MEMBRANE SEPARATION

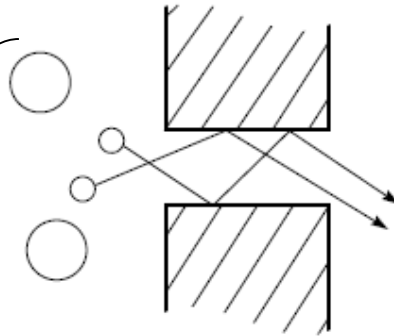# MASS TRANSFER IN MEMBRANE PROCESSES

TRANSPORT MODELS
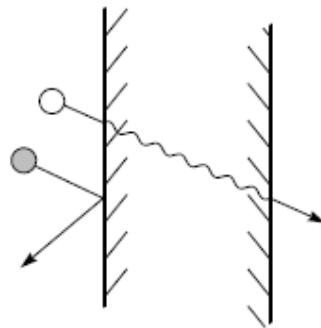
Membrane selective : Ability to control the rate of permeation of different species

Permeation mechanism model

based on pore size

Microporous membranes separate by molecular filtration

ϕ = 5-10Å

Dense solution-diffusion membranes separate because of differences in the solubility and mobility of permeants in the membrane material

Pore-flow/sieving model
- Permeants are transported by pressure-driven convective flow through tiny pores
- Separation occurs because one of the permeants is <u>excluded (filtered)</u> from some of the pores in the membrane through which other permeants move
- The free-volume elements (pores) are relatively large and fixed, do not fluctuate in position or volume on the timescale of permeant motion, and are connected to one another

Solution-diffusion model
- Permeants dissolve in the membrane material and then diffuse through the membrane down a concentration gradient
- The permeants are separated because of the differences in the <u>solubilities</u> of the materials in the membrane and the differences in the rates at which the materials <u>diffuse</u> through the membrane
- The free-volume elements (pores) in the membrane are tiny spaces between polymer chains caused by thermal motion of the polymer molecules

Diffusion:

- is the process by which matter is transported from one part of a system to another by a concentration gradient … **slow process** … kinetic parameter
- simple statistics show that a net transport of matter will occur from the high concentration to the low concentration region
- Fick's law

$$Ji = -D_i \frac{dC_i}{dx}$$

High transport (flux) : thin layer and high concentration difference

Solubility:

- A thermodynamic parameter and gives a measure of the amount of permeants/penetrant sorbed by the membrane under equilibrium conditions

- Solubility of gas ... **Henry's law**

Permeability (P) = Solubility (S) x Diffusivity (D)

For dense/non-porous membranes, e.g. GS, PV, RO, etc.

Pore-flow model:

- Pressure driven convective flow
- In capillary or porous medium
- Darcy's Law

$$Ji = K'C_i \frac{dp}{dx}$$

dp/dx   : is the pressure gradient existing in the porous medium
C_i : is the concentration of component *i* in the medium
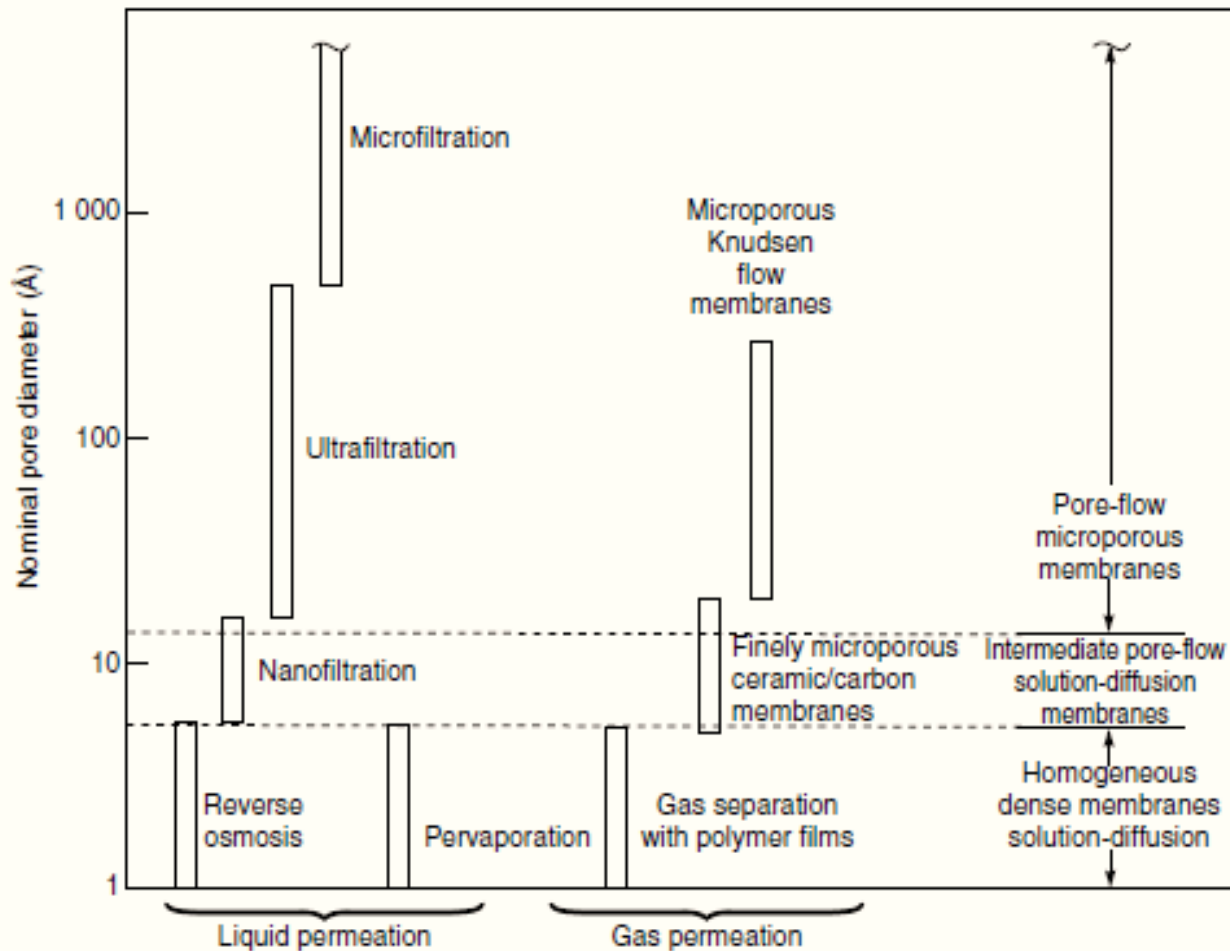K'   : is a coefficient reflecting the nature of the medium

- Fluxes obtained is higher compared to simple diffusion

Pore-flow vs. Solution diffusion **... Membrane pore size**

The average pore diameter in a membrane is difficult to be measured directly and must often be inferred from the size of the molecules that permeate the membrane or by some other indirect technique

Figure : Schematic representation of the nominal pore size and best theoretical model for the principal membrane separation processes

> UF, MF and microporous Knudsen flow gas separation membrane are clearly microporous ... pore flow

> RO, PV, GS ... a dense polymer layer with no visible pores ... for molecule 2-5Å

> NF, fine microporous ... intermediate between truly microporous and truly solution diffusion membranes … for di/trisaccharised (10-13 Å) rejection but freely pass monosaccharides (5-6 Å)

SOLUTION-DIFUSSION MODEL

Molecular Dynamics Simulations

Reverse osmosis

uses a large pressure difference across the membrane to separate water from salt solutions

Pervaporation

the pressure difference across the membrane is small, and the process is driven by the vapor pressure difference between the feed liquid and the low partial pressure of the permeate vapor

Gas Separation

transport of gases down a pressure or concentration gradient

❑ Diffusion process
❑ The pressure, temperature, and composition of the fluids determines the concentration of the diffusing species at the membrane surface in equilibrium with the fluid
❑ Once dissolved in the membrane, individual permeating molecules move by the same random process of molecular diffusion no matter whether the membrane is being used in reverse osmosis, pervaporation, or gas permeation … similar membranes are used in very different processes
❑ The movement or diffusion of individual molecule in free volume (voulme between polymer chain) can be calculated/studied by computer **molecular dynamics simulation**
❑ Molecular dynamics simulations also allow the transition from the solution diffusion to the pore-flow transport mechanism to be seen

SOLUTION-DIFUSSION MODEL

Molecular Dynamics Simulations: example result

Cavity size

Jump length λ

From Smit *et al.* (1992)

Jump

Movement in cavity

Position (Å)

Movement in cavity

Jump length

Cavity size

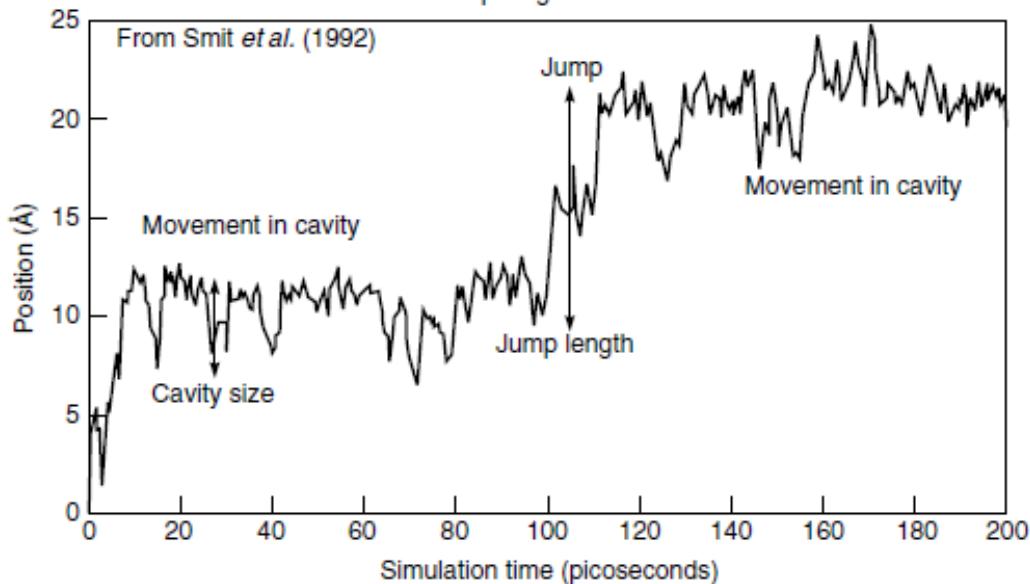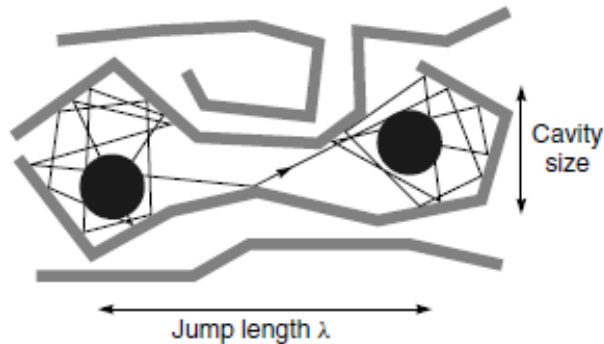Simulation time (picoseconds)

Figure 2.3 Motion of a carbon dioxide molecule in a 6FDA-4PDA polymer matrix [8]. Reprinted from *J. Membr. Sci.* **73**, E. Smit, M.H.V. Mulder, C.A. Smolders, H. Karrenbeld, J. van Eerden and D. Feil, Modeling of the Diffusion of Carbon Dioxide in Polyimide Matrices by Computer Simulation, p. 247, Copyright 1992, with permission from Elsevier

- During the first 100 ps of the simulation, the carbon dioxide molecule bounces around in the cavity where it has been placed, never moving more than about 5 Å , the diameter of the cavity.

- After 100 ps, however, a chance thermal motion moves a segment of the polymer chains sufficiently for the carbon dioxide Molecule to jump approximately 10 Å to an adjacent cavity where it remains until another movement of the polymer chains allows it to jump to another cavity.

- By repeating these calculations many times and averaging the distance moved by the gas molecule, its diffusion coefficient can be calculated.

far from matching the experimental values ... the best quantitative description of permeation uses phenomenological equations, particularly **Fick's law**

Concentration and Pressure Gradients in Membranes

Mathematical description of diffusion in membranes based on thermodynamic: the driving forces of pressure, temperature, concentration, and electrical potential are interrelated and that the overall driving force producing movement of a permeant is the gradient in its chemical potential

$$Ji = -L_i'C_i \frac{d\mu_i}{dx}$$

where $d\mu_i/dx$ is the chemical potential gradient of component i and L_i is a coefficient of proportionality (not necessarily constant) linking this chemical potential driving force to flux.

Restricting the approach to driving forces generated by concentration and pressure gradients, the chemical potential is written as

$$d\mu_i = RT d\ln(\gamma_i n_i) + \upsilon_i dp$$

where n_i is the mole fraction (mol/mol) of component i, γ_i is the activity coefficient (mol/mol) linking mole fraction with activity, p is the pressure, and υ_i is the molar volume of component i.

For incompressible fluid, volume does not change with pressure, thus

$$\mu_i = \mu_i^o + RT\ln(\gamma_i n_i) + \upsilon_i(p - p_i^o)$$

where μ_i^o is the chemical potential of pure i at a reference pressure, p_i^o .

Concentration and Pressure Gradients in Membranes

For incompressible fluid, volume does not change with pressure, thus

$$\mu_i = \mu_i^o + RT \ln(\gamma_i n_i) + \upsilon_i(p - p_i^o)$$

where μ_i^o is the chemical potential of pure i at a reference pressure, p_i^O.

For compressible fluid, volume does change with pressure, thus

$$\mu_i = \mu_i^o + RT \ln(\gamma_i n_i) + RT \ln \frac{p}{p_i^o}$$

reference pressure, p_i^O is defined as the saturation vapor pressure of i, p_i^{sat}, therefore,

$$\mu_i = \mu_i^o + RT \ln(\gamma_i n_i) + \upsilon_i(p - p_{i_{sat}}) \quad \text{for incompressible}$$

$$\mu_i = \mu_i^o + RT \ln(\gamma_i n_i) + RT \ln \frac{p}{p_{i_{sat}}} \quad \text{for compressible}$$

Assumptions

☐ The fluids on either side of the membrane are in equilibrium with the membrane material at the interface
☐ When pressure is applied across a dense membrane, the pressure throughout the membrane is constant at the highest value
☐ The pressure within a membrane is uniform and that the chemical potential gradient across the membrane is expressed only as a concentration gradient

Concentration and Pressure Gradients in Membranes

Solution-diffusion model
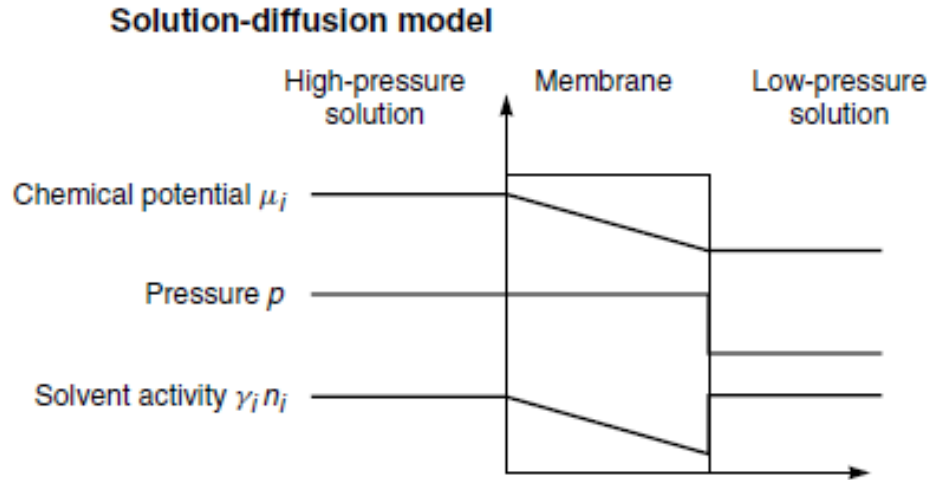
$$J_i = -L_i \frac{\mathrm{d}\mu_i}{\mathrm{d}x}$$

$$\mathrm{d}\mu_i = RT\,\mathrm{d}\ln(\gamma_i n_i) + \upsilon_i \mathrm{d}p$$

$$J_i = -\frac{RT\,L_i}{n_i} \cdot \frac{\mathrm{d}n_i}{\mathrm{d}x}$$

Pressure driven permeation of a one-component solution through a membrane according to the solution-diffusion transport model

$$c_i = m_i \rho n_i$$

$$J_i = -\frac{RTL_i}{c_i} \cdot \frac{\mathrm{d}c_i}{\mathrm{d}x} \qquad \sim \text{Fick's law}$$

c_i: concentration (g/cm³)
m_i: the molecular weight of I (g/mol)
ρ : the molar density (mol/cm³)
o and l represent the position of the feed and permeate interfaces
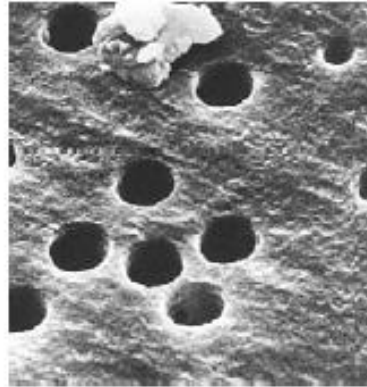
$$J_i = \frac{D_i(c_{i_{o(m)}} - c_{i\ell(m)})}{\ell}$$

Concentration and Pressure Gradients in Membranes

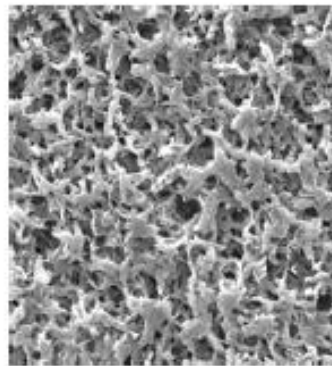*Lack of pore flow model ...* **extremely heterogeneous nature of microporous membranes**

Molecular sieving

Both methods
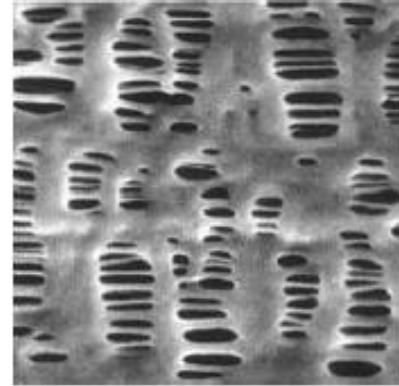
depth filter which captures particles within the interior of the membrane by adsorption
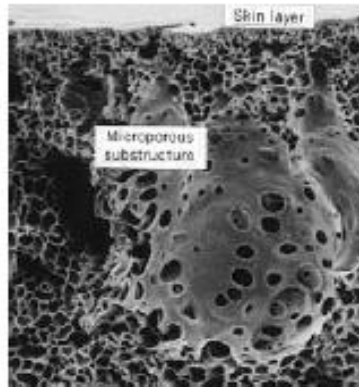
Molecular sieving

(a) Nuclepore (polycarbonate) nucleation track membrane; (b) Celgard® (polyethylene) expanded film membrane; (c) Millipore cellulose acetate/cellulose nitrate phase separation membrane made by water vapor imbibition (Courtesy of Millipore Corporation, Billerica, MA); (d) anisotropic polysulfone membrane made by the Loeb–Sourirajan phase separation process … all have app. similar particle rejection

PORE FLOW MODEL

*Lack of pore flow model ...* **Reasons**

- Pore structure

- Membrane material

- Characterization

Cross-sections of porous membranes of different tortuosity

Membrane thickness ℓ

$\tau = 1.0$ $\tau = 1.5$ $\tau \sim 1.5 - 2.5$

Surface views of porous membranes of equal porosity (ε) but differing pore size

d

average pore size

❑ Porosity (ε) is the fraction of the total membrane volume that is porous
❑ The membrane tortuosity (τ) reflects the actual length of the average pore compared to the membrane thickness
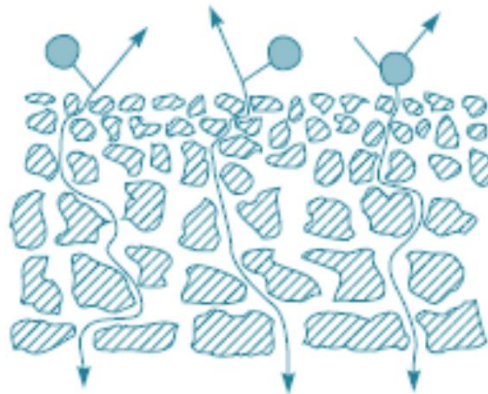❑ pore diameter
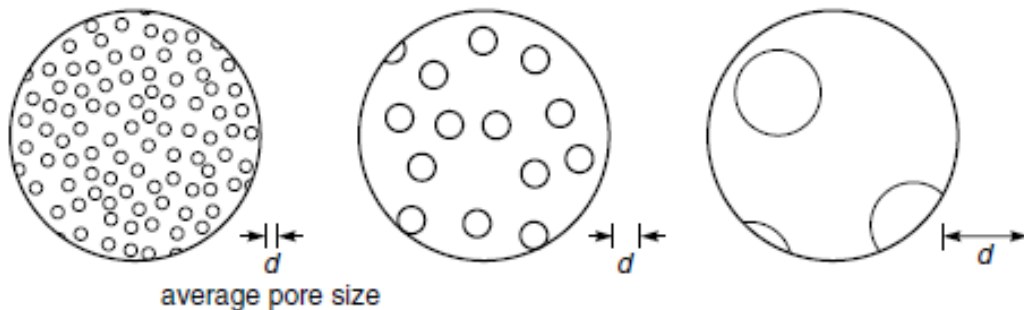
Permeation in Ultrafiltration and Microfiltration Membranes

(a) Screen filtration
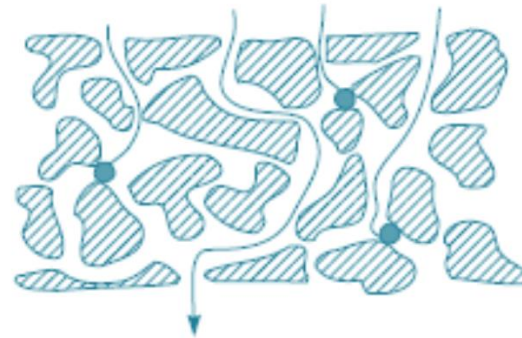
(b) Depth filtration

Figure 2.31 Separation of particulates can take place at the membrane surface according to a screen filtration mechanism (a) or in the interior of the membrane by a capture mechanism as in depth filtration (b)

- Contain surface pores smaller than the particles to be removed
- Anisotropic
- Capture and accumulated on the surface

- Captures the parti-cles to be removed in the interior of the membrane
- Isotropic
- Constrictions and adsorption

Screen filtration
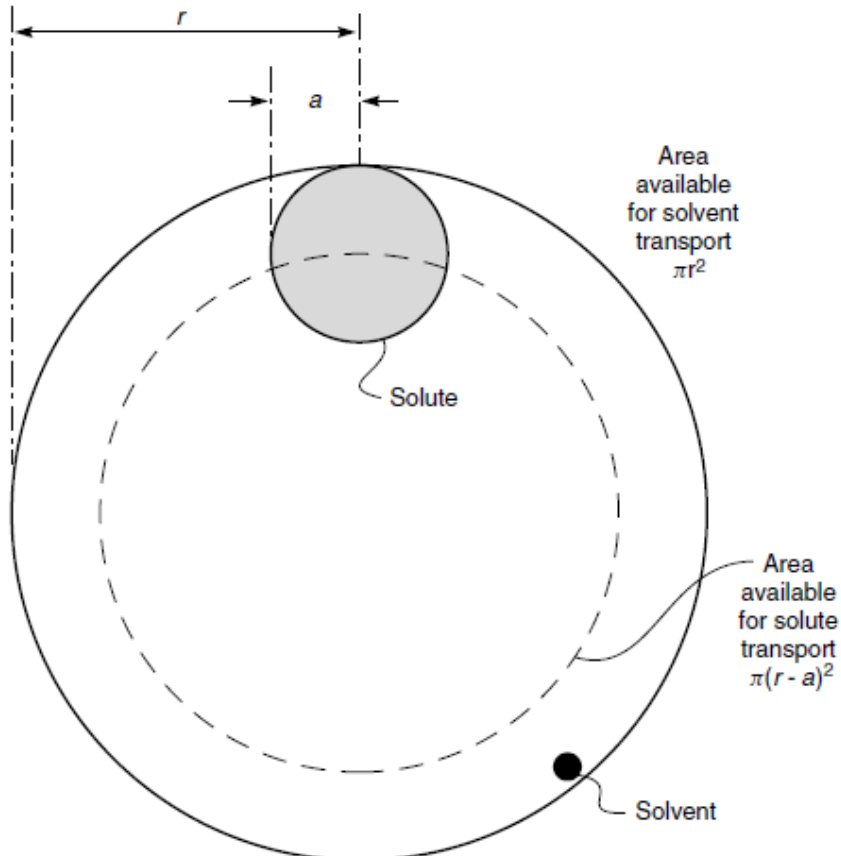
The area, A, of the pore available for solute transport

$$A = \pi(r - a)^2$$

$$\frac{A}{A_o} = \frac{\pi(r-a)^2}{\pi r^2} = \frac{(r-a)^2}{r^2}$$

to account for the parabolic velocity profile of the fluid as it passes through the pore

$$\left(\frac{A}{A_o}\right)' = 2\left(1 - \frac{a}{r}\right)^2 - \left(1 - \frac{a}{r}\right)^4$$

$$\left(\frac{A}{A_o}\right)' = \frac{C_p}{C_o}$$

Ferry-Renkin equation

$$R = \left[1 - 2\left(1 - \frac{a}{r}\right)^2 + \left(1 - \frac{a}{r}\right)^4\right] x100\%$$

Co and Cp are solute concentration in feed and permeate, respectively

Area available for solvent transport πr^2

Solute

Area available for solute transport $\pi(r-a)^2$

Solvent

❑ Pores are assumed to be equal circular capillaries with a large radius (r)
❑ Solvent can freely pass through the pores

Depth filtration

Electrostatic adsorption

Brownian diffusion

Inertial impaction

Sieving

Fluid stream lines

Fiber cross-section