Nanofiltration Membrane Characterization using Mass Transfer Data with Emphasis on Temperature Effects

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Importance of Nanofiltration

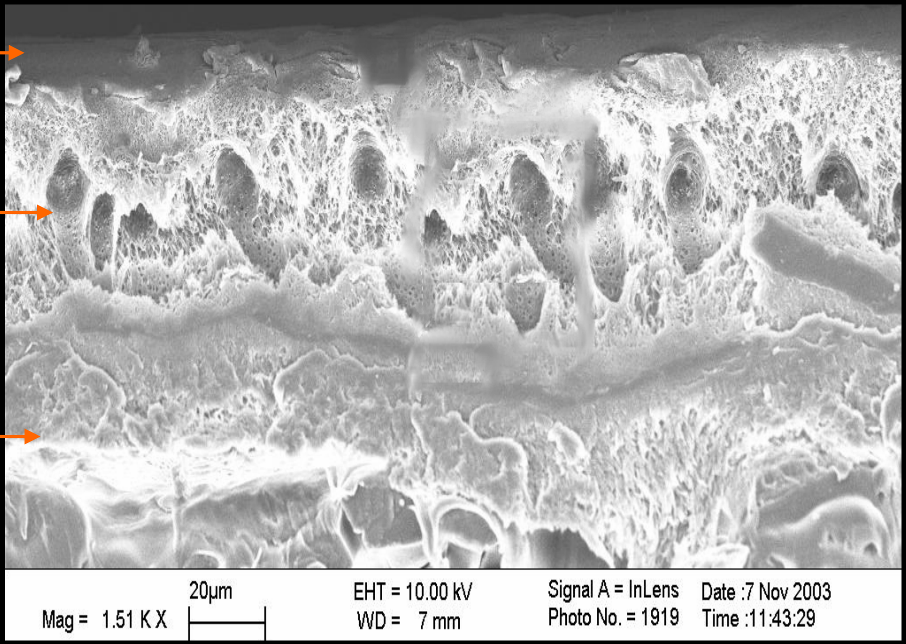
- Capable of achieving high removals of natural organic matter, disinfection by-products, pesticides, arsenic, hardness, etc.
- Lower cost than reverse osmosis technology
- However, transport mechanisms are not yet fully understood

Thin Film Composite Nanofilter

Thin skin ~ 1 μm

Porous support
~ 40 μm

Reinforcing fabric
~ 120 μm



EFFECTIVE skin layer parameters: pore size distribution, porosity, tortuosity, thickness, and charge density

Temperature – Important Variable

NF/RO feed water temperature changes over time

- **1 - 26 °C – River Oise, France**
  37 MGD NF Plant, (Ventresque et al., 1997)

- **1 - 26 °C – Occoquan Reservoir, Virginia, USA**
  NF Pilot scale Study (Chellam et al., 1997)

- **10 - 25 °C – Ehime, Japan (Sea Water)**
  3.7 MGD RO plant (Taniguchi and Kimura, 2000)

- **10 - 35 °C – Kuwait (Sea Water)**
  32 MGD RO plant (Abdel-Jawad et al., 2001)

Motivation – Temperature Effects

With increase in temperature

- **Salt passage↑ (*Mehdizadeh, et al. 1989*)**
- **Natural organic matter passage↑ (*Her, et al. 2000*)**
- **Arsenic passage↑ (*Waypa, et al. 1997*)**
- **Water permeability↑ (*Sharma, et al., 2003*)**

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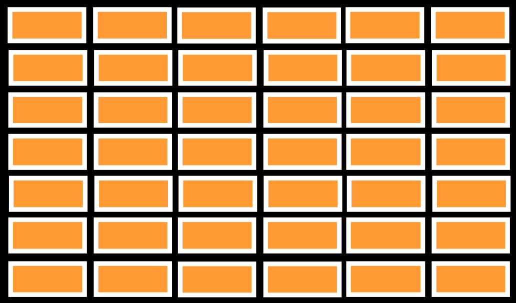

IDEALIZED NF PORE STRUCTURE

Motivation – Temperature Effects

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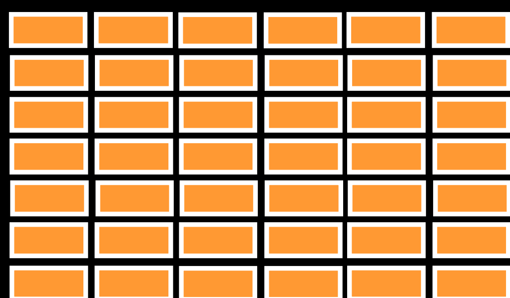
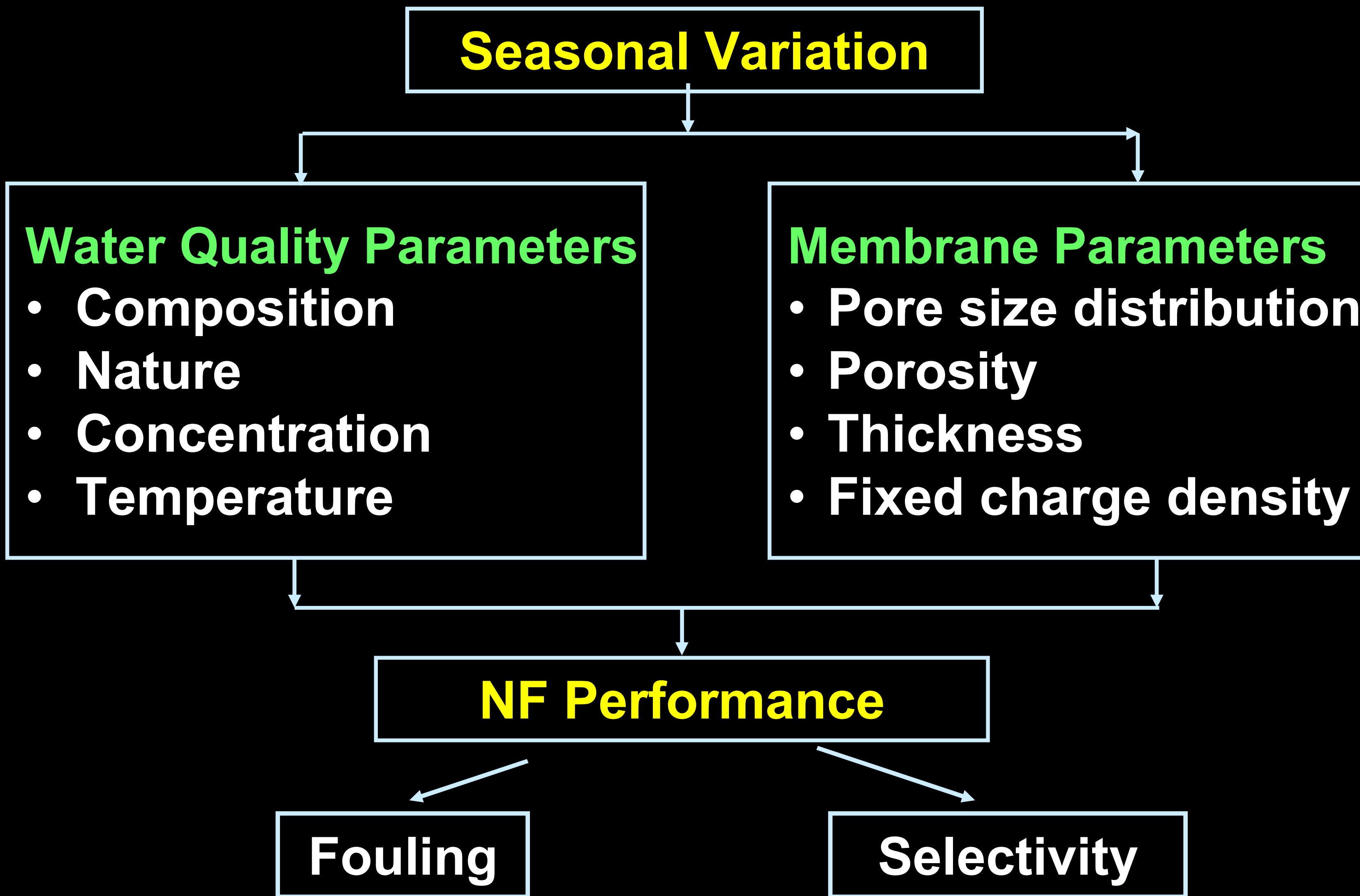


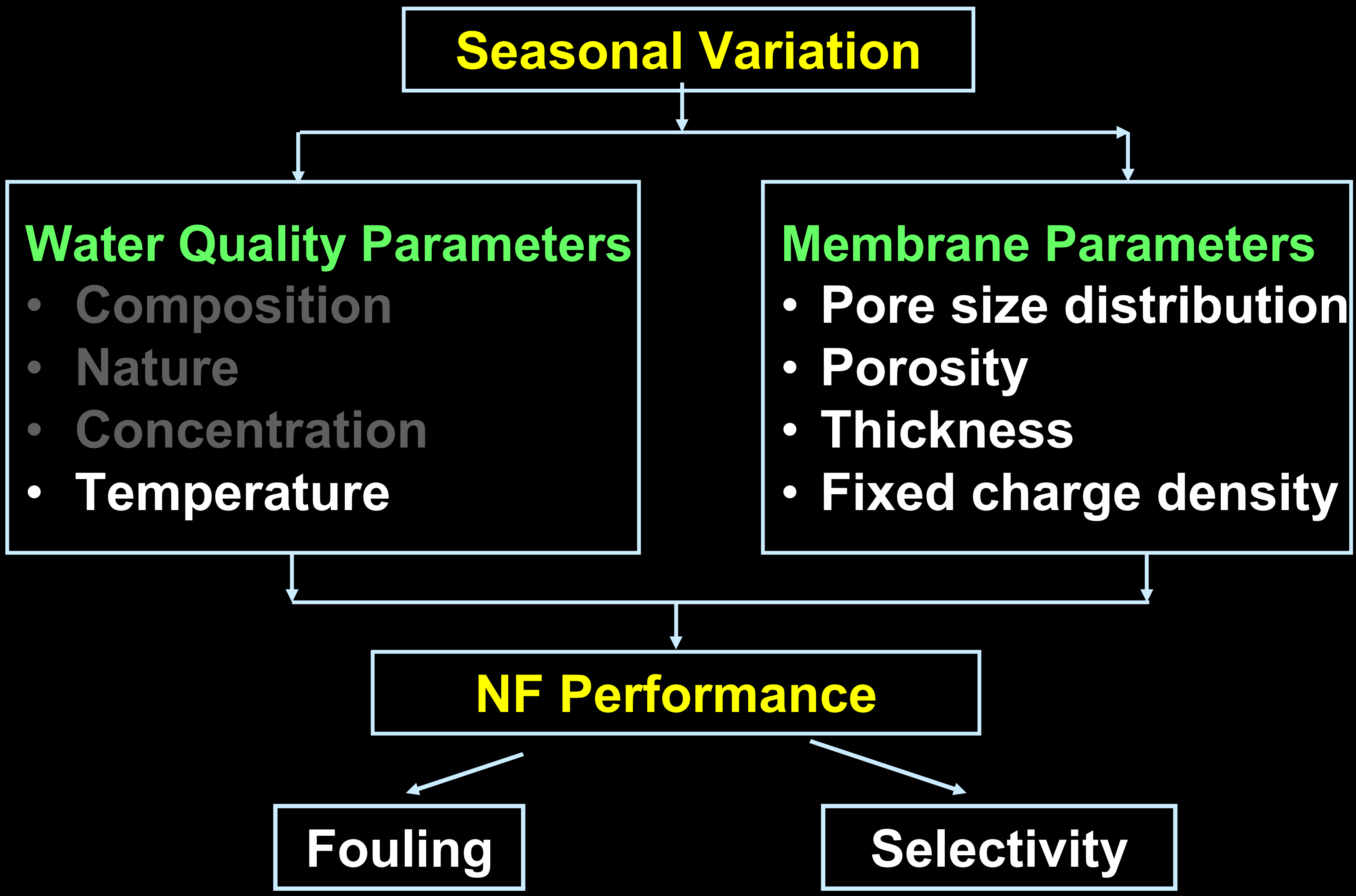
Low Temperature

High Temperature

Motivation – Temperature Effects



Motivation – Temperature Effects



Objectives

Investigate temperature (5 – 41°C) effects

- Water Permeation
- Convective transport
  - Pore size distribution and sieving
- Diffusive transport
  - Solute permeability
- Develop insights into pore structure, morphology from selectivity measurements

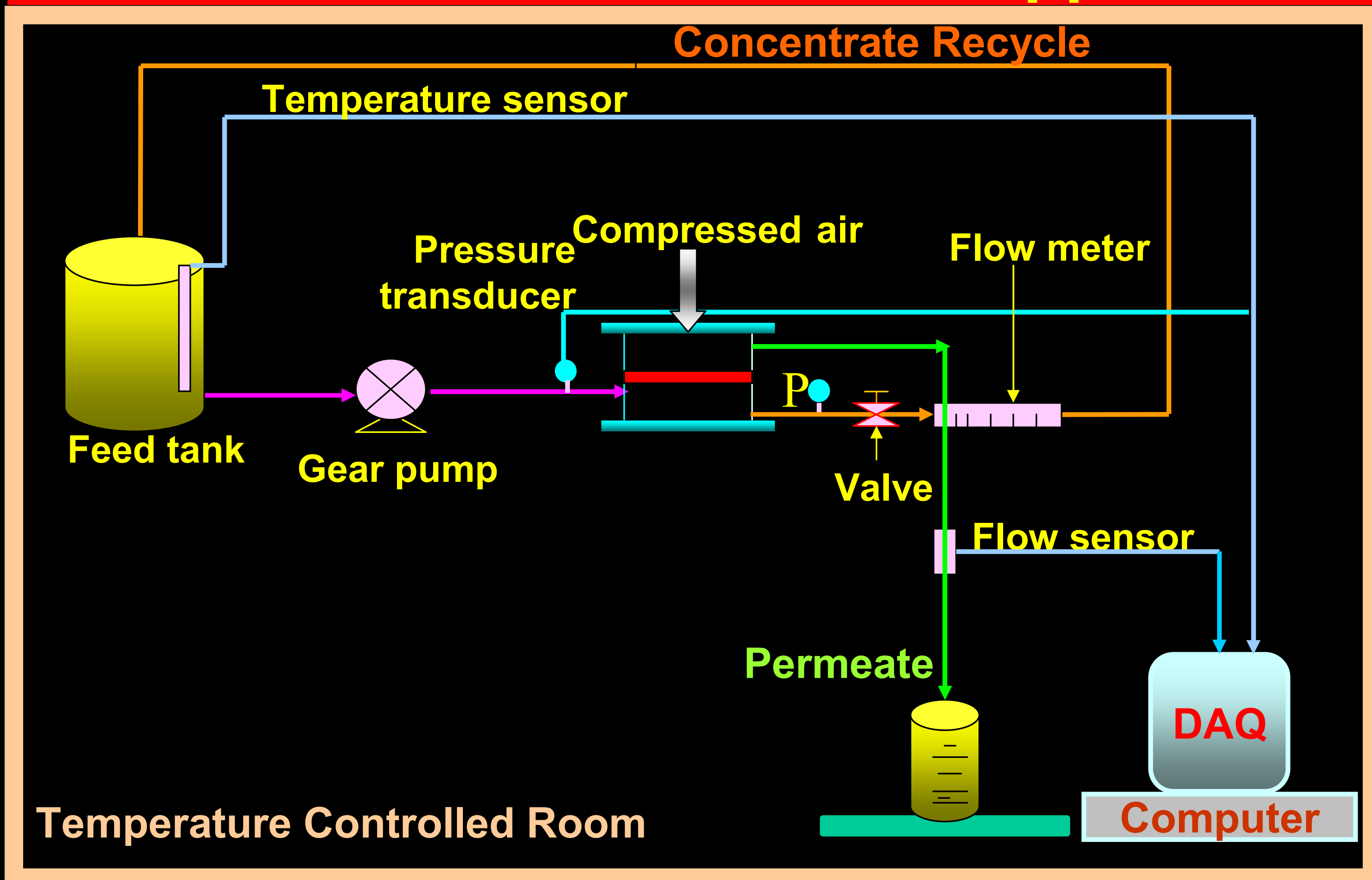
Membranes Employed

Manufacturer	Model	Composition	MWCO
Osmonics, Minnetonka, MN	DL	Polyamide	~200
Koch Fluid Systems, San Diego, CA	TFCS	Polyamide	~ 300

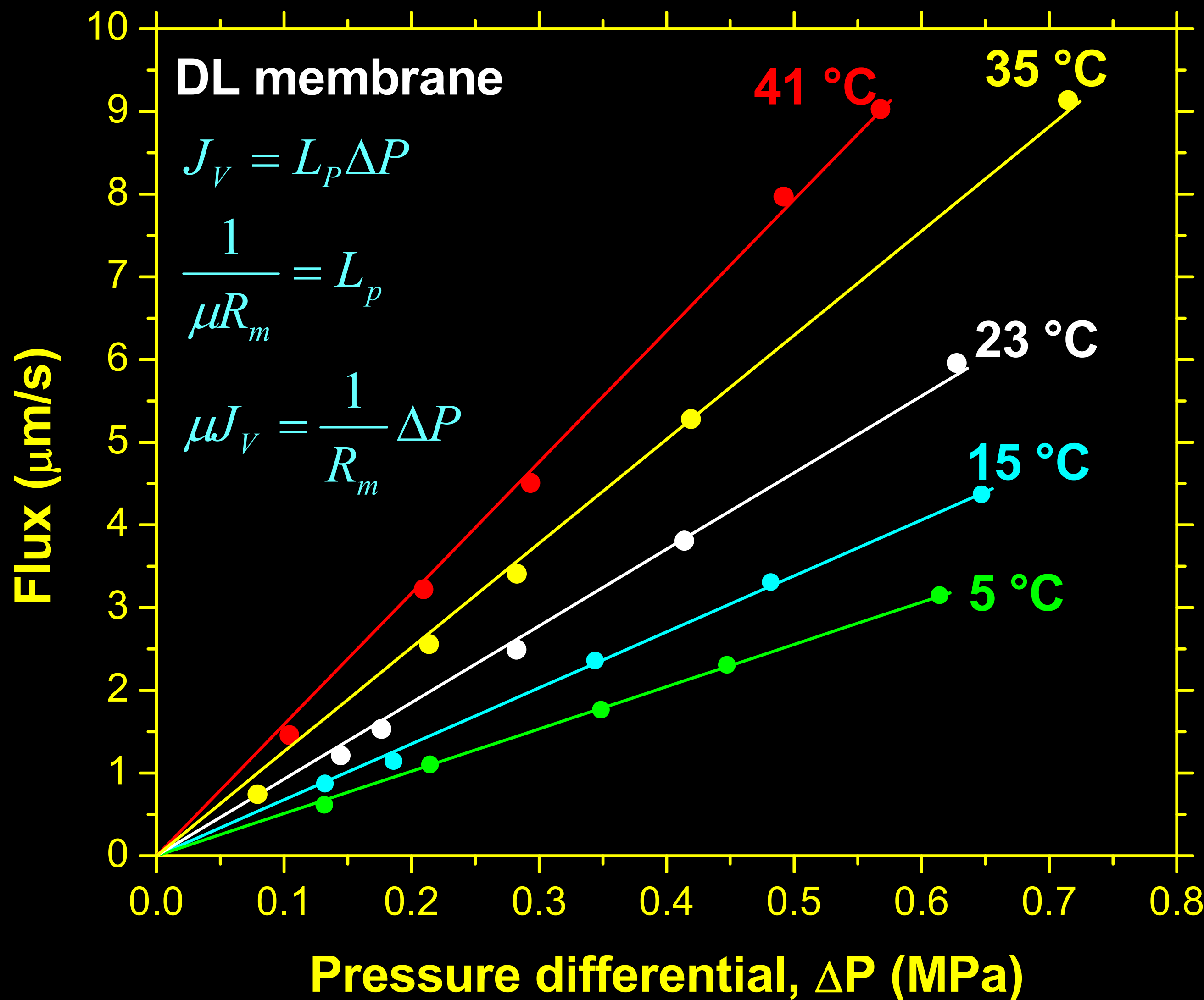
Manufacturer specifications

Water Permeation

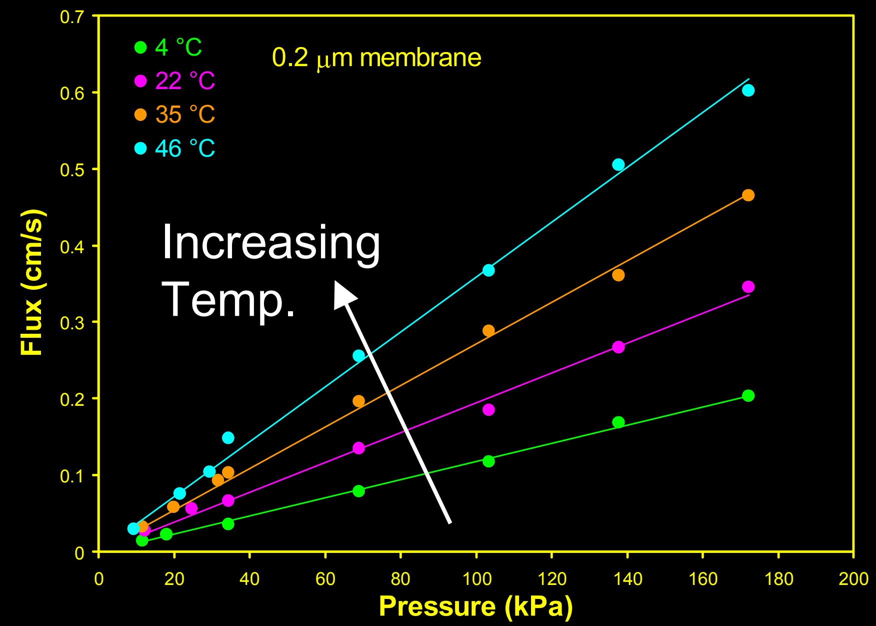
Schematic of Nanofiltration Apparatus

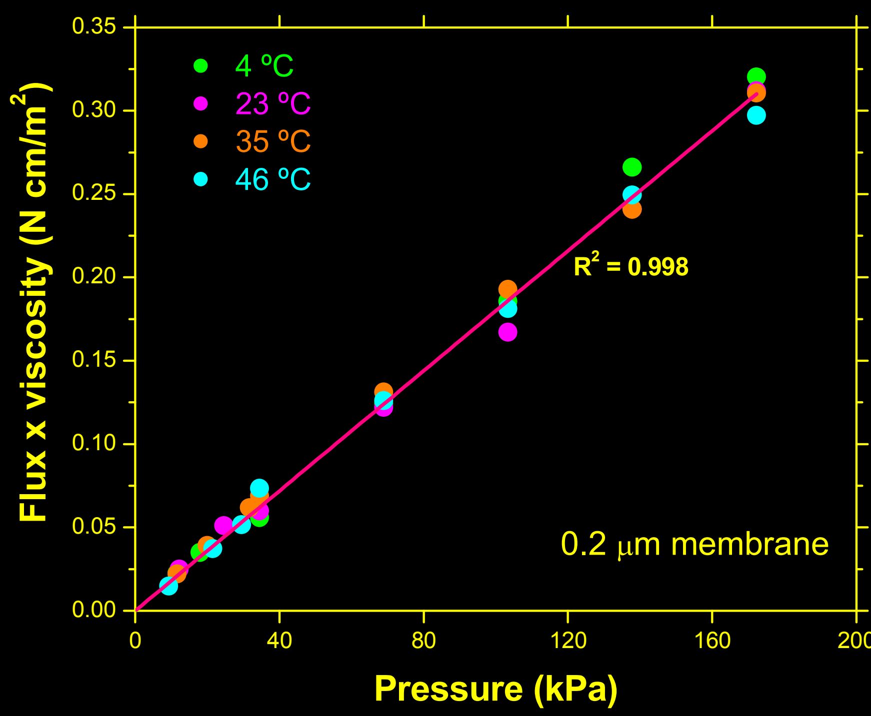


Validity of Darcy's Law – Nanofiltration

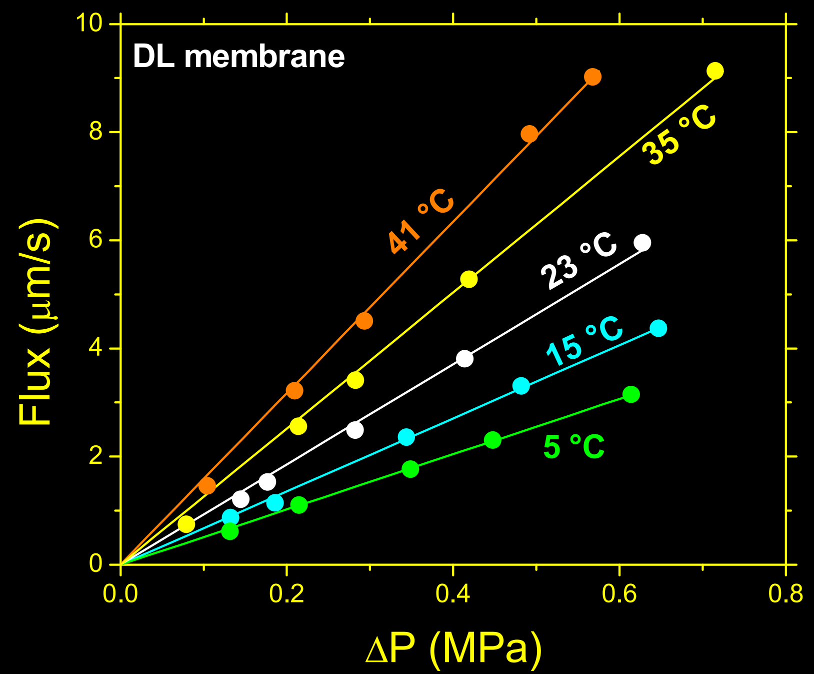


Validity of Darcy's Law – Microfiltration



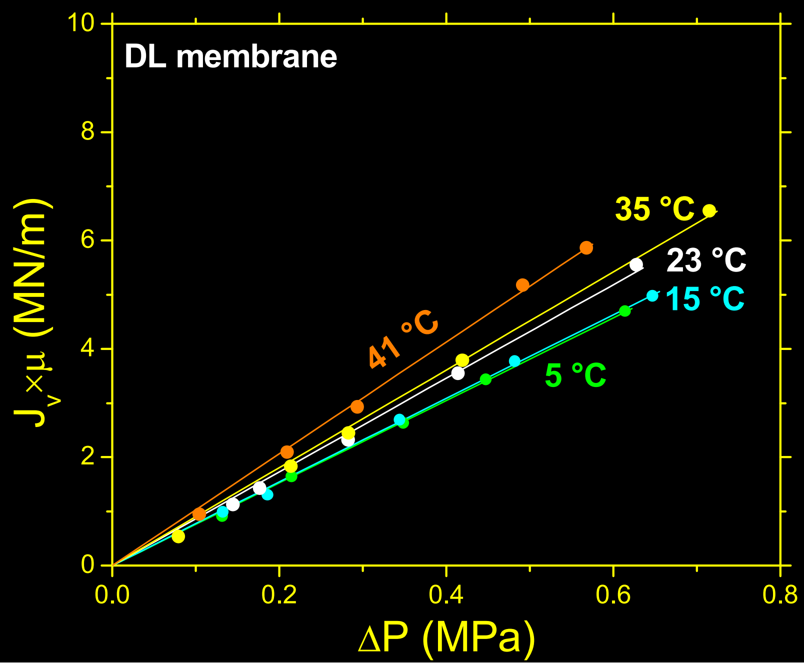


Temperature Effects on Water Permeation



$$J_V = L_P \Delta P$$

$$\mu J_V = \frac{1}{R_m} \Delta P$$



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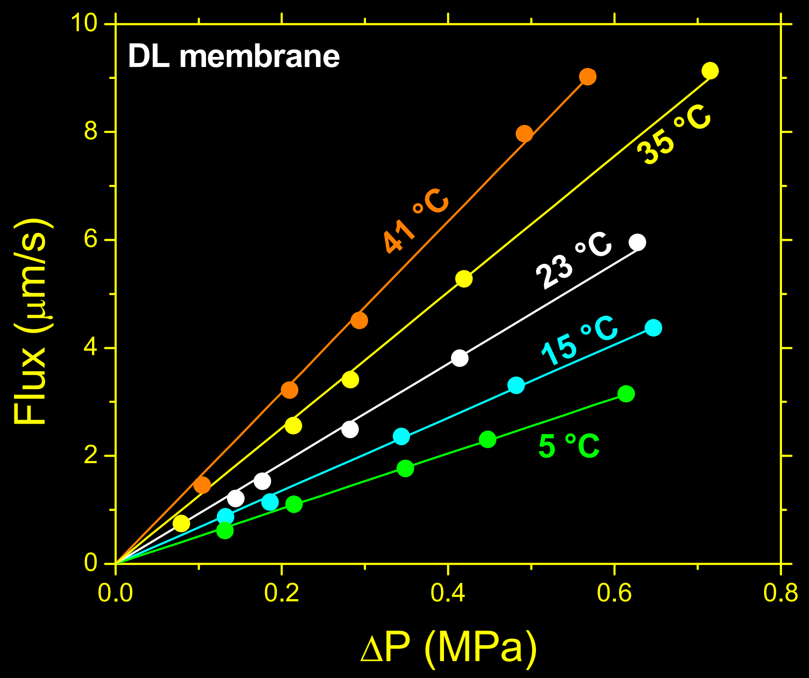

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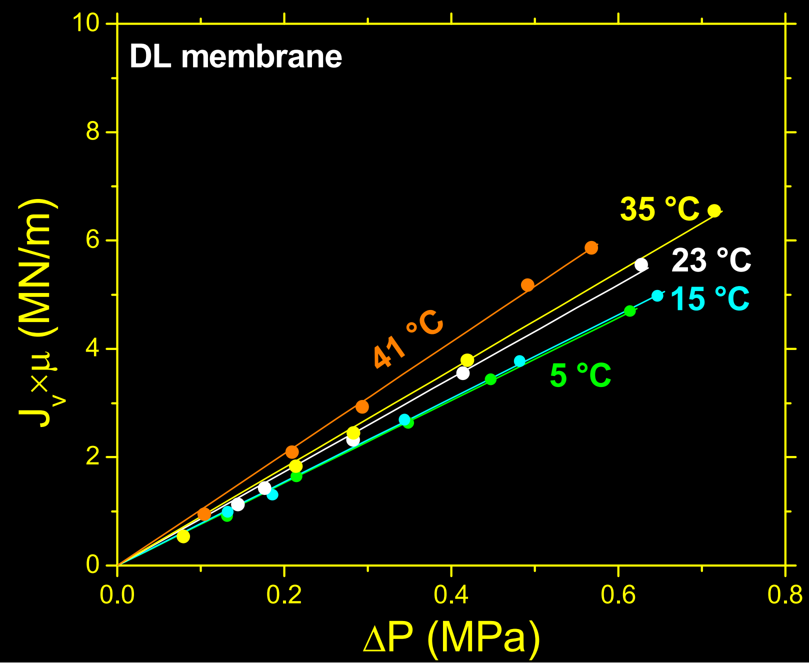

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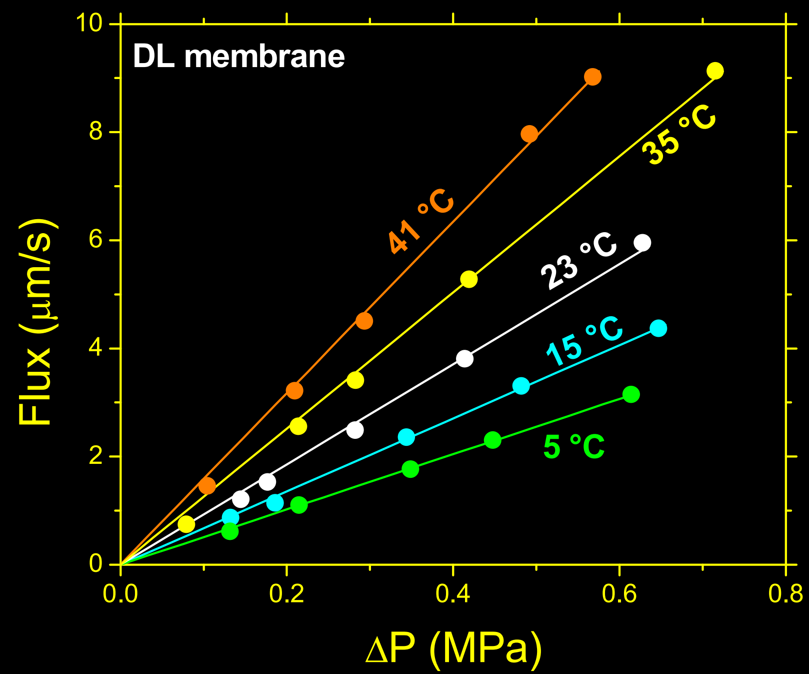
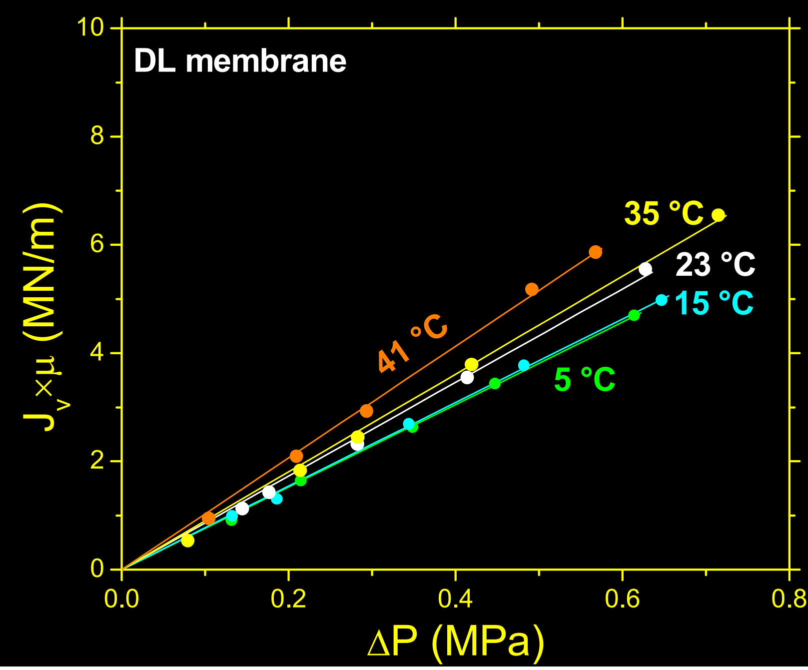


$$\frac{J_v(T)}{J_{v,23^\circ C}} = \exp\left[TCF\left(\frac{1}{296} - \frac{1}{273+T}\right)\right]$$

$$J_V = L_P \Delta P$$

$$\frac{1}{R_m} = \mu L_p$$



Temperature Effect on Transport

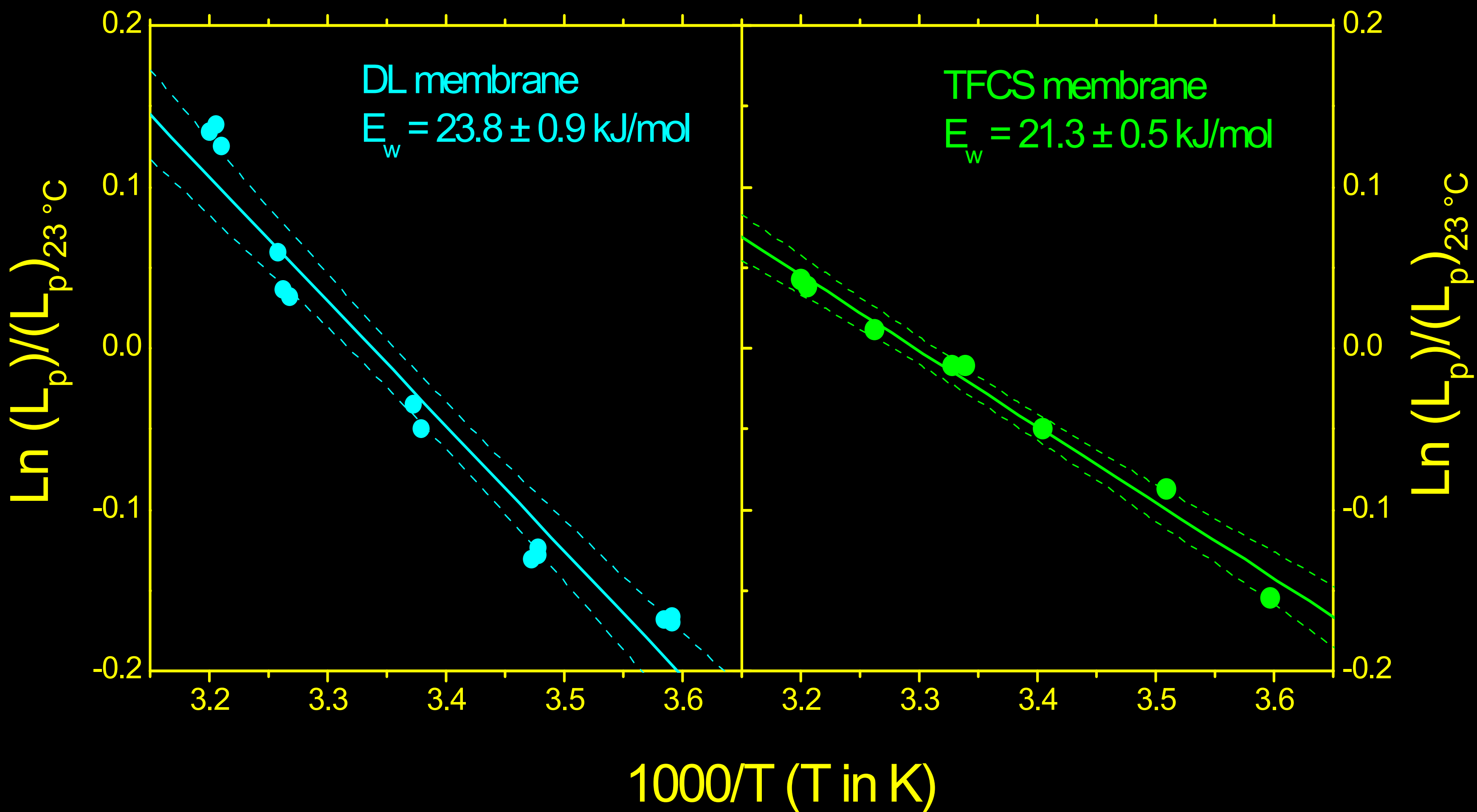
Arrhenius Equation

$$\ln\left(\frac{L_p}{L_{P23°C}}\right) = -\frac{E}{R}\left(\frac{1}{T} - \frac{1}{296}\right)$$

where

- **L_p = Water or solute permeability**
- **E = Activation energy**
- **T = Temperature (K)**
- **R = Universal gas constant**

Pure Water Permeability



Temperature Correction Equations

$$\frac{J_v(T)}{J_{v,25^\circ C}} = \exp\left[\frac{E_{act}}{R}\left(\frac{1}{298} - \frac{1}{273+T}\right)\right]$$

TFCS Membrane

$$\frac{J_v(T)}{J_{v,25^\circ C}} = \exp\left[2617\left(\frac{1}{298} - \frac{1}{273+T}\right)\right]$$

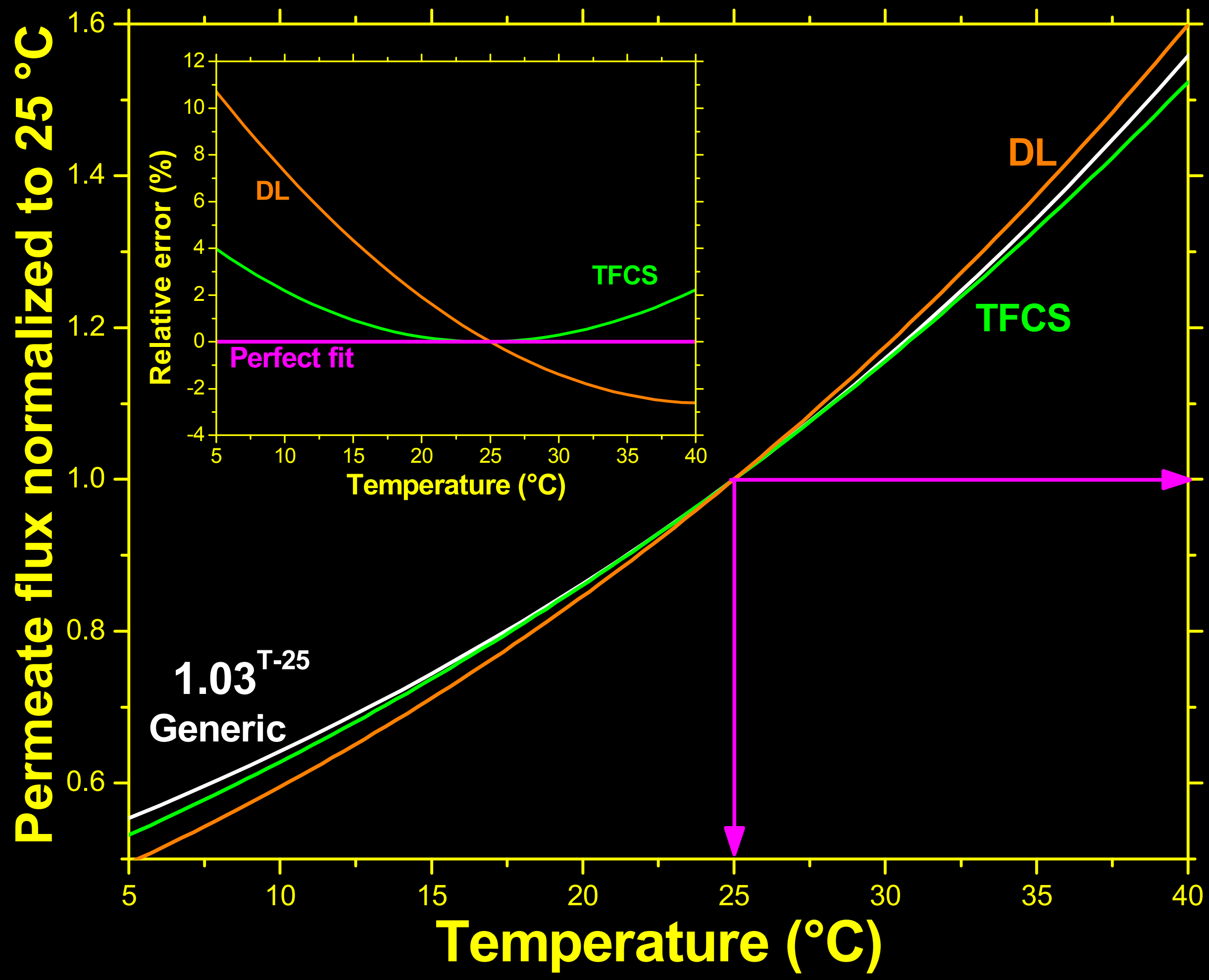
DL Membrane

$$\frac{J_v(T)}{J_{v,25^\circ C}} = \exp\left[2918\left(\frac{1}{298} - \frac{1}{273+T}\right)\right]$$

MF/UF Membrane

$$\frac{J_v}{J_{v,25^\circ C}} = \exp\left[2100\left(\frac{1}{298} - \frac{1}{273+T}\right)\right]$$

Need for Membrane-Specific TCFs

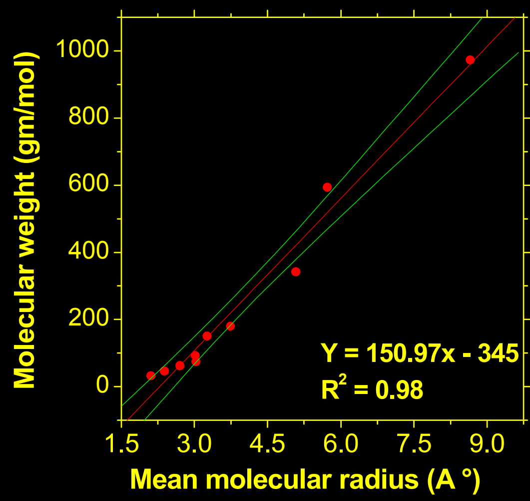


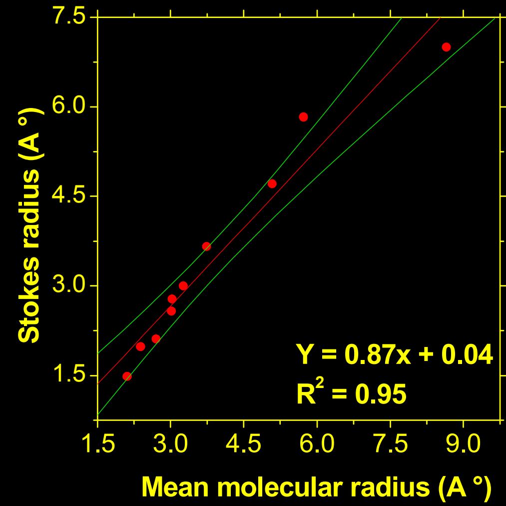
Neutral Solute Transport and Changes in Membrane Morphology

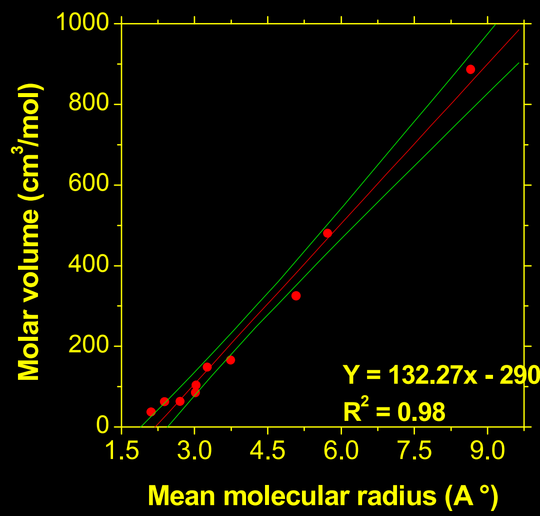
Solutes Employed

Solute	Molecular weight (g/g-mol)	Molar volume (cm^3/mol)	Stokes radius (nm)	Mean molecular radius (nm)
PEG (100K)	100,000	5,180,014.8	8.26	NA
PEG (35K)	35,000	1,813,014.8	4.87	NA
PEG (20K)	20,000	1,036,014.8	3.68	NA
α-cyclodextrin	973	886.8	0.700	0.866
Raffinose	594	480	0.583	0.573
Sucrose	342	325	0.471	0.508
Dextrose	180	166	0.366	0.374
Xylose	150	148	0.300	0.326
t-butyl alcohol	74	103.6	0.278	0.303
Glycerol	92	85.1	0.258	0.302
Ethylene glycol	62	63.5	0.211	0.270
Ethanol	46	62.6	0.198	0.239
Methanol	32	37	0.148	0.211
Water	18	14.8	0.150	0.140

Choice of Solute Size Parameter







MMR as a representative solute size parameter

Experimental Conditions

Flux: 1 to 50 L/m^2 h

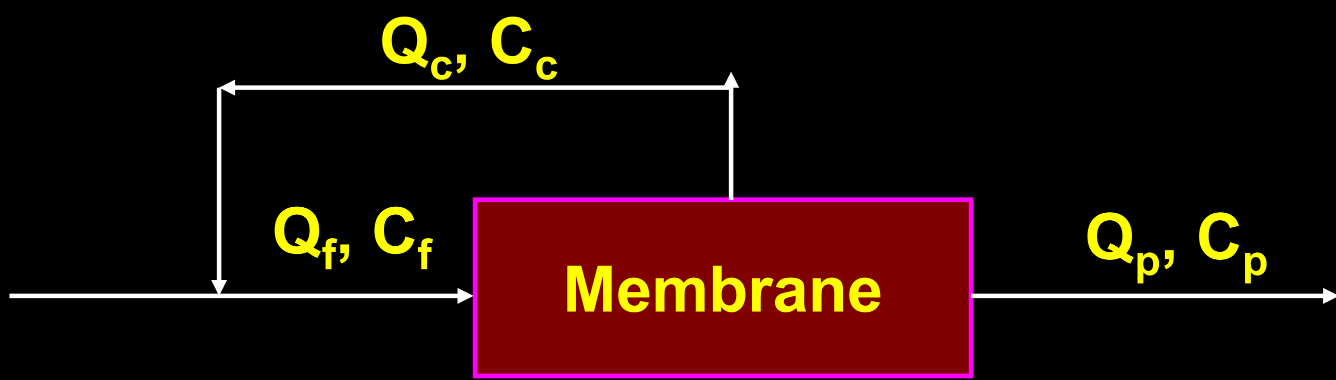
Constant and low recovery (< 1%)

Constant cross flow velocity: 9 and 19 cm/s

Feed water TOC: 20 mg/L

Temperature: 5 , 15, 23, 35 and 41 °C

Irreversible Thermodynamics Model



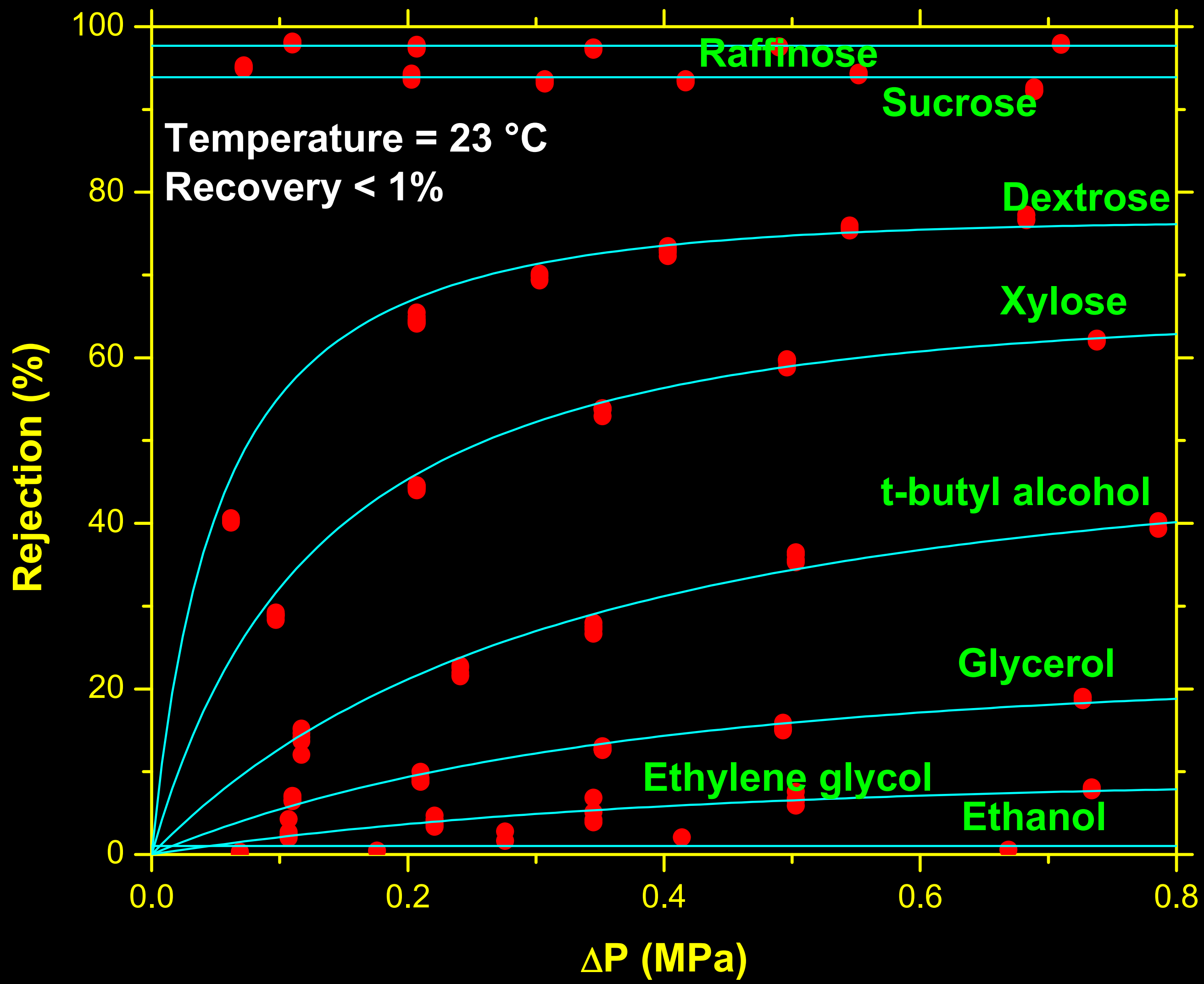
$$J_S = -P\Delta x\left(\frac{dc}{dx}\right) + (1-\sigma)J_V c$$ (Spiegler and Kedem 1966)

$$\text{Rejection} = 1 - \frac{C_p}{C_m} = \frac{\sigma(1-F)}{(1-\sigma F)} \qquad \text{where } F = \exp\left(-\frac{1-\sigma}{P}J_v\right)$$

$$\Delta P \to 0 \Rightarrow J_v \to 0 \Rightarrow F \to 1 \text{ and Rejection} \to 0$$

$$\Delta P \to \infty \Rightarrow J_v \to \infty \Rightarrow F \to 0 \text{ and Rejection} \to \sigma$$

Rejection – Transmembrane Pressure



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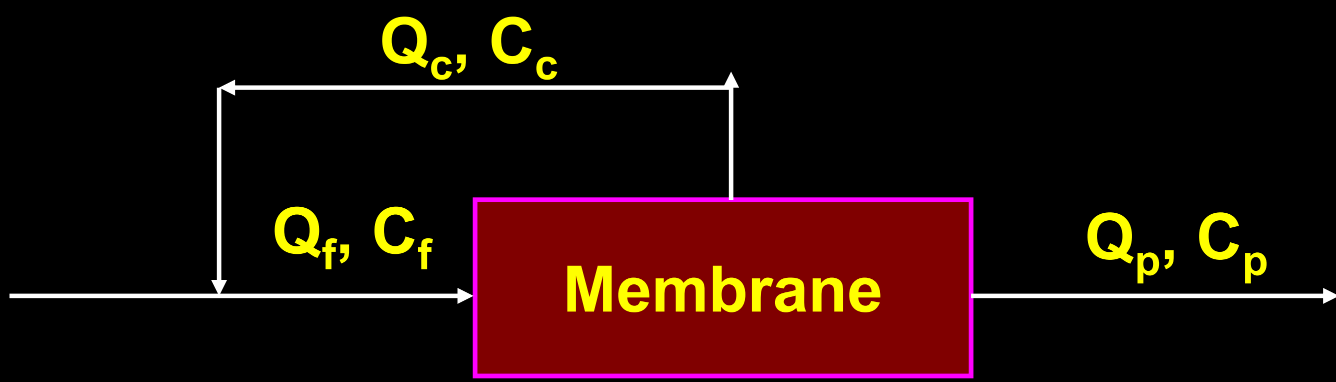

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$$\text{Note: } J_v \to \infty \Rightarrow \frac{1}{J_v} \to 0 \text{ (intercept)}$$

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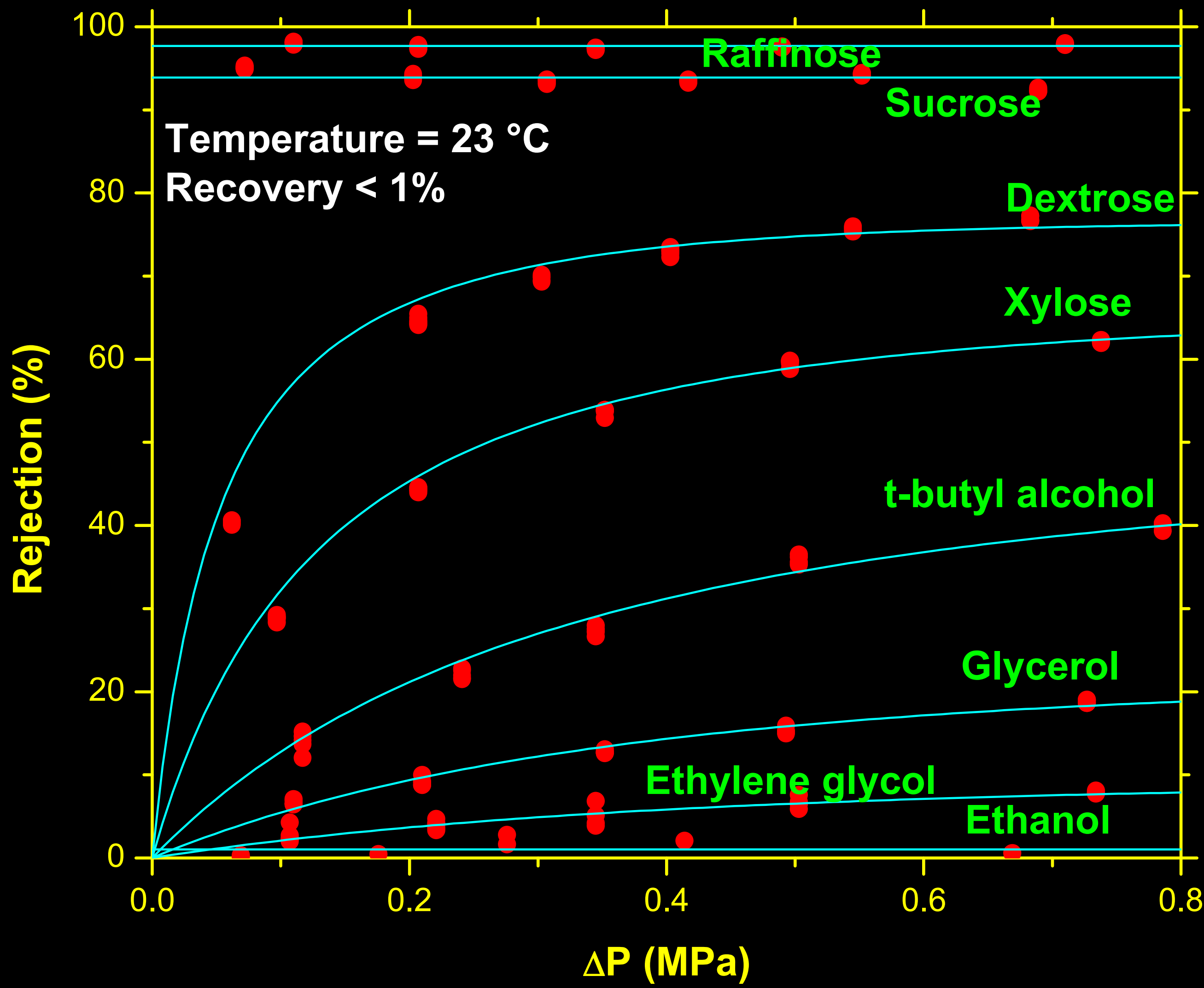
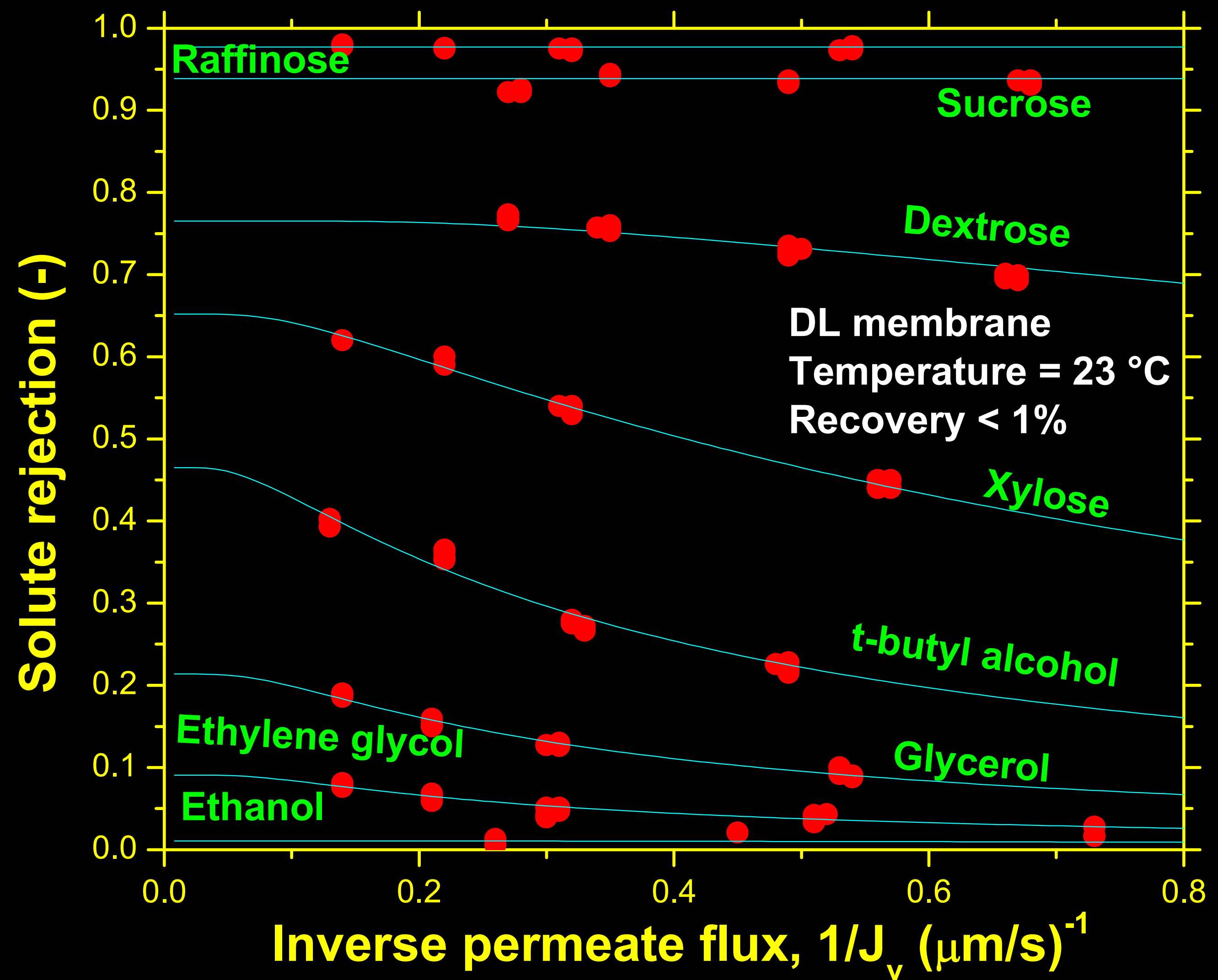


Rejection – Inverse Flux



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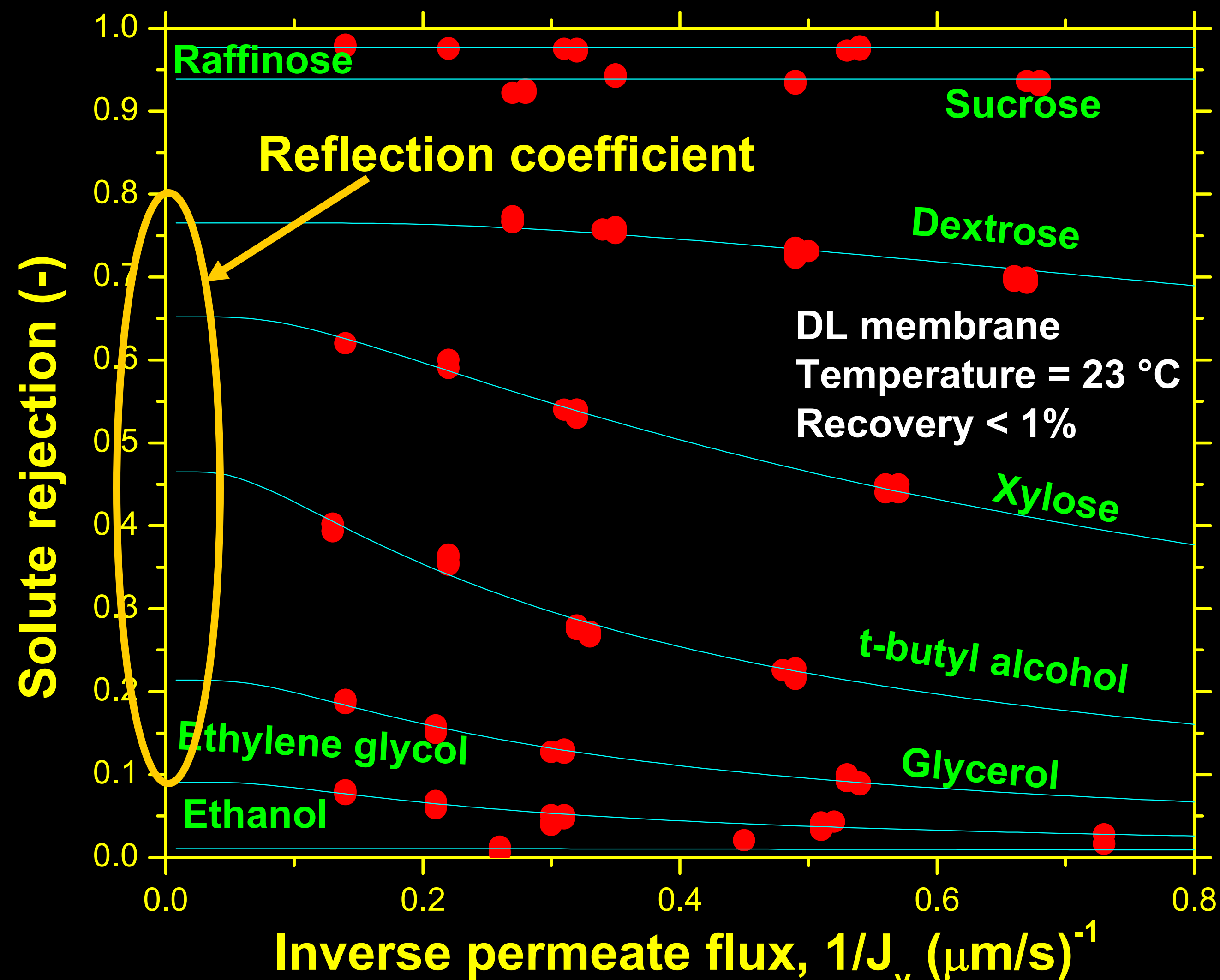

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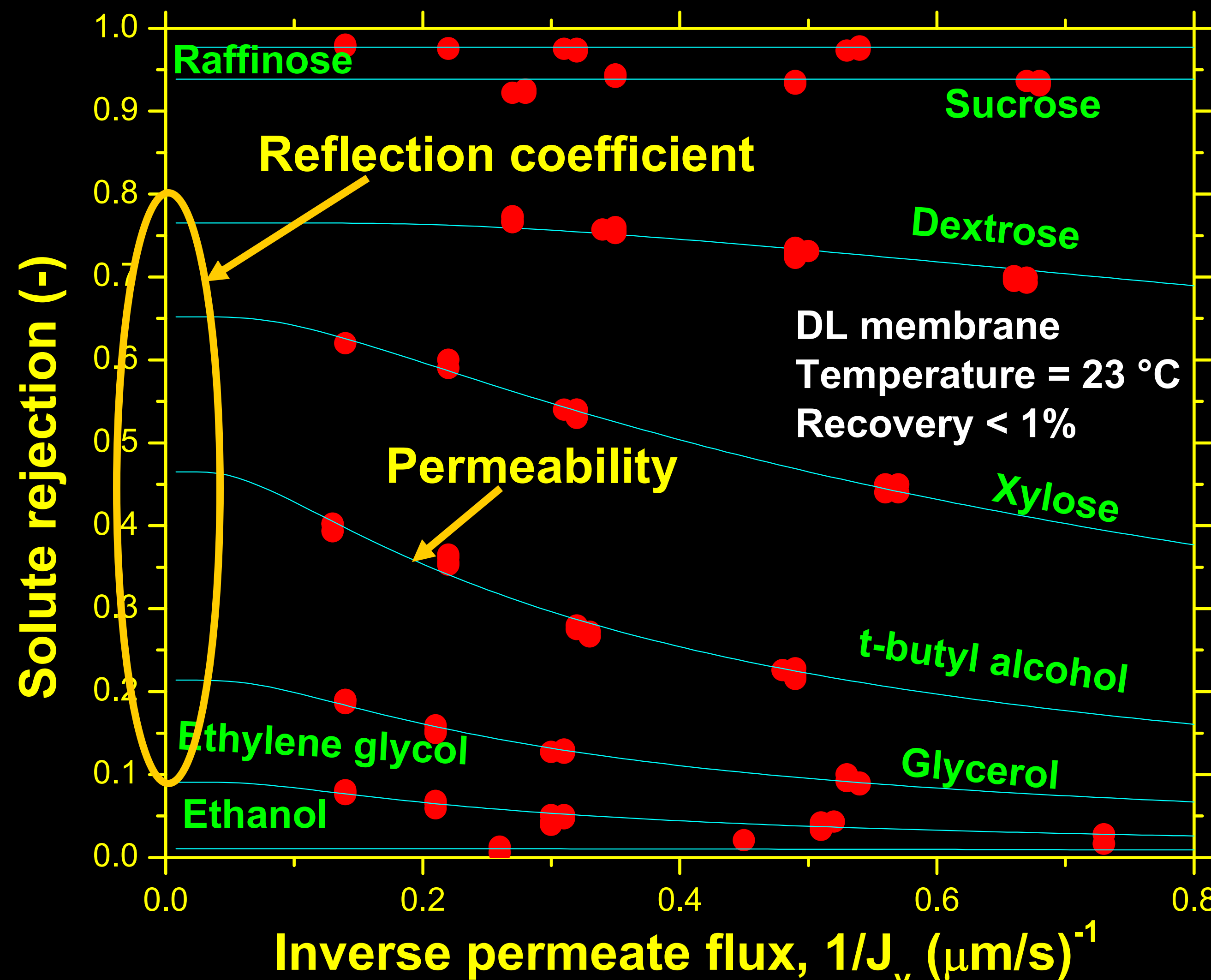


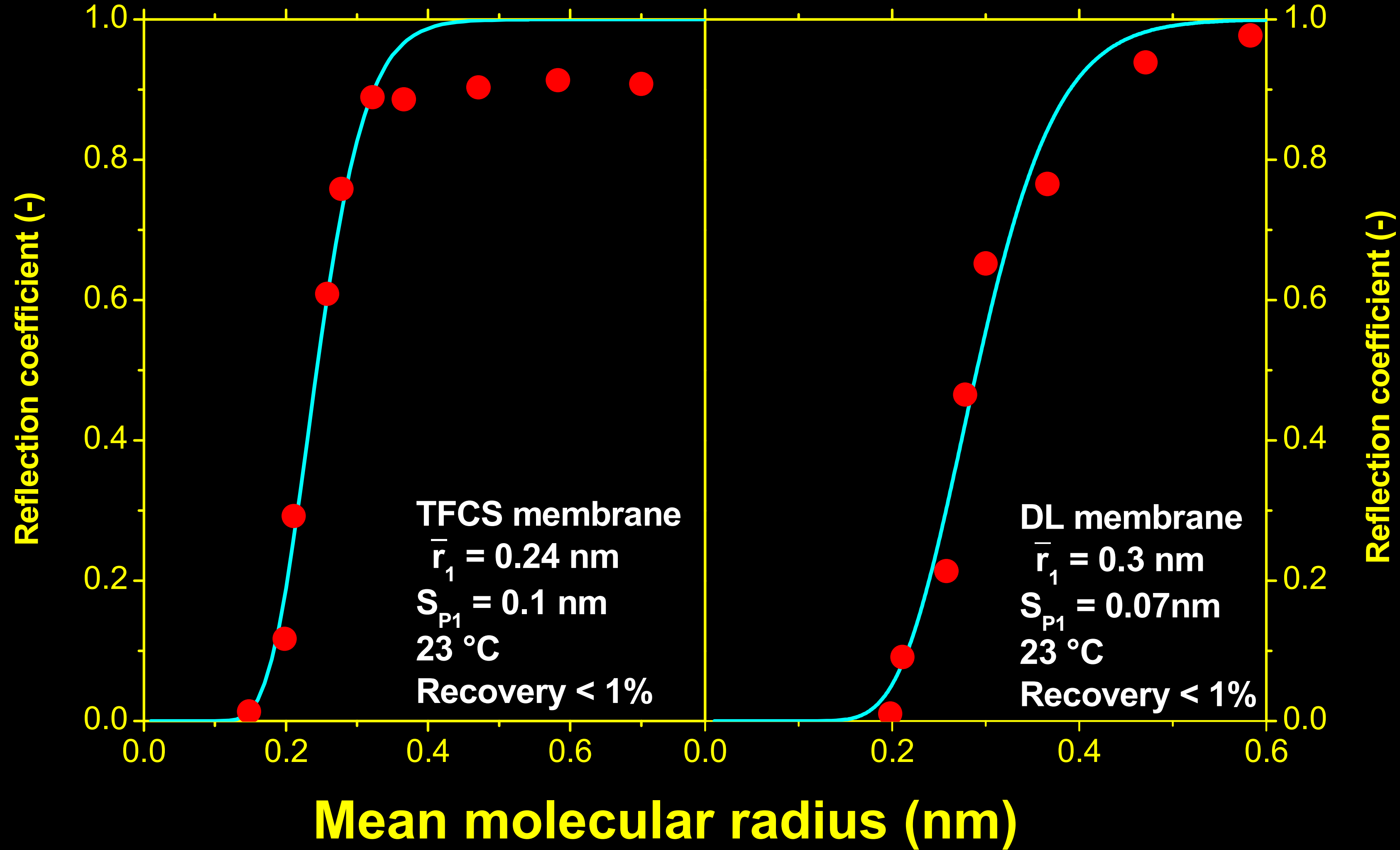
Lognormal Model

- Assumption of lognormal distribution of pore sizes
- No hydrodynamic lag involved

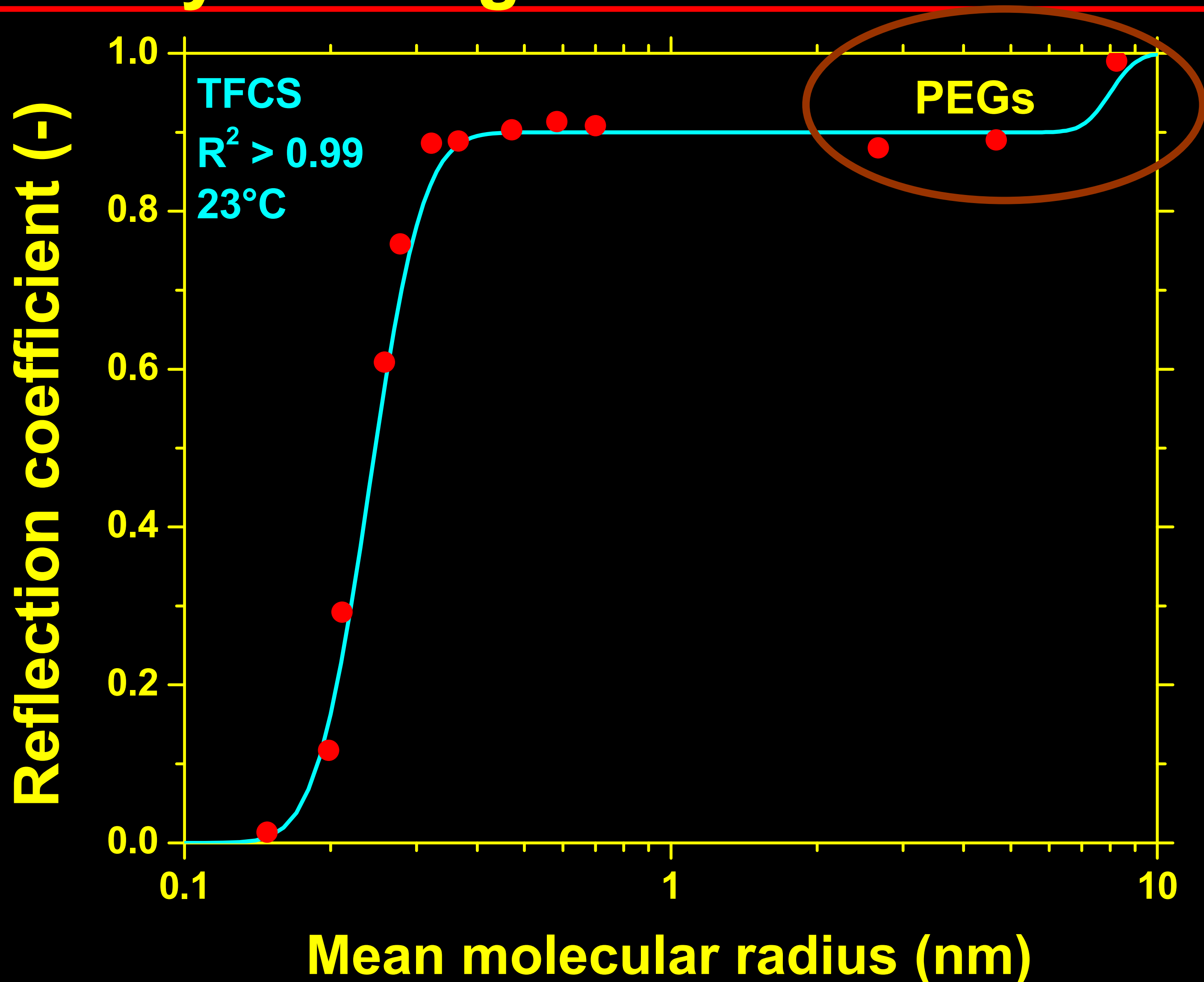
$$\sigma(r^*) = \int_0^{r^*} \frac{1}{S_p\sqrt{2\pi}}\frac{1}{r}\exp\left(-\frac{\left(\ln(r)-\ln(\bar{r})\right)^2}{2S_p^2}\right)dr$$

Rejection at $J_v \rightarrow \infty$

Lognormal Distribution



Purely Sieving Bimodal Distribution



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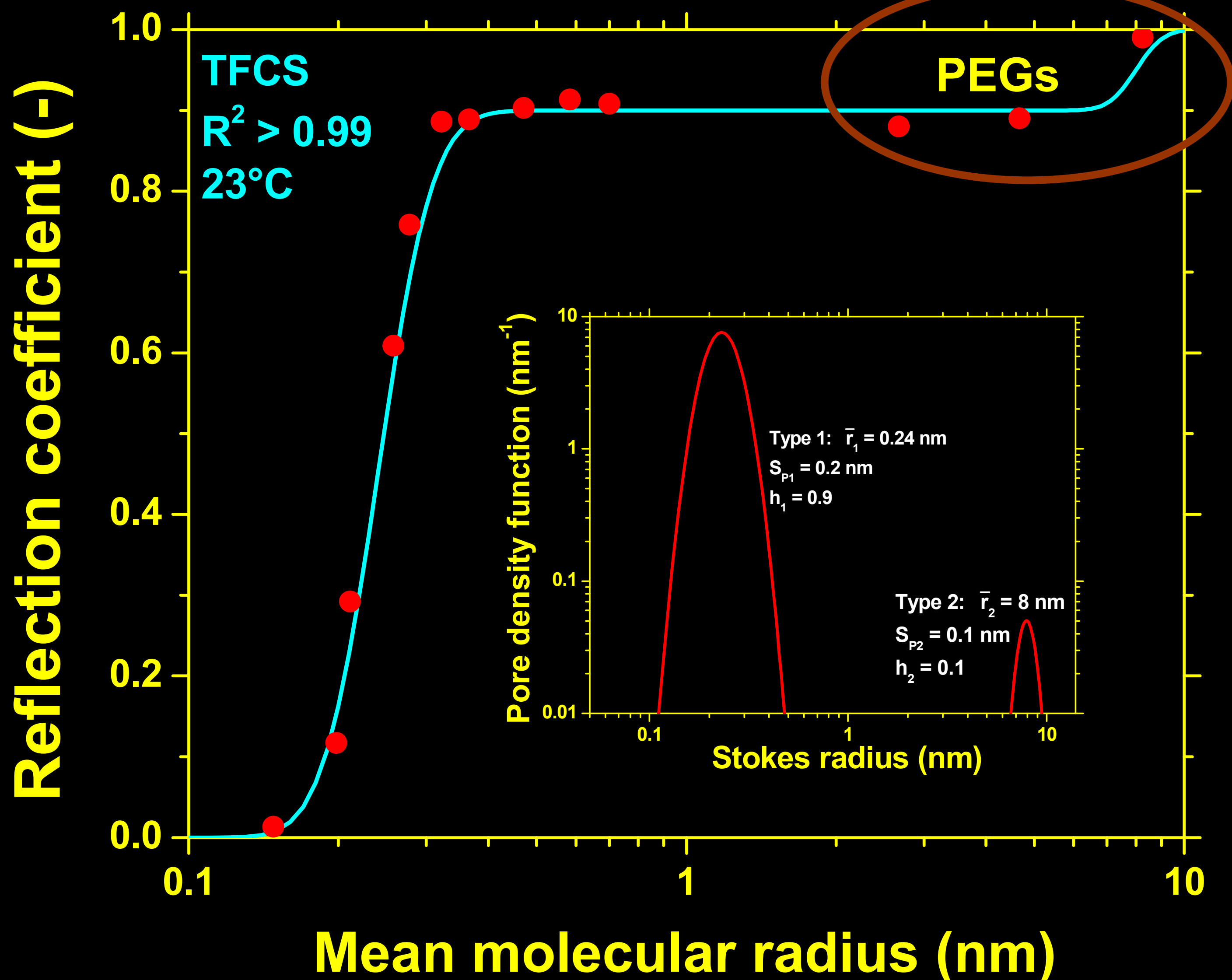
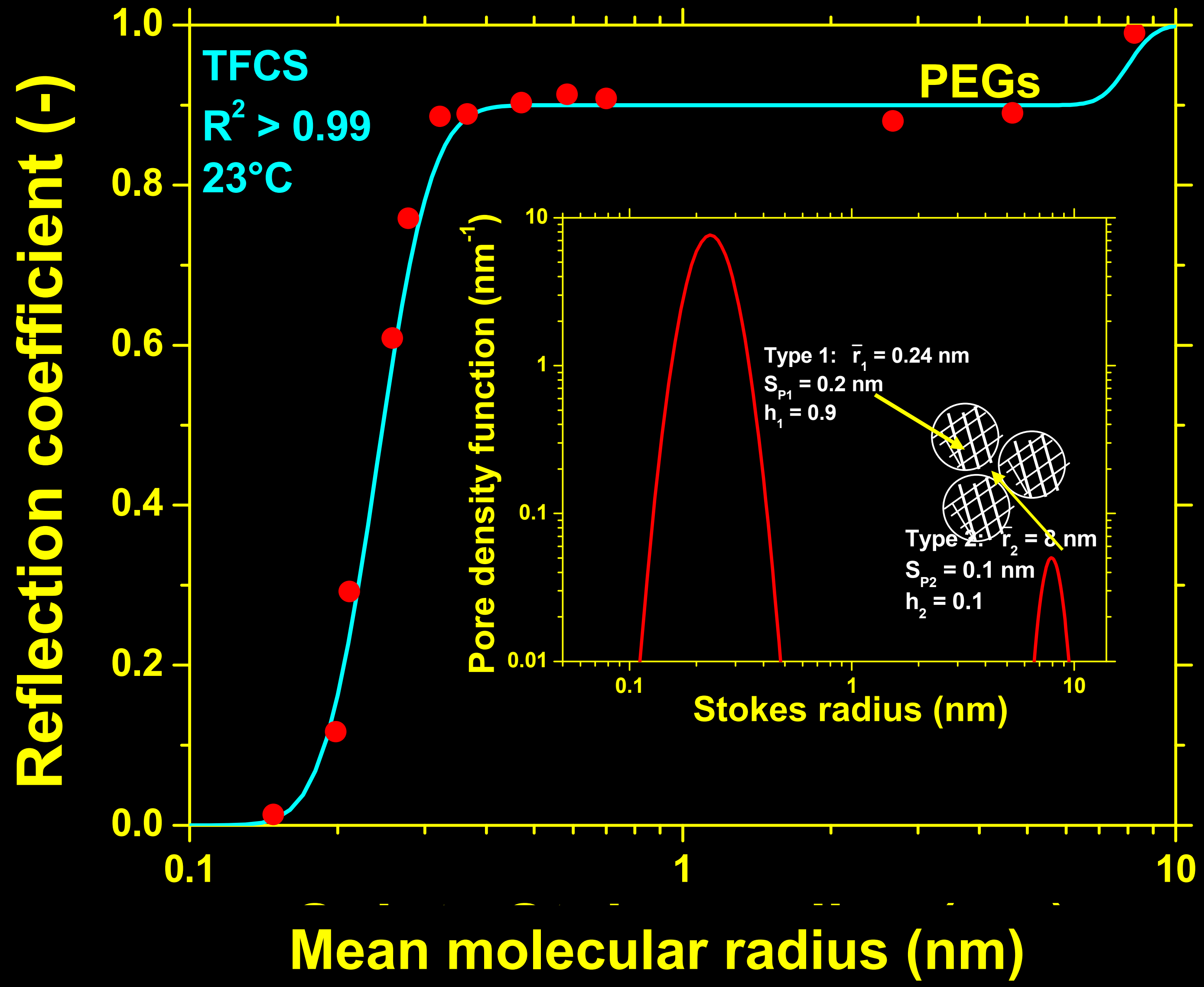
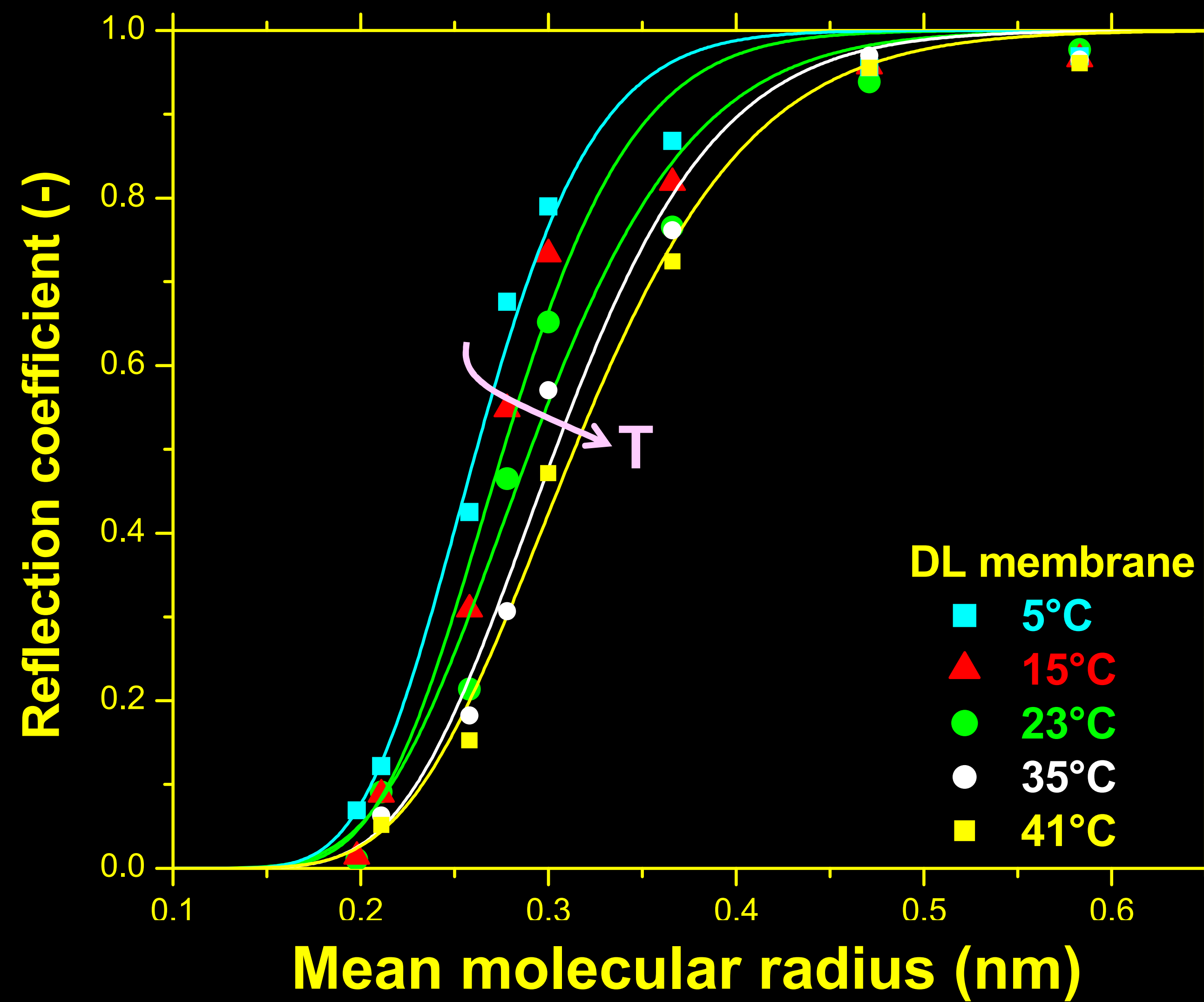


Purely sieving bimodal distribution



Temperature Effect on PSD



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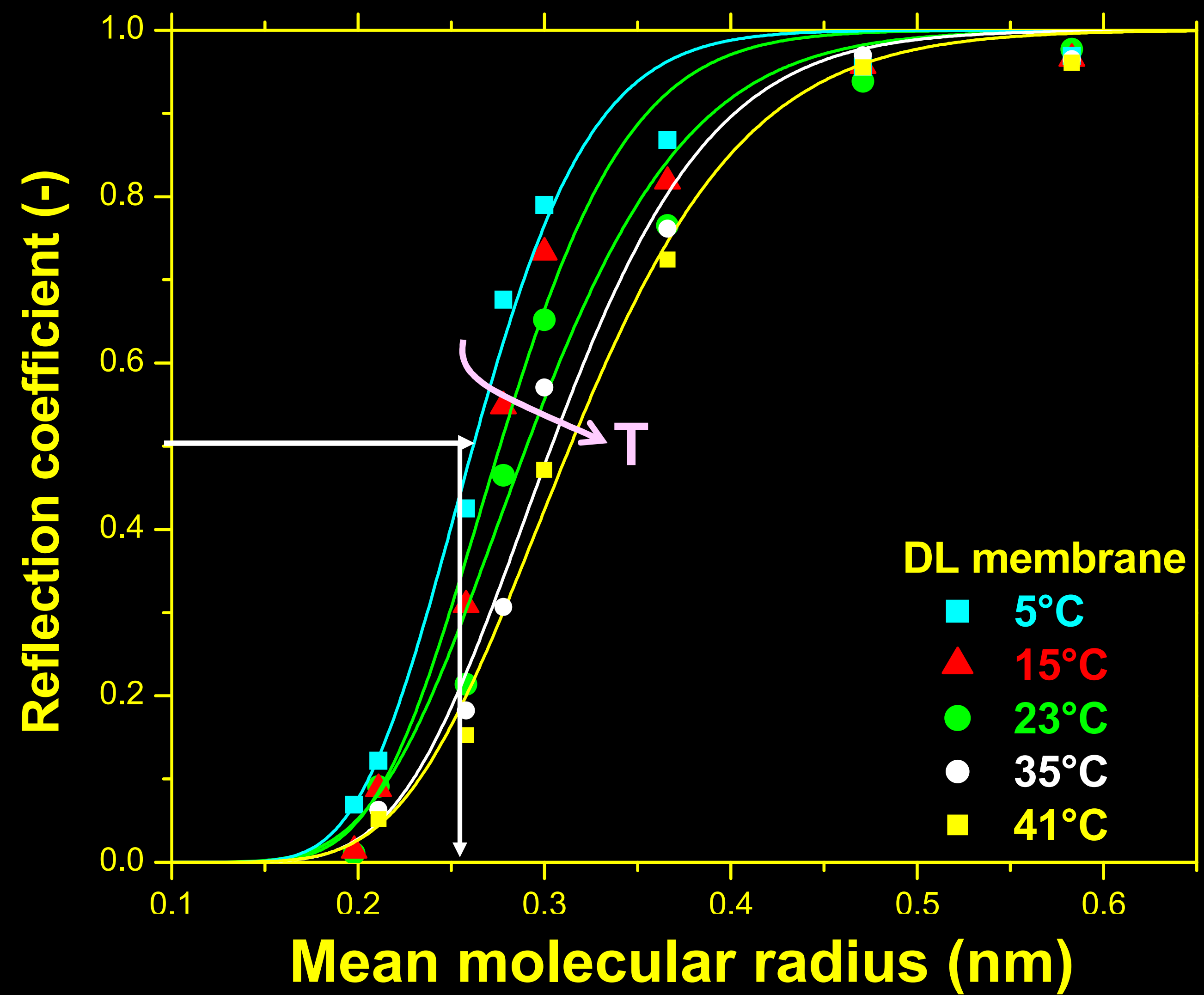
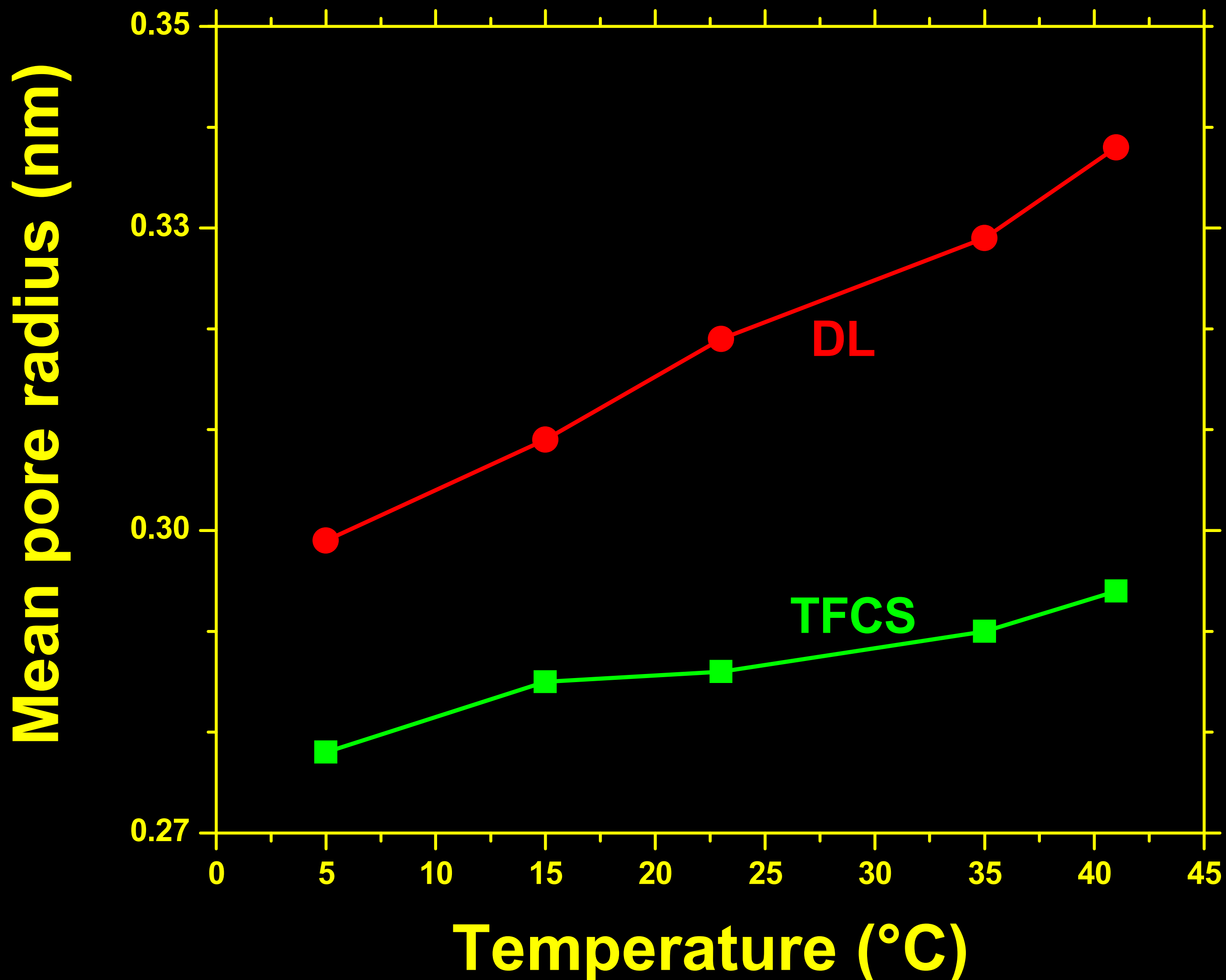


Increasing Mean Pore Radii



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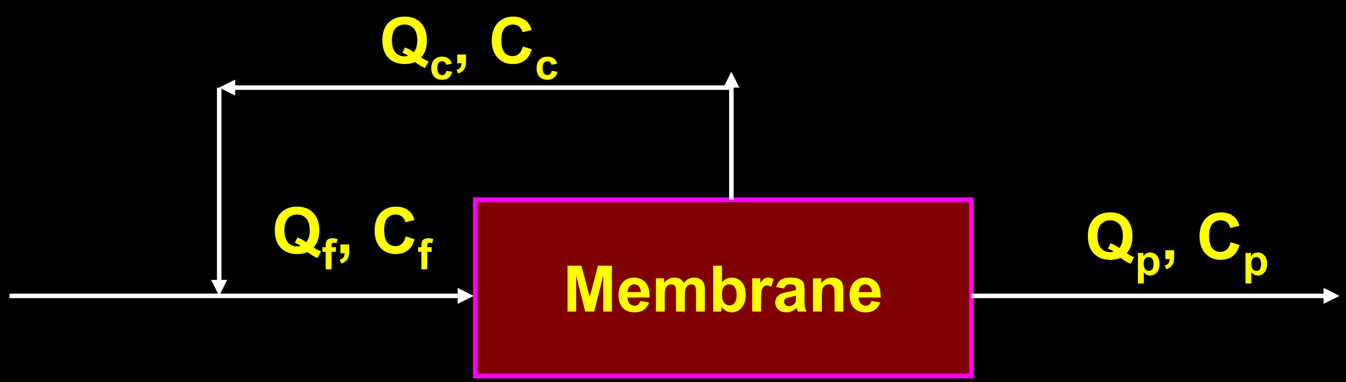

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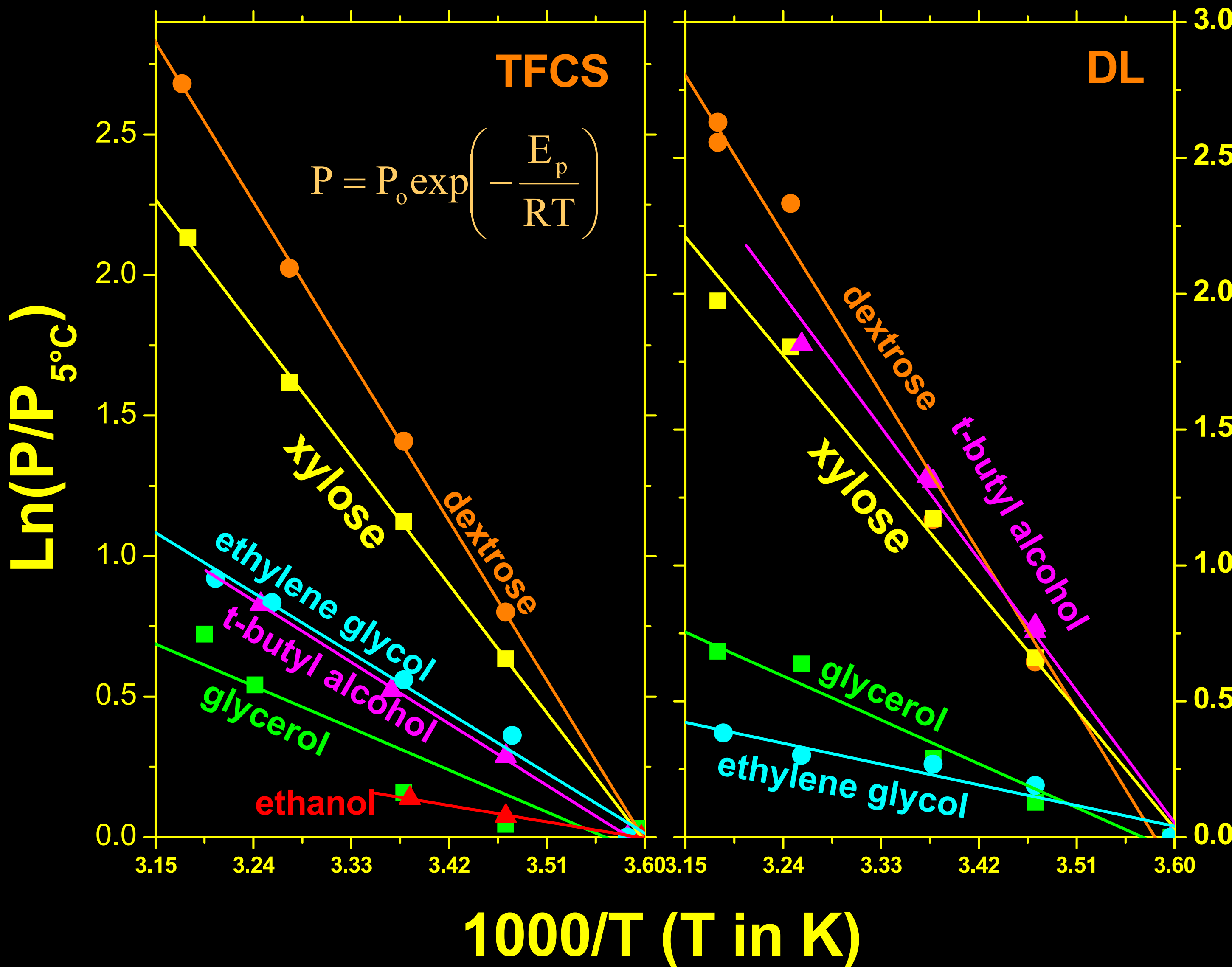
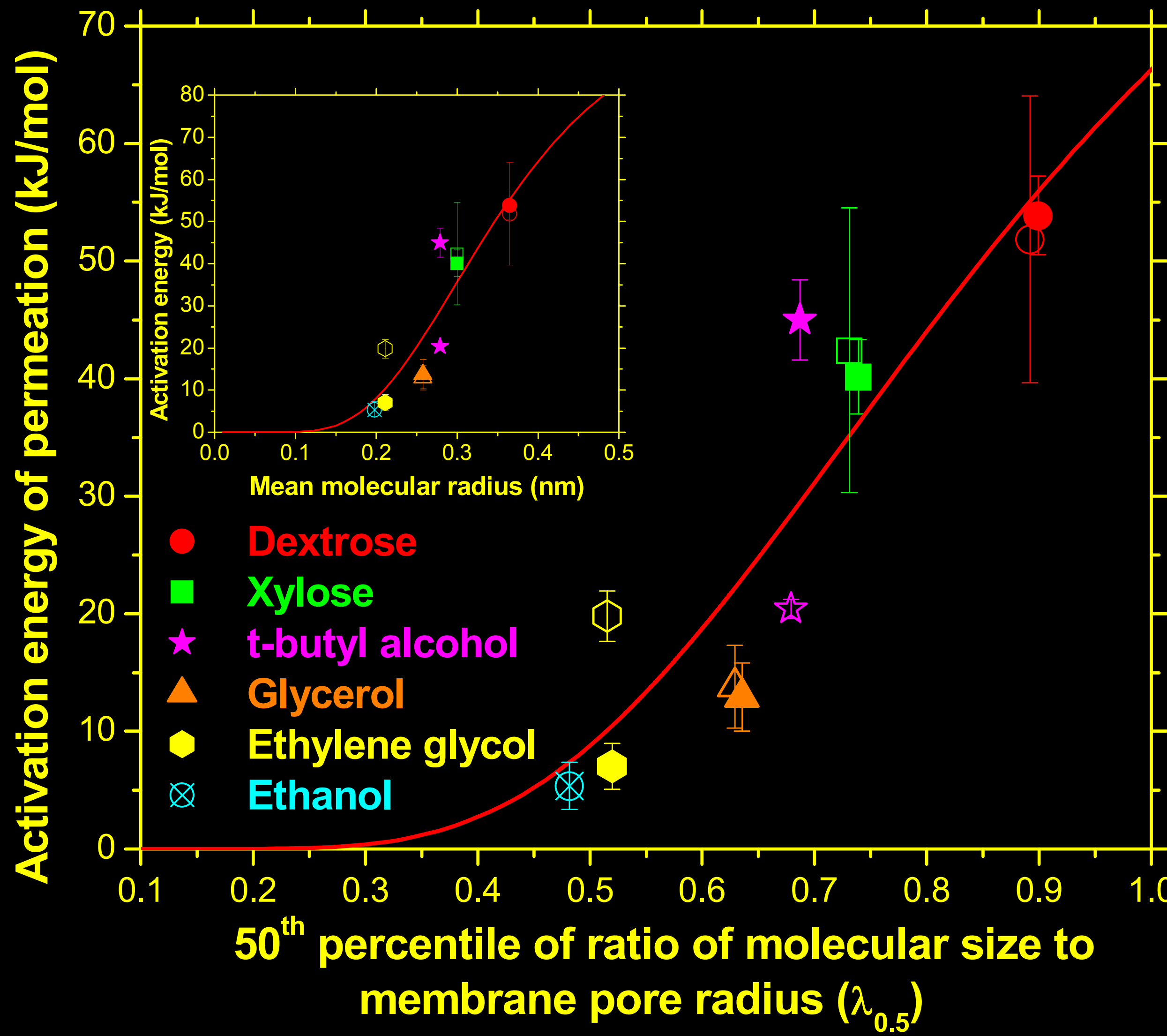
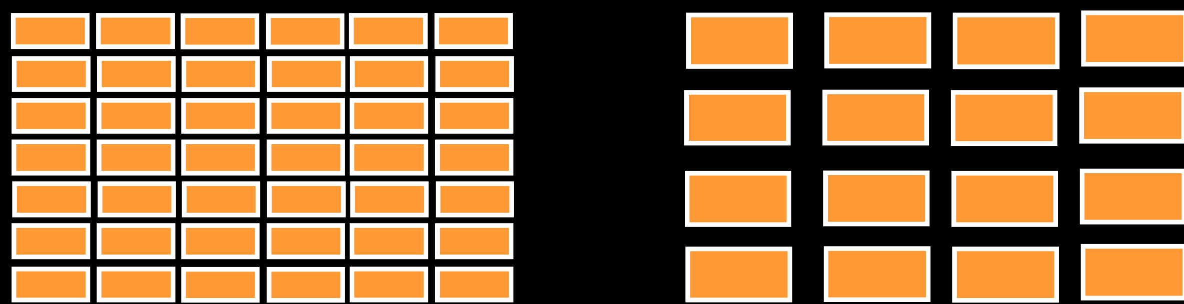
Arrhenius Relationship



Activation Energy – Mean Molecular Radius



Conclusion



Low Temperature High Temperature

With increase in temperature

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- **Arsenic passage↑ (*Waypa, et al. 1997*)**
- **Water permeability↑ (*Sharma, et al., 2003*)**

Lessons Learned!

- **NF membranes are <u>NOT</u> like RO membranes**
- **Because pore sizes are lognormally distributed, even a few large pores may determine membrane selectivity**
- **Need for a membrane specific temperature correction factor**
- **Rejection of larger size contaminant is more sensitive to temperature**

Peer Reviewed Articles

- **Temperature Effects on Sieving Characteristics of Nanofiltration Membranes: Pore Size Distributions and Transport Parameters.** ***JMS*** **(2003) 223, 69-87**

- **Temperature Effects on Morphology of Porous Nanofiltration Membranes.** ***ES&T*****, (2005) 39, 5022-5030.**

- **Temperature and Concentration Effects on Electrolyte Transport across Porous Nanofiltration Membranes.** ***JCIS*****, (2006) 298, 327-340.**

- **Frictional interpretation of thermodynamic transport parameters for porous nanofiltration membranes.** ***Journal of Water Supply: Research and Technology—AQUA Vol 55 No 7-8 pp 571–587***

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Questions!

Trussell
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