Removal of organic substances by RO and NF composite membranes: mechanism and limitations

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Outlook

- Problem: organic contaminants in water
- RO/NF as a potential solution
- Experiments:
  - ATR-FTIR
  - Retention in RO/NF tests
- Rejection mechanism
- Limitations of polyamide membranes
- Conclusions

Trace contaminants in water sources

- **U.S. Geological Survey** [Kolpin et al (EST, 2002)]:
  95 OWCs of 139 streams across 30 states during 1999 and 2000.

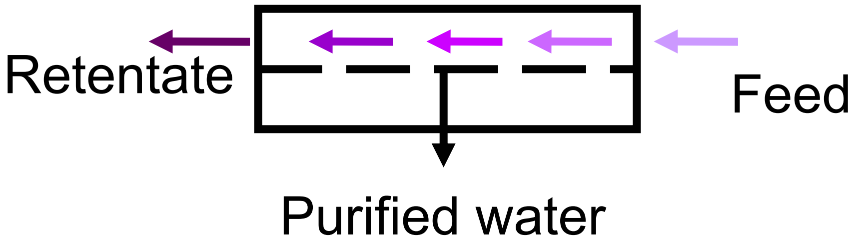
- 82 of the 95 OWCs found.

- The most frequently detected:

  coprostanol (fecal steroid)
  cholesterol (plant and animal steroid)
  N, N-diethyltoluamide (insect repellant)
  caffeine (stimulant)
  triclosan (antimicrobial disinfectant)
  tri(2-chloroethyl)phosphate (fire retardant)
  4-nonylphenol (nonionic detergent metabolite).

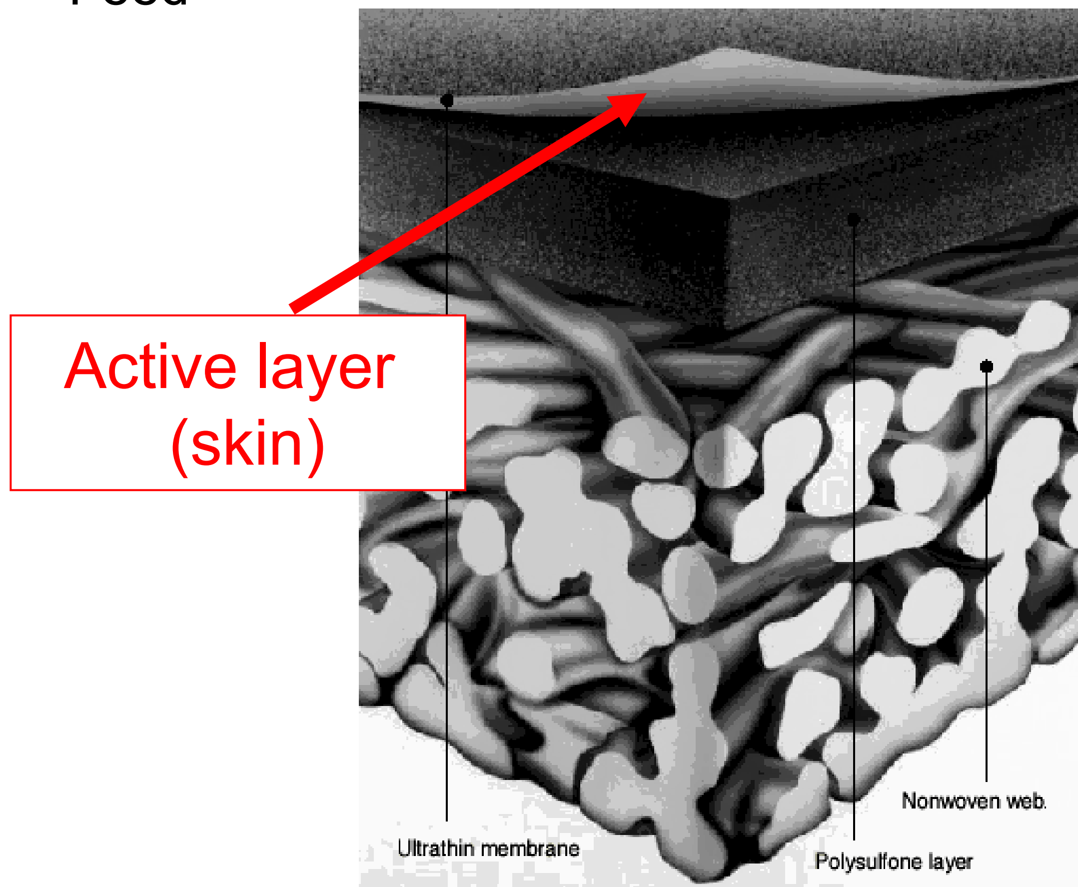
- Potential damages: endocrine disruption, toxicity …

Membrane filtration (RO and NF)



Membrane modules

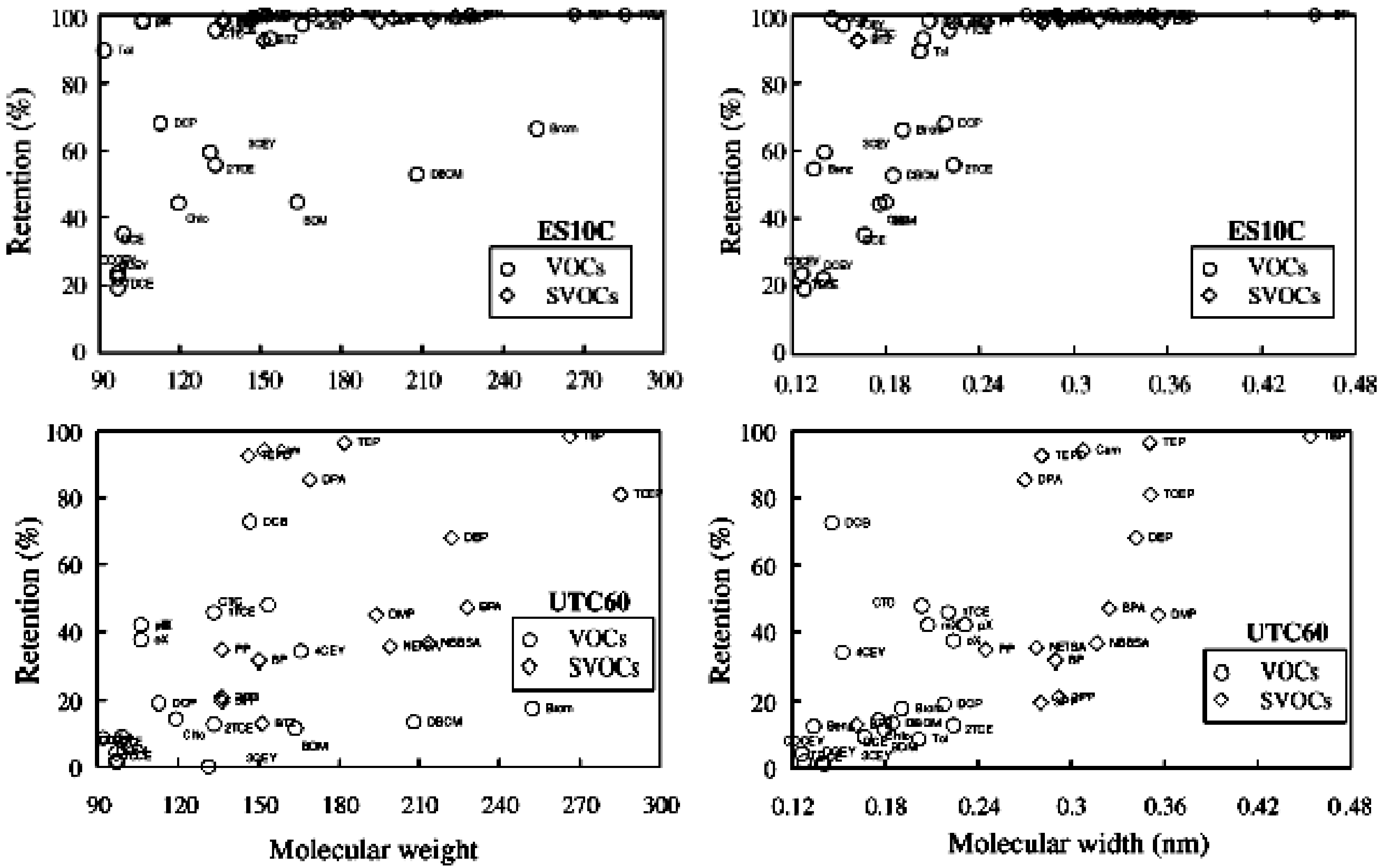
The structure of a composite membrane (TFC)



Freger
ISEEQS 2005

Retention of various compounds by RO/NF

Agenson et al. (JMS, 2003)

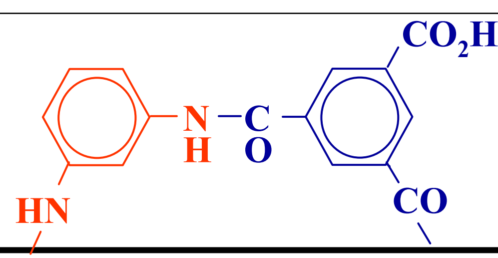
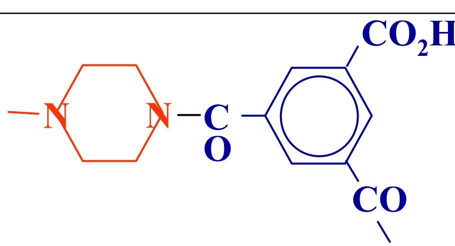


NF rejection of various compounds

Van der Bruggen et al., JMS, 1999

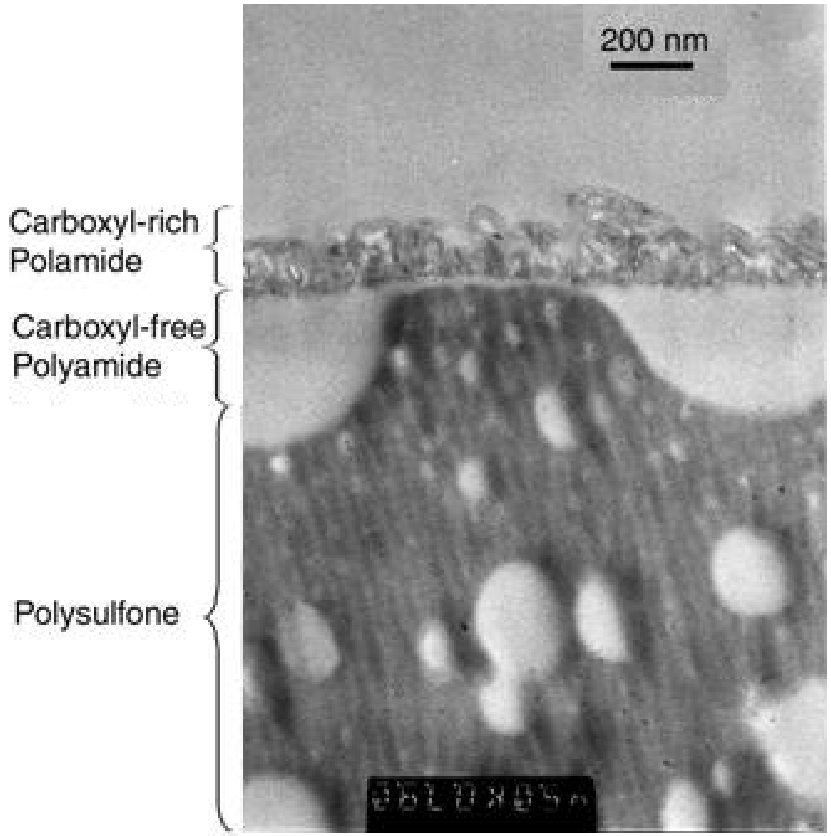
Molecule	MW	μ(Debye)	Retention (NF70)
Methanol	32.04	1.6	10.8
Ethanol	46.07	1.7	28.2
Isopropanol	60.11	1.8	76.4
Methylethylketon (MEK)	72.12	2.8	54.4
Ethylacetate	88.12	1.7	60.9
Toluene	92.15	0.4	77.6
Aniline	93.13	1.5	42.3
Phenol	94.11	1.7	47.7
Cyclohexanon	98.15	2.8	80.4
Methylmetacrylate	100.13	2.0	51.4
Isobutylmethylketon (BMK)	100.16	2.7	86.7
Benzonitrile	103.13	3.9	40.1
Benzylalcohol	108.15	1.7	76.7
Caprolactam	113.16	3.9	71.2
Nitrobenzene	123.11	3.8	22.4
Benzoic acid	122.13	4.2	69.3
Xylose	150.13	1.0	88.0

Two main types of TFC polyamide membranes

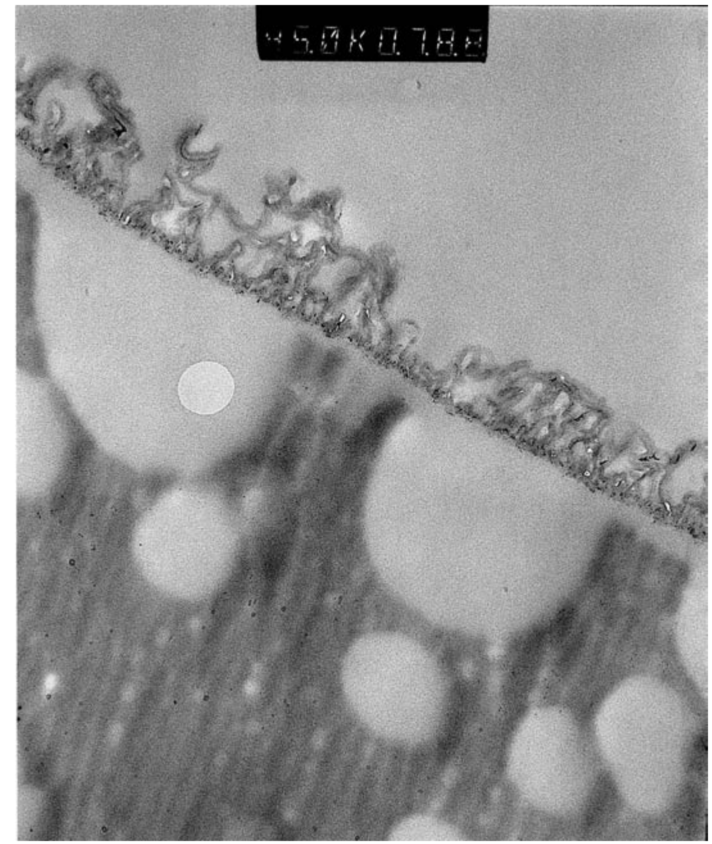
Typical characteristics	RO membranes (fully aromatic) all manufacturers	NF membranes (semi-aromatic) e.g., NF270 (Dow)
Thickness, nm	100-300	15-100
Roughness, nm	20-50	2-10
Salt rejection, %	>99	<90
Intrinsic permeability, nm*L/(m^2*h*bar)	~100	~300
Chemical Structure		

TEM observations: RO membranes

uranyl stain



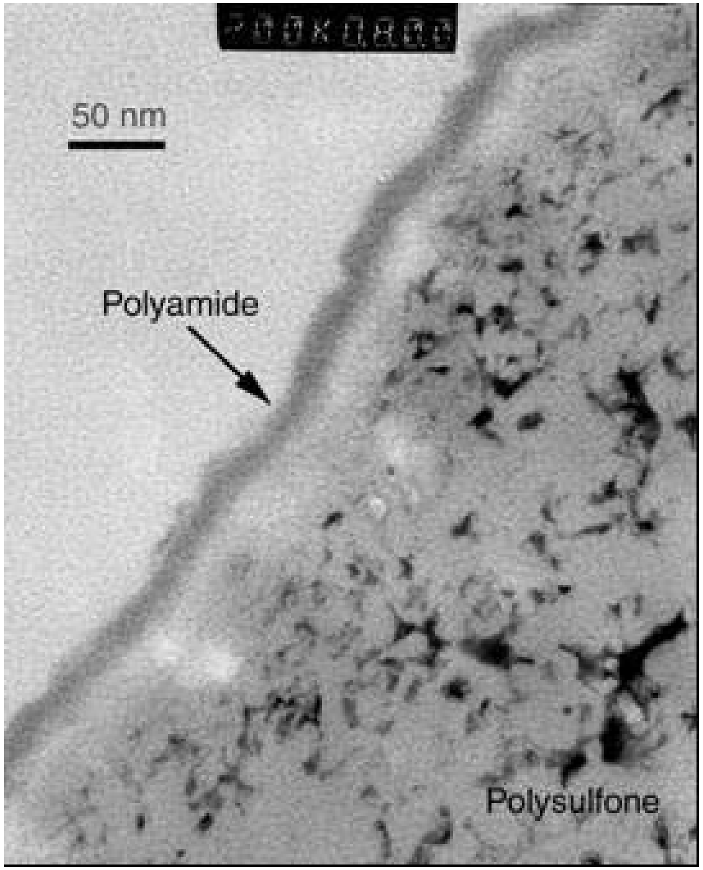
SWC1- high pressure RO membrane
A thick dense structure of polyamide



ESPA1- low pressure RO membrane
Thick but a very thin dense barrier !

NF membranes: TEM observations

uranyl stain



More permeable film - a nearly homogeneous dense structure

Permeation, sorption and diffusion

$$J = J_v C K(1-\sigma) + D K\, dC/dx$$

C – equilibrium concentration in solution;

K - partitioning coefficient between membrane and solution,

for pure size exclusion $K = (1-r/r_p)^2$;

D - diffusivity in the membrane (skin);

σ - reflection coefficient (extent of convective drag by water).

The ultimate goal: quantify the effects of ***K***, ***D*** and σ.

A particular goal: correlation of retention to the parameter ***K***, i.e., thermodynamic affinity of solute to polyamide.

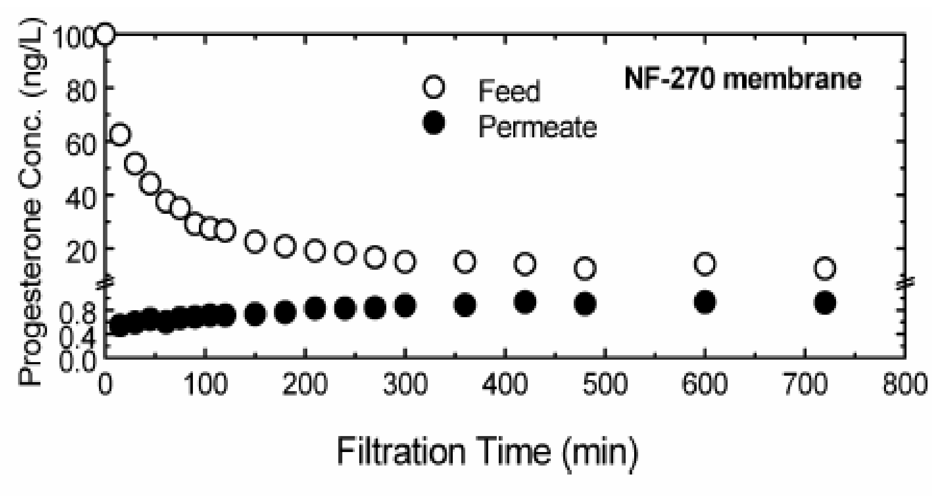
Experiments: (1) Filtration (retention), (2) Sorption (partitioning).

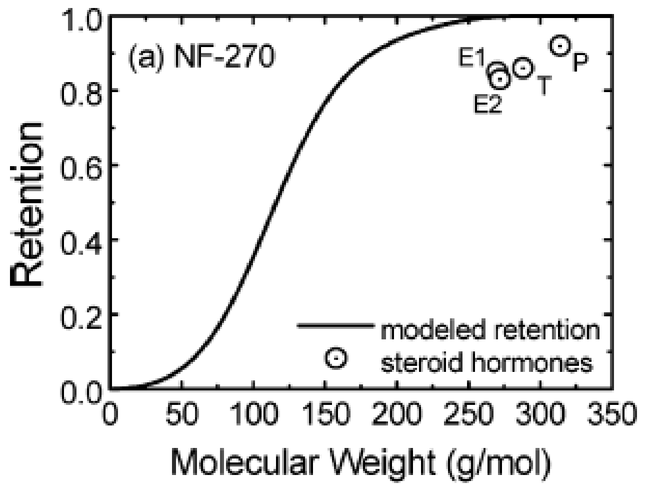
How to measure partitioning in polyamide?

1. Equilibration of a whole membrane with solution.
2. Closing material balance in batch filtration experiments.

The results of such measurements and modeling indicate that RO/NF separation is not just sieving and there is a significant sorption effect.

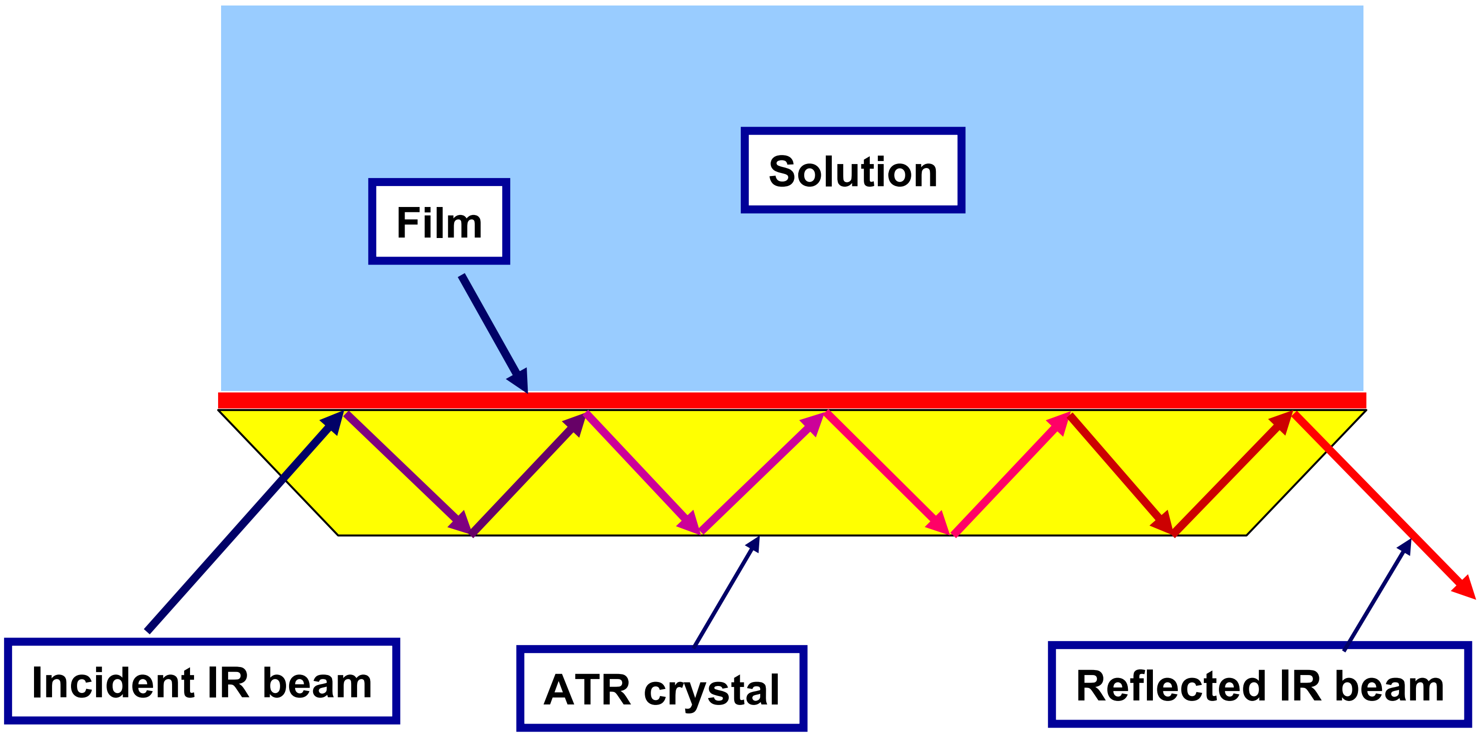
However, none of these approaches may distinguish sorption by the support, which may be very large.





Nghiem, Schaefer and Elimelech, EST, 2004

A new approach: partitioning in a polyamide film by ATR-FTIR



$$A = aC\left(1 - b + dK\right)$$

$$b, d = t_{film} f\left(n_{film}, n_{sol}, n_{cryst}, \lambda, polarization\right)$$

SEM/ellipsometry and AFM results

Freger, ES&T, 2004, Ben-David et al. , 2005

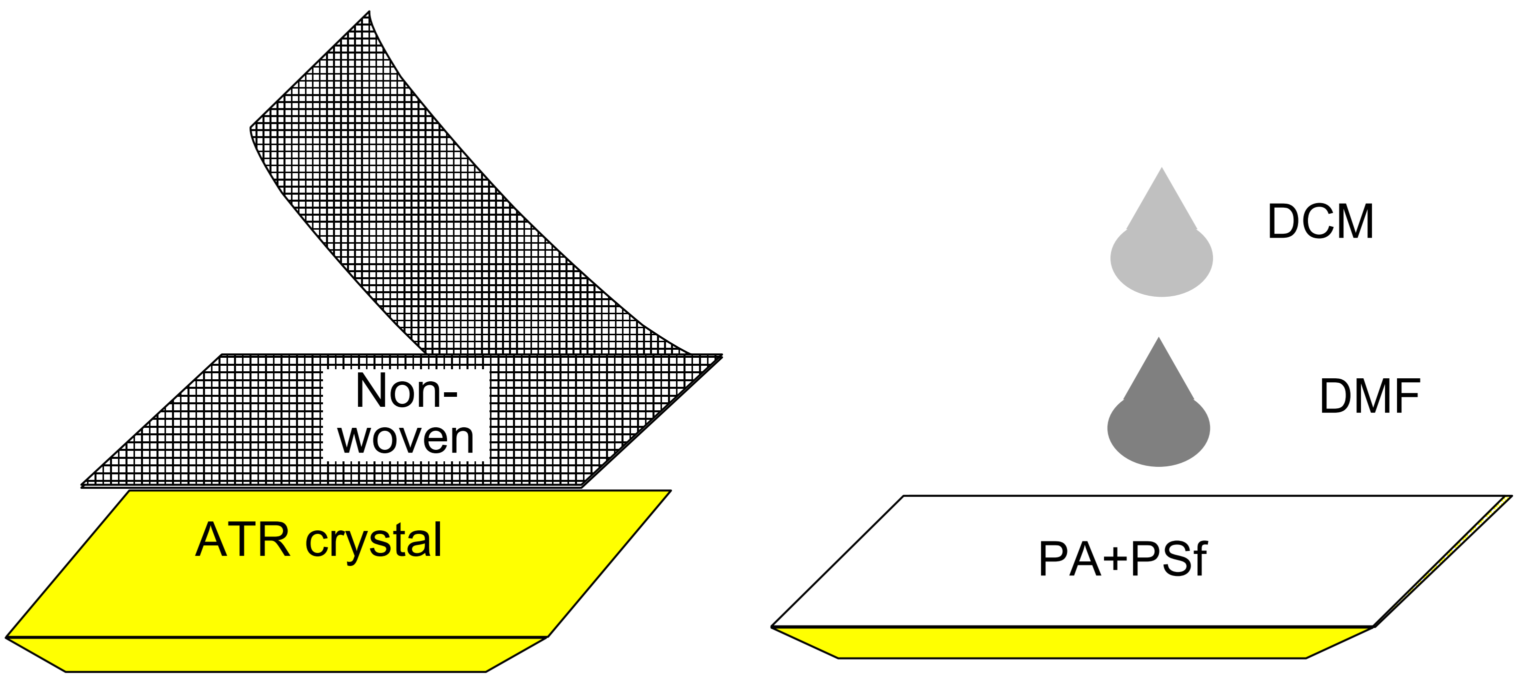
Membrane	Type, manufacturer	Average effective thickness, nm	Degree of swelling, %
SWC1	high pressure RO, Hydranautics	96±30	7.3 ± 6.5
ESPA1	low pressure RO, Hydranautics	184±23	6.0 ±1.1
NF-200	NF, Dow-Filmtec	29.5±5.5	20 ±5

For a dry film n_{film} = 1.70 (both RO and NF).

For a swollen film n_{film} may be calculated from swelling and void fraction.

Sample preparation for ATR measurements

1st stage 2nd stage



Organic solutes used in this study

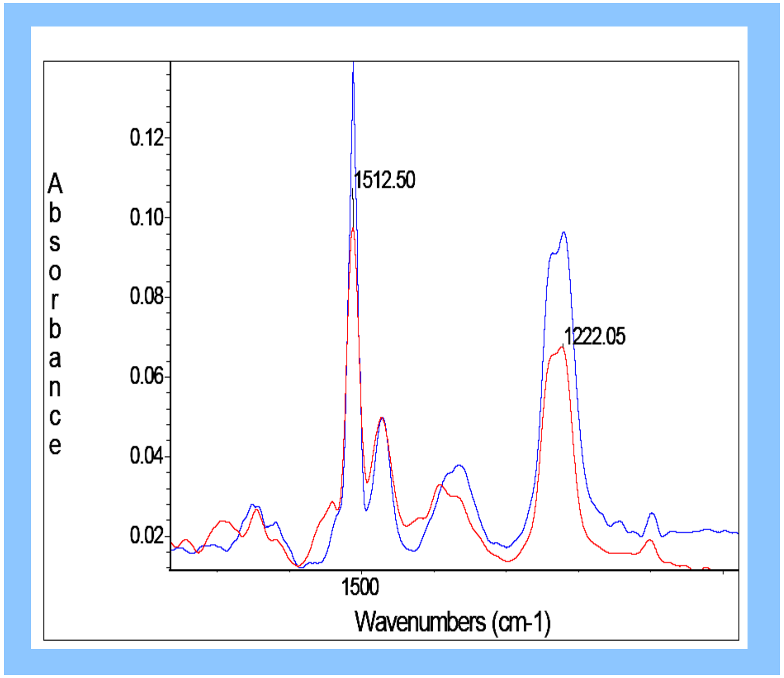
3 groups of solutes:

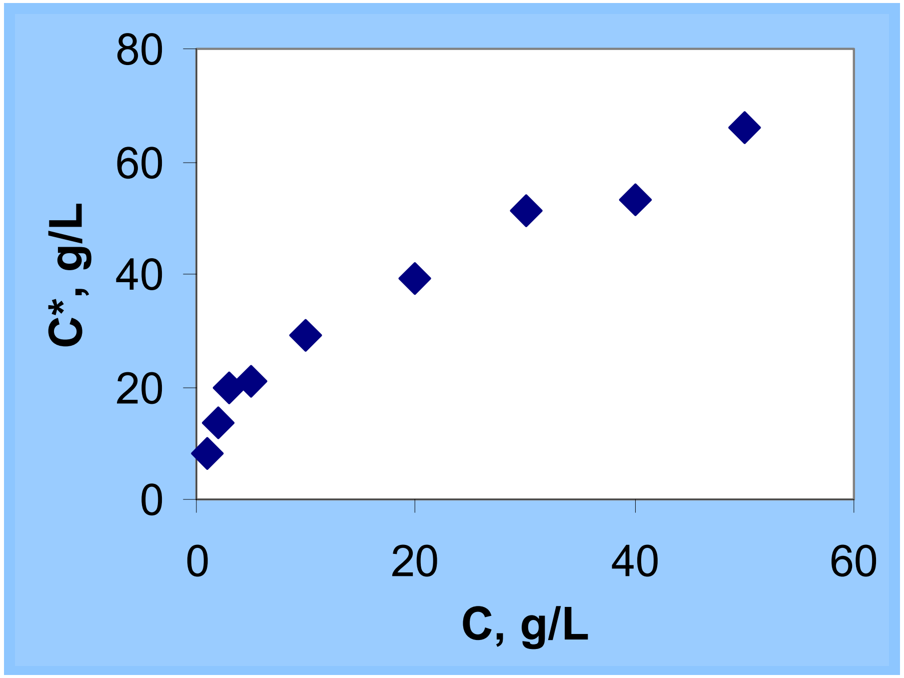
1) Mononuclear aromatics (similar size, different chemistry)
   - Aniline (amine)
   - Hydroquinone (diphenol)
   - Benzyl alcohol

2) Low *n*-alcohols (increasing size, decreasing polarity)
   - Methanol to Pentanol (C1 to C5)

3) Low polyols $C_nH_{n+2}(OH)_n$ (increasing size, similar high polarity)
   - Methanol to Meso-erythritol (C1 to C4)

Example: hydroquinone in ESPA1





Typical spectra
with and without film
(20 g/L HQ)

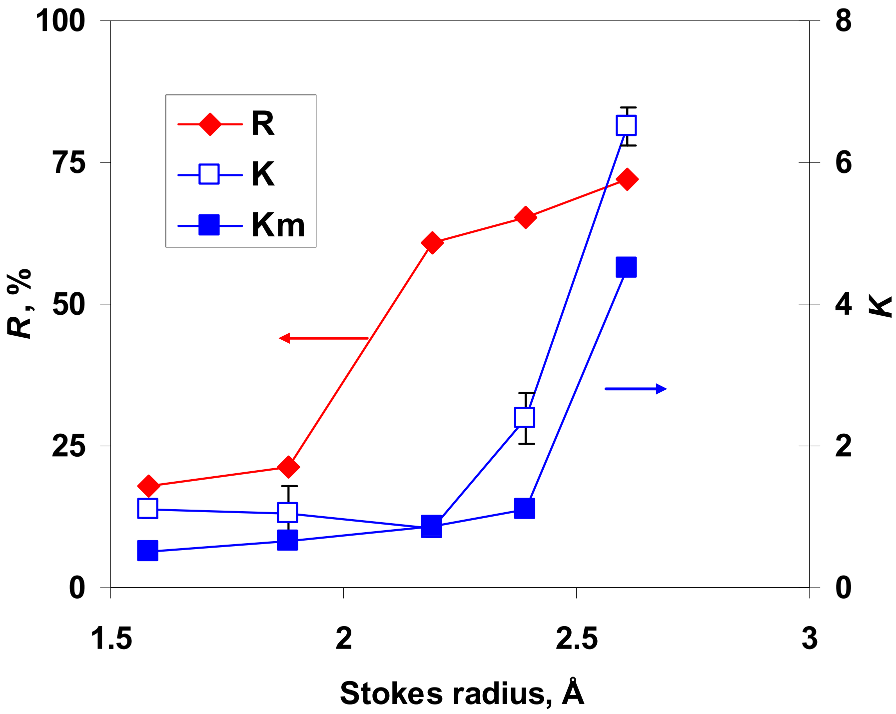
A calculated
isotherm for HQ

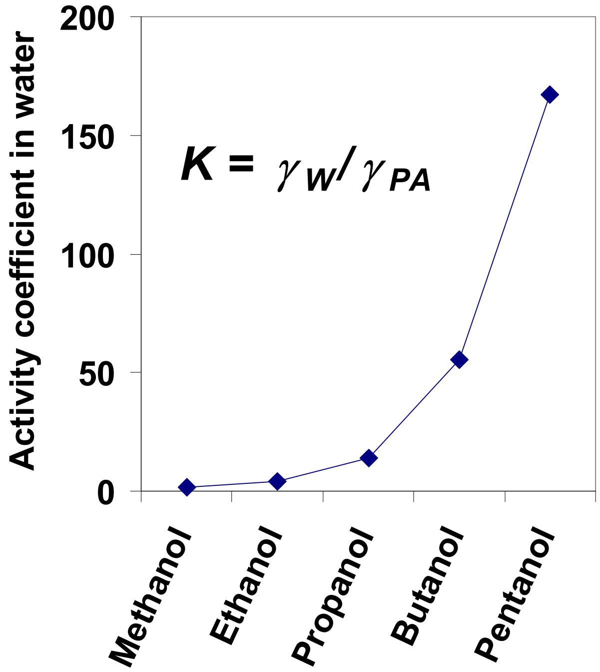
Partitioning and rejection of small aromatics

Solute	Stokes radius, Å	ESPA1		NF-200	
		Rejection, %	$K(K_m)$	Rejection, %	K_m
Hydroquinone	2.12	63	4(1.3)	20	23
Aniline	2.61	76	4(3)	22	6
Benzyl alcohol	2.87	45	6(2.4)	15	3.4
Urea	1.66	-32	0.5(0.5)	-9.5	0.6
Swelling (water)	0.88	–	0.06	–	0.20

Difficult to observe any trend for chemically different solutes

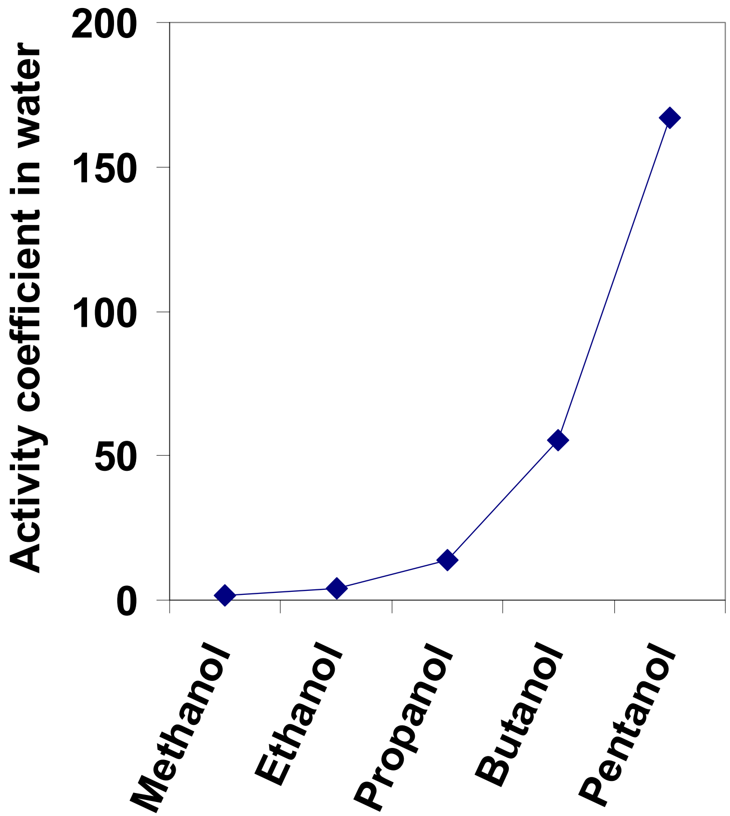
Partitioning and rejection of alcohols - RO





K grows with decreasing polarity of alcohols (solubility in water) and counterbalances the increase of rejection with size.

Partitioning of alcohols in RO polyamide: thermodynamics

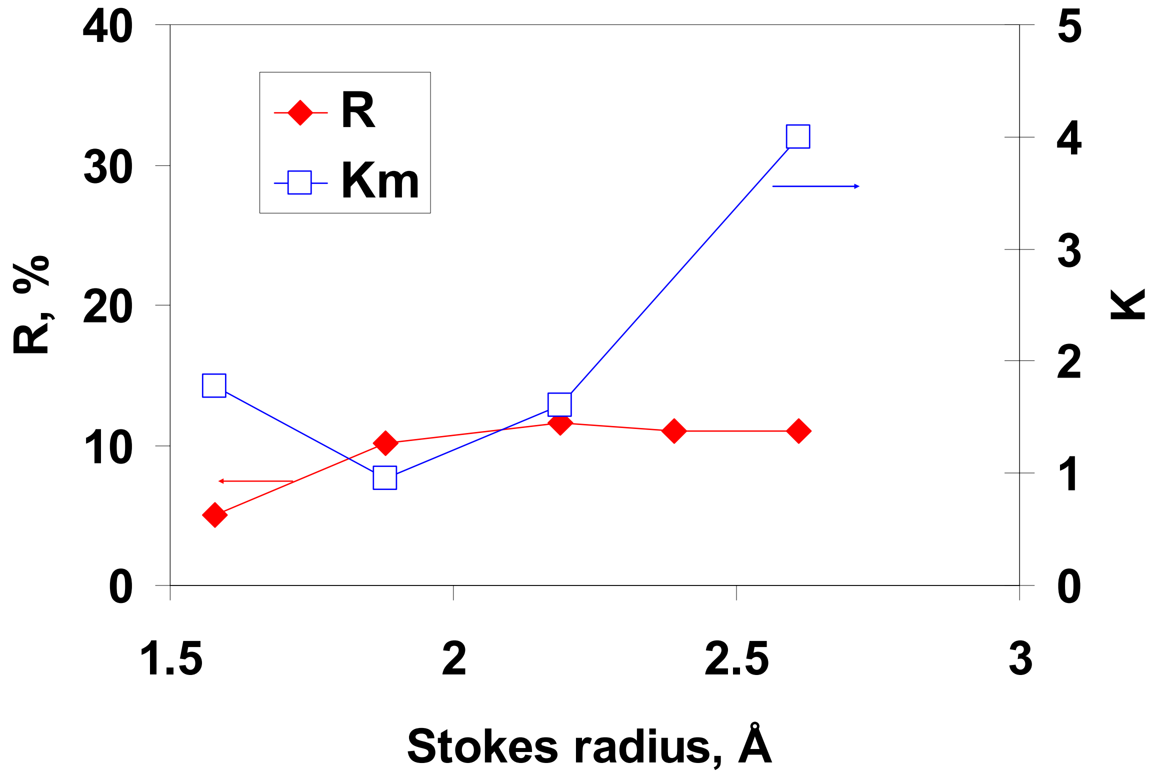


Substance	Solubility parameter δ, $(MPa/m^3)^{0.5}$
Methanol	29.7
Ethanol	26.0
n-Propanol	24.4
n-Butanol	23.3
n-Pentanol	22.3
Polyamide	23

$$K = \frac{\gamma_W}{\gamma_{PA}}$$

$$\gamma_{PA} = \frac{V_m}{RT}\left[(\delta_{alc} - \delta_{PA})^2 + \mathbf{steric}\right]$$

Partitioning and rejection of alcohols - NF

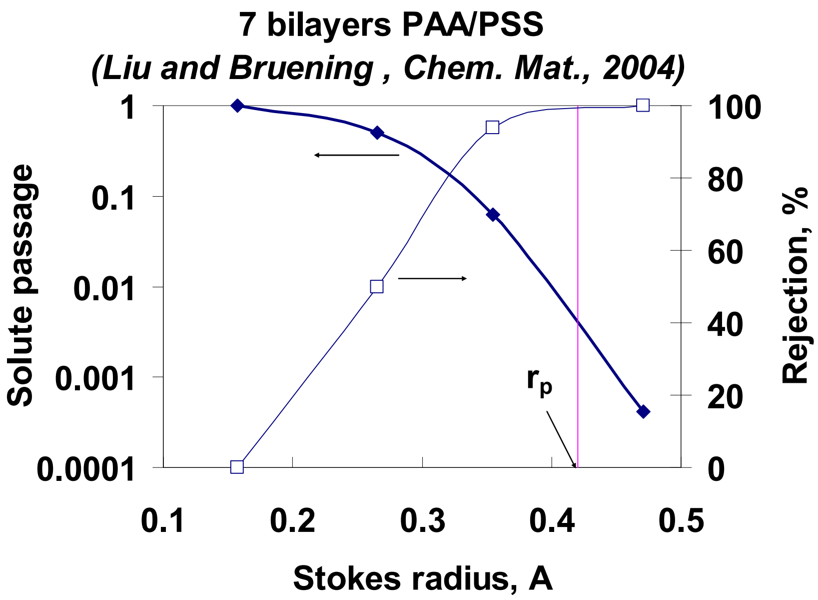


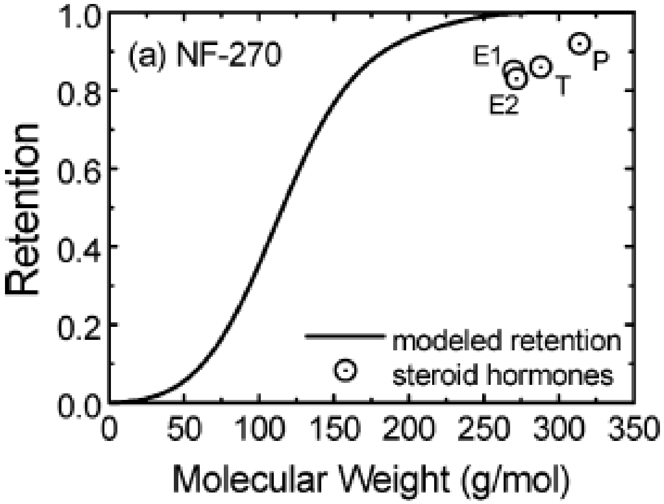
The same trend as for RO: the 2 effects combine.

How to assess the steric effect ?

Assessment of size exclusion in RO/NF

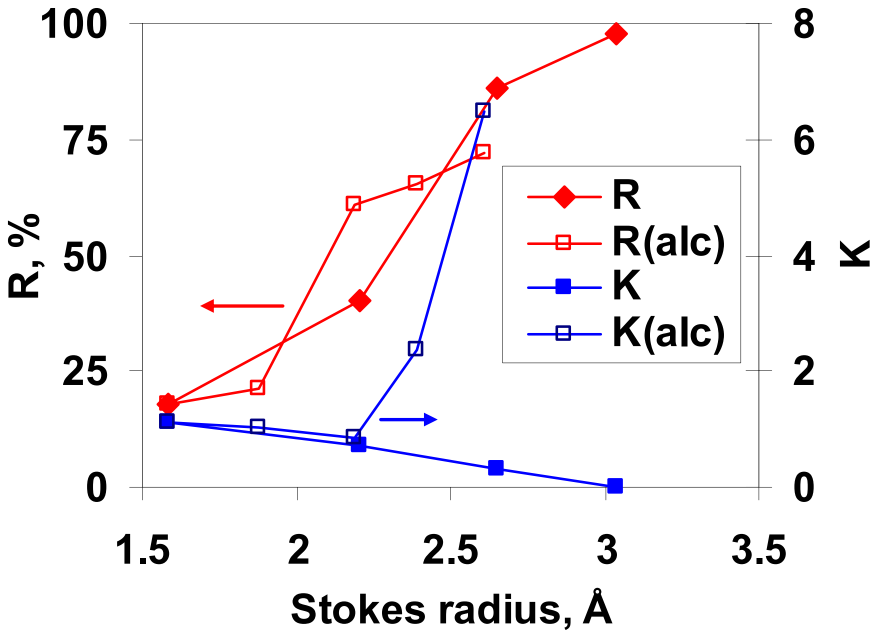
- Polyols/sugars were suggested for examining the effect of molecular size on rejection.

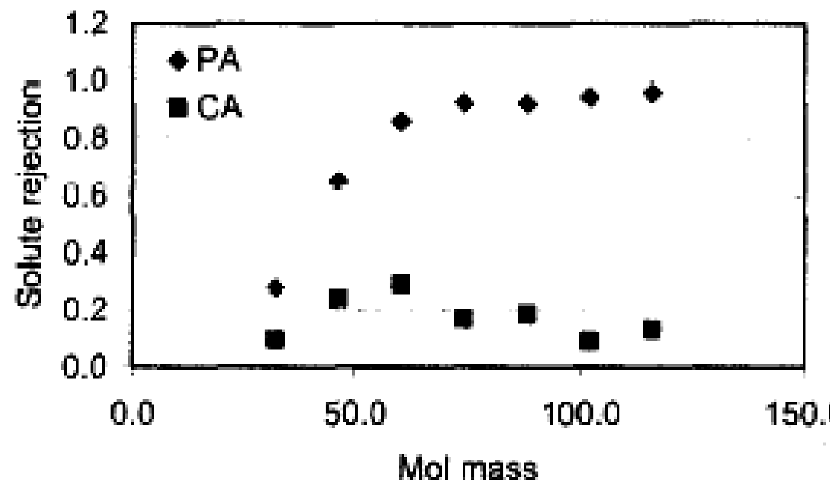




- A similar idea could be employed for steric effect in partitioning

Polyols vs. *n*-alcohols: RO





Shutte, Deslination, 2003

The monotonous effect of size on ***K*** is clearly seen for polyols.

For alcohols the effect of hydrophobicity is superimposed on the size effect and dominates for ***r*** > 2.2 Å.

As a result, the rejection of large alcohols is lower than for polyols.

Polyamide membranes: limitations

Unique properties crucial for good salt removal:

- polarity (hydrophilic-hydrophobic balance, H-bonding)
  - mildly hydrophilic (H-bonding, some charge) for high water flux
  - mildly hydrophobic for good ion exclusion
- molecular packing and heavy crosslinking (small pore size, limited swelling, high strength and rigidity)

<u>The polyamides are not necessarily optimal for removal of organics</u>. Large thermodynamic mismatch ($\delta_{org} \neq \delta_{mem}$) is required to minimize partitioning. Thus more hydrophilic membranes might have an advantage along with a potentially higher water flux.

Conclusions

- Strong partitioning in polyamide negatively affects the rejection of organic contaminants in RO and NF filtration, though the correlation is not straightforward for chemically different contaminants.
- The effect may be very significant for larger contaminants having low solubility in water. In extreme cases this may counterbalance the sieving effect and limit the applicability of RO/NF to removal of moderately hydrophobic substances (e.g., hormones or nonyl phenol).
- The hydrophobicity of polyamides is good for salt rejection, yet it may be unfavorable in removal of organics.
- To date, the main effort has been directed towards optimal membranes for desalination, yet efficient removal of organics might need a larger diversity of membranes (in terms of polarity, presence of specific groups etc.).

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