{binding ratio of counterion on micelles}$$

$$1 + K_i C_i e^{\frac{-z_i \psi}{k_B T}} + K_{\text{NaCl}} C_{\text{NaCl}} e^{\frac{-z_i \psi}{k_B T}} \quad \psi \rightarrow \text{zeta P.R.E.}$$

C_i → bulk conc of i-th component of micellae
 K_i → binding constant of i-th component of micellae

for 2 cations:

$$\beta_1 = \frac{K_{11} e^{-\frac{\gamma_1 \psi}{k_B T}}}{1 + K_{Na} C_{Na} e^{-\frac{\gamma_1 \psi}{k_B T}} + \sum_{i=2}^n K_{i1} e^{-\frac{\gamma_i \psi}{k_B T}}}$$

Experimental evaluation of β_1 :

$\beta_1 \exp = \frac{c_1 - c_{11}}{C_0 - c_{11}}$ conc of 1st cation in
initial conc of c_{11} the permeate
cations K_1 's and ψ are unknown in
isotherm expression.

K_1 's can be evaluated

$$S = \sum_{i=1}^n (\beta_{i1} \exp - \beta_{i1} \text{cal})^2 + \sum_{i=2}^n (\beta_{i1} \exp - \beta_{i1} \text{cal})^2$$

- (1) Start with guess value of K_1
- (2) Evaluate S
- (3) Use an optimisation technique to minimize S .
- (4) Result at new set of K_1 's
- (5) Check $S < 10^{-3}$

for single system: $(SDS + Cu^{2+}) \rightarrow K_{Cu} = 70.87$
 $K_{Na} = 0.06; V_p = 11.15 \text{ m}^3$

$\Rightarrow SDS \text{ or } Cu^{2+} \rightarrow K_{Cu} = 192; K_{Na} = 0.06; V_p = 16 \text{ m}^3$

\Rightarrow Removal of organic pollutant using MEUF

$\Rightarrow SDS + Phenol. S = 2.34 \times 10^{-3} \text{ mg/mg}$

$C_0 \rightarrow$ feed conc of surfactant $\rightarrow 10 \text{ kg/m}^3$

$C_0 \rightarrow$ feed conc of phenol $\rightarrow 20 \text{ mg/l}$

$$S = \frac{c_1 c_p}{1 + b_1 c_p} [s] + \frac{mg}{mg} \quad c_1 = 0.1 \text{ mg/l} \quad b_1 = 9 \times 10^{-1} / \text{mg}$$

$$c_p = 280 \text{ kg/m}^3$$

$$K = 2 \times 10^{-5} \text{ m/l} \quad \text{cmc of SDS} = 2.3 \text{ kg/m}^3$$

$$V_{10} = ? \quad c_p = \text{permeate conc of phenol?}$$

$$V_{10}^S = K \ln \left(\frac{c_p}{C_0} \right) \rightarrow V_{10}^S = 2 \times 10^{-5} \ln \left(\frac{280}{10} \right)$$

$$\rightarrow V_{10}^S = 2 \times 10^{-5} \ln \left(\frac{280}{10} \right) \text{ m}^3/\text{m}^2 \cdot \text{s}$$

$$2.34 \times 10^{-3} = \frac{0.1 \times 9 \times 10^{-2} \times c_p}{1 + 9 \times 10^{-2} c_p}$$

$$\Rightarrow 2.34 \times 10^{-3} + 2.706 \times 10^{-5} c_p = 9 \times 10^{-3} c_p$$

$$\Rightarrow 2.34 \times 10^{-3} = c_p \times 10^{-3} (9 - 0.2106)$$

$$\Rightarrow c_p = \frac{2.34}{8.7894} = 0.266 \text{ mg/l}$$

$$\text{observed retention of phenol} = 1 - \frac{c_p}{C_0} = 98.61\%$$

Ex 2 SDS micelle \rightarrow $c_1 = 10^{-5} \text{ mol/l}$

$Cu^{2+} \rightarrow 4 \text{ kg/m}^3 \quad K \rightarrow 10^{-5}$

permeate flux F . $R_o, Cu^{2+} = ? \quad C_0 = 10 \text{ kg/m}^3$

$$g = 292 - 3C_{Cu} (\text{copper in bulk})$$

$$CMC = 2.3 \text{ kg/m}^3$$

Localized Adsorption Isotherm & various binding constants:

$$\beta = K_{Cu} C_{Cu} \exp \left(-\frac{2C_{Cu}\psi}{k_B T} \right)$$

$$1 + K_{Cu} C_{Cu} \exp \left(-\frac{2C_{Cu}\psi}{k_B T} \right) + K_{Na} C_{Na} \exp \left(-\frac{2C_{Na}\psi}{k_B T} \right)$$

$$K_{Cu} = 71; K_{Na} = 0.06; 2C_{Cu} = 2 \quad \frac{-2C_{Na}\psi}{k_B T} = 1 \quad \psi = 11 \text{ mV}; T = 300 \text{ K}$$

$$V_{10} = K \ln \left(\frac{c_p}{C_0} \right) \rightarrow V_{10} = 280 \text{ kg/m}^3$$

$$c_p = 292 - 3 \times 4 = 280 \text{ kg/m}^3$$

$$\beta = 71 \times \exp \left(-\frac{2 \times 1.6 \times 10^{-19} \times 11 \times 10^{-3}}{1.38 \times 10^{-23} \times 300} \right)$$

$$1 + 71 \times 4 \times \exp \left(\frac{1}{0.4273} \right) + 0.06 \times 20 \exp \left(\frac{-4 \times 11 \times 10^{-3}}{1.6 \times 10^{-23} \times 300} \right) = 0.9855$$

$$\beta_{exp} = 2 \left[\frac{c_1 - c_{11}}{C_0 - CMC} \right]$$

$$\Rightarrow 0.985 = 2 \left[\frac{4 - C_p}{10 - 2.3} \right] \Rightarrow C_p = 0.21 \text{ kg/m}^3$$

$$R_o = 1 - \frac{C_p}{C_0} = 94.7\%$$

INDIAN INSTITUTE OF TECHNOLOGY

DATE

SHEET NO.

Liquid Membrane! - Emulsion Lq. Membranes

• A lq. phase \rightarrow emulsion config.

• Double Emulsion \rightarrow water/oil/water or oil/water/oil
for water-oil-water sys. !

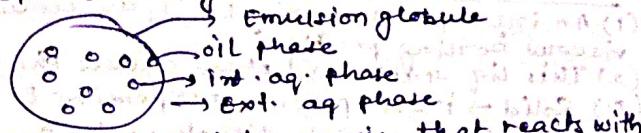
oil phase separates to aqueous phase and is known as the membrane \rightarrow since it is a lq. \rightarrow lq. membrane

Surfactants are used to stabilize emulsion prep!:-

(1) Precipitate the emulsion b/w 2 lq. immiscible phases (high stirring) 10000 rpm

(2) Emulsion is dispersed in a 3rd cont. phase under constant stirring (\sim 400 rpm)
Membrane phase \rightarrow lq. phase that separates the encapsulated internal phase from ext. phase

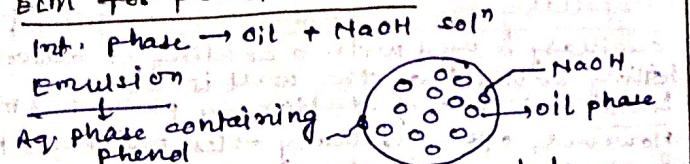
Surfactant (additives) are used to stabilize
Typical size of int. droplets \rightarrow 1-3 μm and of emulsion globules \rightarrow 100-2000 μm



Int. phase contains species that reacts with the pollutant. Pollutant diffuses from ext. phase to the int. phase through the oil phase.

In int. phase \rightarrow pollutant reacts with int. phase. Ext. phase will have less conc. of pollutant.

BLM for phenol removal!:-

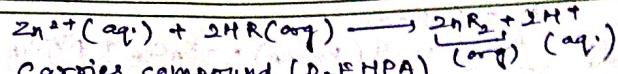


$\text{NaOH} + \text{Phenol} \rightarrow \text{Sodium Phenolate}$
After sometime (insoluble in oil phase (trapped within the globule)) globule will be loaded in

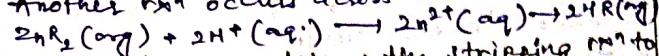
Driving force & facilitated Medium!:-

TYPE I! - facilitation
1) reactant present in inner phase.
2) Solute conc in inner phase \rightarrow 0.
3) Maxm Conc grad. is maintained.

TYPE II! - facilitation process (we have a facilitator or a carrier)
oil (ext. phase) $\xrightarrow{\text{X}} \text{X}$ take place at the ext. interface b/w ext. & membr. carrier phase



Carries compound (D_2EHPA) form a complex with Zn^{2+} (ZnR_2) complex diffuses across the membrane phase to internal phase (H_2SO_4 soln). Another rxn occurs across membr. & int. phase



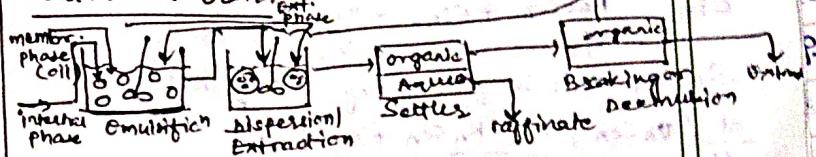
Acid in int. phase drives the stripping rxn to the right and maintain a low concentrated Zn complex (ZnR_2)

Adv. of ELM

fed $\xrightarrow{\text{H}^+}$ HR $\xrightarrow{\text{H}^+}$ Receiving phase (inner phase)

Simultaneous Extraction & stripping in one step only.

Continuous BLM:



Modeling of BLM!:-

Batch Extractor

TYPE I Facilitation! - Transport Mechanism \rightarrow Diffusion,

A spherical shell approach

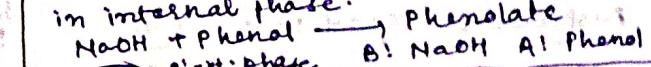
Salient features: - (1) Solute A from ext. phase diffuses to the int. phase and after rxn becomes 'B' (mass transfer coeff. k_1)

(2) 'B' diffuses through to the ext. phase via diffusion

(3) breakage

Add in the int. phase drives the stripping rxn to the right and maintain a low concentrated Zn complex.

(4) In ext. phase, B can get converted to A. Thus 'A' can exist only in ext. phase. 'B' can exist only in internal phase.



A: ext. phase B: NaOH At Phenol
 $\frac{\text{rate of breakage of vol. of internal phase at any t}}{\text{rate of breakage of vol. of internal phase at any t}}$

Breakage of internal phase!:-

$$-\frac{dV_i}{dt} = \phi V_i \rightarrow \text{Breakage coefficient}$$

$$\text{Integrate } V_i = V_{i0} \exp(-\phi t)$$

initial internal phase vol.

Total volume of the system, $V_0 = V_{i0} + V_{e0}$

At any pt. of time, $\frac{\text{Total initial vol.}}{\text{Total initial vol.}} = \frac{\text{Total ext. vol.}}{\text{Total ext. vol.}}$

$$V_e + V_i = V_0 \rightarrow V_e = V_0 - V_{i0} e^{-\phi t}$$

Vol. of ext. phase at any pt. of time

P.R.E.

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DATE

SHEET NO.

Size Exclusion Chromatography (SEC) :-

No Adsorpⁿ takes place
static exclusion of solutes causes separⁿ
useful for separⁿ of larger from smaller molecule
solid matrix is cross linked polymers gels →
Agarose Polycelxtran (Sephadex)

Principle:- Migration chromatography where
solute absorb & desorb and all solutes
move at finite but different velocities.

Solute movement through Col. :- depends
on packing
Solid particles → high porosity Str. & nature
large surf. area/gm of solvent of packing
particiles must be porous → more separⁿ. (Efficiency)

$$\begin{aligned} \epsilon_p &= \text{Avg. intraparticle porosity} = \frac{\text{Vol. inside particles}}{\text{Total vol. of all particles}} \\ \epsilon_e &= \text{Avg. interparticle porosity} = \frac{\text{Vol. b/w particles}}{\text{Total vol. of packed bed}} \end{aligned}$$

$$\epsilon_t = \text{Total bed porosity} = \frac{\text{Sum of voids within & b/w particles}}{\text{Total vol. of the particles}}$$

$$\text{Bulk density}! - P_B = (1 - \epsilon_t) P_p + \epsilon_t P_f$$

$$P_p = (1 - \epsilon_p) P_s + \epsilon_p P_f$$

L_c = crystalline density of solid after crushing and compressing the solids.
Pores in solid particles are not of uniform size!

Large molecules such as proteins/synthetic polymers may be sterically excluded from some of pores.

$$(ii) \text{Fraction of pores that a molecule can penetrate} \\ K_d = \frac{V_e}{V_i} \quad V_e \rightarrow \text{elution Vol. (Vol. of fluid at which species exit from Col.)} \\ V_i \rightarrow \text{ext. void vol. b/w particles} \\ V_i \rightarrow \text{Int. void vol.}$$

for small molecules that penetrate entire interparticle vol. :- $V_e = V_i + V_o$ & $K_d = 1.0$

for large molecules that cannot penetrate $V_e = V_o$ & $K_d = 0.0$

processes involved in a typical chromatographic column :- fluid with solid flow through void vol. outside the particle.

Basic processes involved :-
Basic processes involved :-

i) Solute diffuses through an ext. film to the particle.

ii) Solute may be adsorbed on external surface of solid or they can diffuse through the fluid occupying intraparticle void

the forces are smaller in size diffusion of solute hindered. $\rightarrow D_H \sim 2-3$ orders of magnitude less than bulk diffusion

(iii) Adsorpⁿ of solute

- Physical Adsorpⁿ → Chemical Adsorpⁿ
- Adsorpⁿ by electrical forces
- (iv) While Adsorbed solute may diffuse along the surface of the solid → surface diffusion
- (v) Solute desorbs
- (vi) Solute diffuses through the pores and comes back to ext. film and into moving film/mobile phase

A given molecule can be adsorbed or desorbed a no. of times.

While in moving fluid, solute is carried by interstitial fluid vel., until it encounters and enters another particle, where the whole process is repeated.

$$\text{Migration of solute through col.} = f(\epsilon_p, \epsilon_e, K_d, V, \text{sorption})$$

$$\Delta z \quad \text{An elemental area of col.} \\ \text{Ext. void vol.} = G_e A_c \Delta z$$

$$A_c = \text{cross sectional area of bed} = \frac{\pi D^2}{4}$$

$$\text{Internal void vol. (within particle)} = (1 - \epsilon_e) \epsilon_p A_c \Delta z$$

Solute inside the bed is located,
(i) in the mobile phase (ii) in the stagnant (iii) adsorbed in ext. vol. liq. phase inside the particle

Solutes that exit the column can be in mobile phase only. Considers the movement of an incremental mass added to the bed. → lead to change in fluid concentration SC
change in amt. adsorbed by age

$$\text{fraction of solute in mobile phase} = \frac{\text{Amt. of solute in mobile phase}}{\text{Total amt. of solute present}}$$

$$\text{Amt. of solute in mobile phase} = \frac{\text{Amt. in (mobile fluid + stationary + sorbed)}}{\text{Total amt. of solute present}}$$

$$\text{Amt. of solute increment} = \frac{\text{Vol. of segment}}{\text{segment length}} \times \frac{\text{fraction of mobile phase}}{\text{molar concn. in mobile phase}}$$

$$\text{Total amt. of solute in segment} = (\Delta z A_c) (E_e) A_c$$

$$\text{Amt. of solute in mobile phase} = \frac{\Delta z A_c E_e}{\Delta z A_c E_e}$$

$$\text{Total amt. of solute in segment} = (\Delta z A_c) E_e A_c + \frac{\Delta z A_c (1-E_e)}{E_e A_c K_d}$$

$$P_s \rightarrow \text{solid density}$$

$$q_{1C} \rightarrow \text{related by adsorpⁿ isotherm}$$

$$\text{interstitial rel. vol.} \rightarrow \text{then amp. vol. of solute phase}$$

$$\text{solute in the bed, } u_s$$

$$u_s = v \times (\text{fraction of solute in the mobile phase})$$

$$u_s = v \times \frac{1 + (\frac{1 - E_e}{E_e}) \epsilon_p K_d + (\frac{1 - E_e}{E_e}) (1 - \epsilon_p) P_s A_q}{E_e}$$

$$\text{If isotherm is linear!} - q = mC \quad m(T) \quad \frac{\Delta q}{\Delta C} = m$$

$$\text{if isotherm nonlinear} \rightarrow q = A(T) \quad \text{(Freundlich isotherm)}$$

$$A(T) \rightarrow \text{Temp.}$$

$$\text{(iv) Solute desorbs.}$$

$$\text{rel. of solute} = f(\text{change in concn.})$$

$$\text{Packed bed}$$

Defn: for very large molecule $K_d = 0$

Case 2: for small molecule $K_d = 1/00$

Movement of smaller molecules will be much slower.

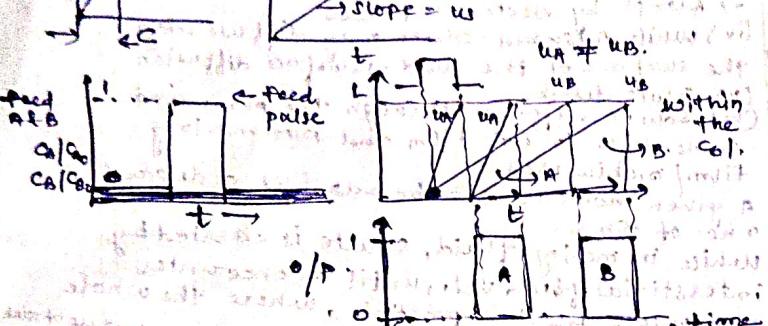
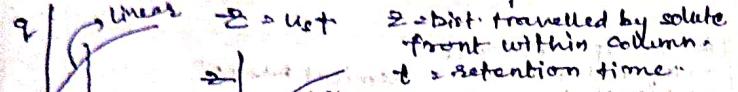
Case 3: In case of strong adsorpⁿ → molecules move

slower as rel. \downarrow

For linear adsorpⁿ Isotherm → solute rel. is indep. of solute conc.

For nonlinear adsorpⁿ Isotherm → solute rel. depends on solute conc.

At lower solute conc., linear adsorpⁿ isotherm is valid.



for small feed pulse :- $t_R = \frac{L}{u_s}$

for fairly wide feed pulse :- $t_R = \frac{L}{u_s} + \frac{t_f}{2}$ t_f = duration of feed pulse

Ex:- In a chromatographic col. an organic acid is passed through a solid matrix! $P_s = 1.5 \text{ g/kg}$; $K_d = 1/00$, $e_0 = 0.4$, $G_p = 0.6$; $q = 2.5 C^{0.4}$ C → molar conc.

(a) initially a clean col. is fed with organic acid solⁿ containing 0.2 M . It is fed with organic acid solⁿ containing 0.2 M at superficial vel. of 5 cm/min col. length $= 23 \text{ cm}$. Find the residence time of the shockwave - if a conⁿ stream displaces a dilute solⁿ, the ligⁿ front is known as shockwave. If dil. displaces conc. → diffused wave.

(b.) after the column is saturated with $C = 0.2 \text{ M}$ solⁿ of organic acid is removed with an aqueous solⁿ of a superficial vel. 20 cm/min ; predict the shape and time distribⁿ at the outlet of the col.

solⁿ ! $V_{super} = 5 \text{ cm/min}$ $v =$ interstitial vel. = $\frac{V_{super}}{e_0}$

Corresp. to $C = 0.2 \text{ M}$

$$q_2 = 2.5 C^{0.4} = 2.5 (0.2)^{0.4} = 1.813 \text{ g/mol/kg}$$

$u_{sh} = \text{rel. of lig. front (shockwave)} = \frac{1}{1 + \left(\frac{1+e_0}{e_0}\right) \epsilon p K_d} \frac{v}{e_0}$

$$= \frac{1}{1 + \left(\frac{1+0.4}{0.4}\right) 0.6 + \left(\frac{1-0.4}{0.4}\right) \left(\frac{1-q_2}{1-q}\right) \frac{1-e_0}{e_0} \left(\frac{1-q}{1-q_2}\right) \frac{1+e_0}{e_0} \frac{p}{p_0}}$$

$$= \frac{1}{1 + \left(\frac{1+0.4}{0.4}\right) 0.6 + \left(\frac{1-0.4}{0.4}\right) \left(\frac{1-0.2}{1-0.1813}\right) \frac{1-0.4}{0.4} \times 1.5 \times \frac{(1.319 - 0)}{0.2 - 0}}$$

$$= \frac{1}{1.52} = 1.478 \text{ cm/min}$$

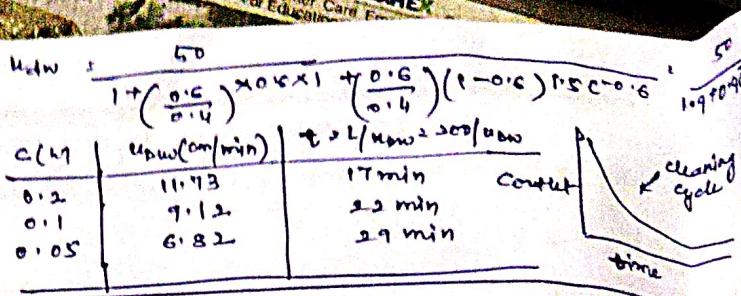
$$t_{out} = \frac{L}{u_{sh}} = \frac{200}{1.475} = 136 \text{ min.}$$

(b.) Diffused wave cleaning cycle of the col. $V_{interstitial} = V_{super} = 20 \text{ cm/min}$

$$u_{dw} = \frac{V_{interstitial}}{1 + \left(\frac{1+e_0}{e_0}\right) \epsilon p K_d + \left(\frac{1-e_0}{e_0}\right) \left(\frac{1-p}{p}\right) \frac{dp}{dc}} = 50 \text{ cm/min}$$

$$q = 2.5 C^{0.4}$$

$$\frac{dq}{dc} = 2.5 \times 0.4$$



Rough :-

$$1 + \frac{2V_0}{K} = \frac{V_0}{\alpha C} \quad V_0 = \frac{R_m A}{\alpha C} \quad K = \frac{2A^2}{(P_0 - P)}$$

$$\frac{t}{V} = \frac{1}{K} (V_0 + 2V_0) \quad \frac{t}{V} = \frac{V_0}{K} + \frac{2V_0}{V} \quad V = 7.01 \times 10^{-5} x + 0.0272$$

$$\frac{1}{K} = 7.01 \times 10^{-5} \quad K = 0.1426 \times 10^5$$

$$\frac{2V_0}{K} = 0.0272 \rightarrow V_0 = \frac{K \times 0.0272}{2}$$

$$\rightarrow V_0 = 204 \quad \rho_c = 1.8 \text{ kgm/gf.s}^2$$

$$K = \frac{(2A^2)}{\alpha P C} \Delta P \rho_c = \frac{2 \times (0.28)^2}{4 \times 2.9 \times 10^{-3} \times 1920} \Delta P \times 98$$

$$\rightarrow \Delta P = \frac{1.5 \times 10^4 \times 7 \times 1920 \times 2.9 \times 10^{-3} \times 98}{2 \times (0.28)^2 \times 98}$$

$$\rightarrow \Delta P = 217409 \times 10^{-6} \text{ m}^3 \text{ XM} \times \frac{\text{kg}}{\text{m}^3} \times \frac{\text{kg}}{\text{m}^2}$$

$$60.5 \text{ kg/m}^2$$

$$\Delta P = 20.3 \times 10^{-4} \text{ N/m}^2$$

$$100L/h \quad C_P = 18/L \quad P_0 = 10L/h$$

$$C_B = 100 C_P^2$$

$$R = F = 100 L/h$$

$$F = 100 L/h$$