MEMBRANE DEVELOPMENT FOR THE NEXT GENERATION OF CHEMICAL BIOLOGICAL PROTECTIVE CLOTHING

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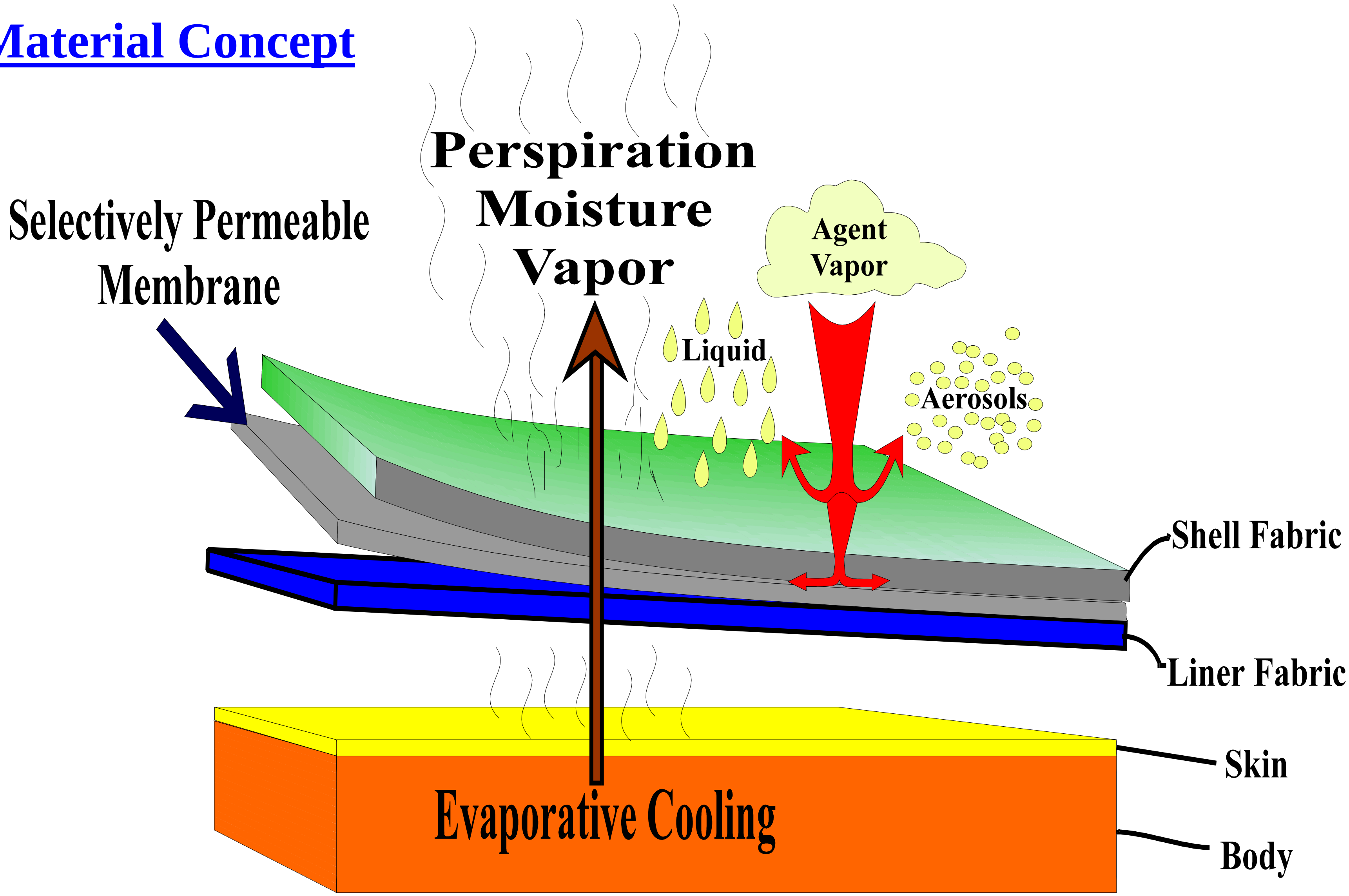
Material Concept



Vapor (V) Chemical Agent Protective Closure Systems

Vapor, Aerosol, Liquid, (VAL) Chemical, and Biological Agent Protective Closure Systems

All Purpose Personal Protective Ensemble (AP-PPE)

- **Based on selectively permeable membranes**
- **Increased protection from liquids and aerosols**
- **Reduced weight and bulk**
- **Improved comfort and compatibility**
- **Improved operational suitability**
- **Reduced shelf-life burden**

Membranes – Where do we go from here?

- Optimize permselectivity
- Ensure protection vs. toxic industrial chemicals (TICs)
- Introduce self-detoxification
- Integrate compatible closures

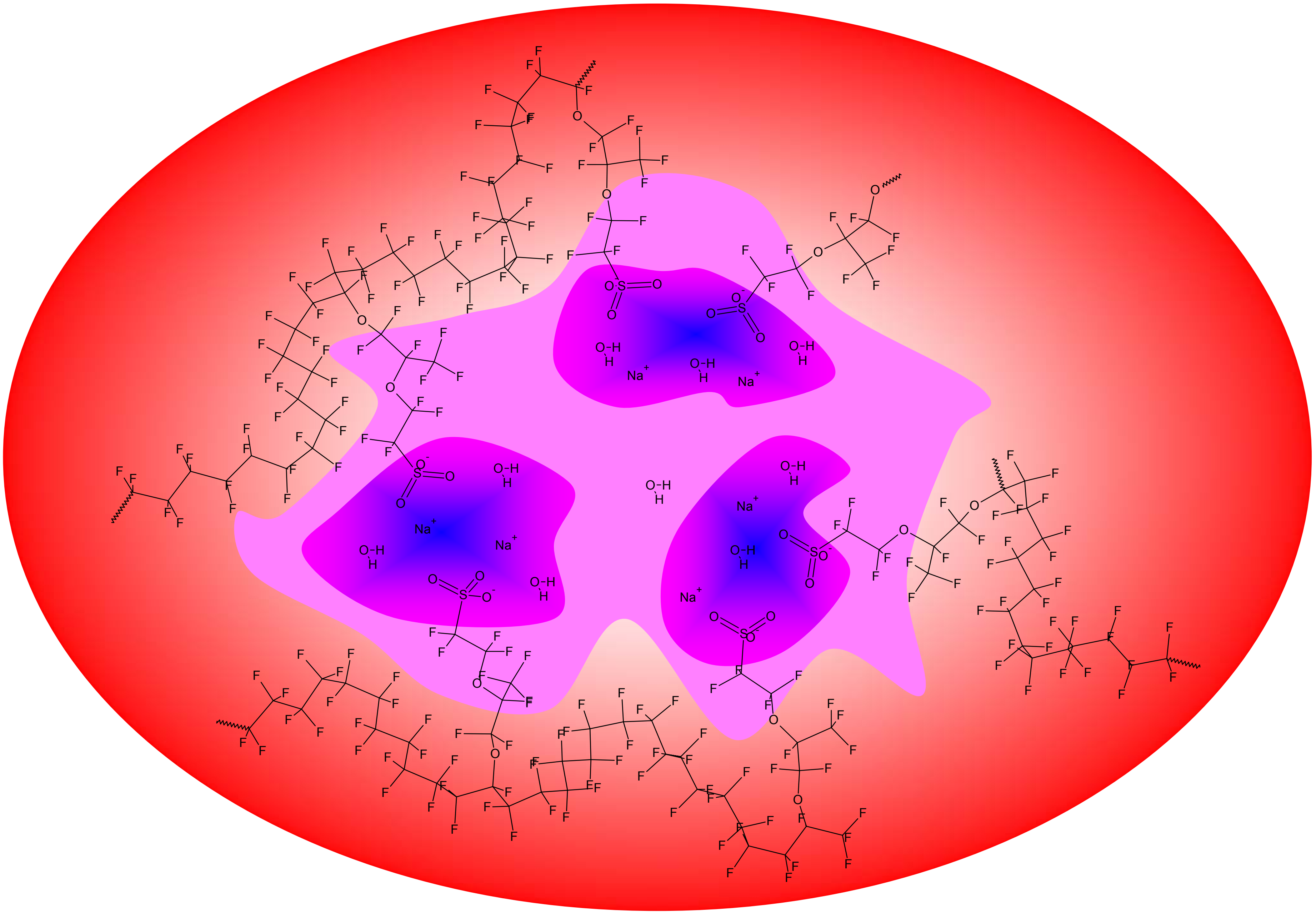
Ion Implanted Membranes

- Improve the permselectivity of membrane materials for use in chemical/biological (CB) protective clothing through the ion beam modification of the surface layers of available membranes

- Two-fold approach: computer modeling of the irradiation process to develop a better understanding of the process at the molecular level and irradiation experiments of materials at different energy levels and with different ions for permselectivity measurements.

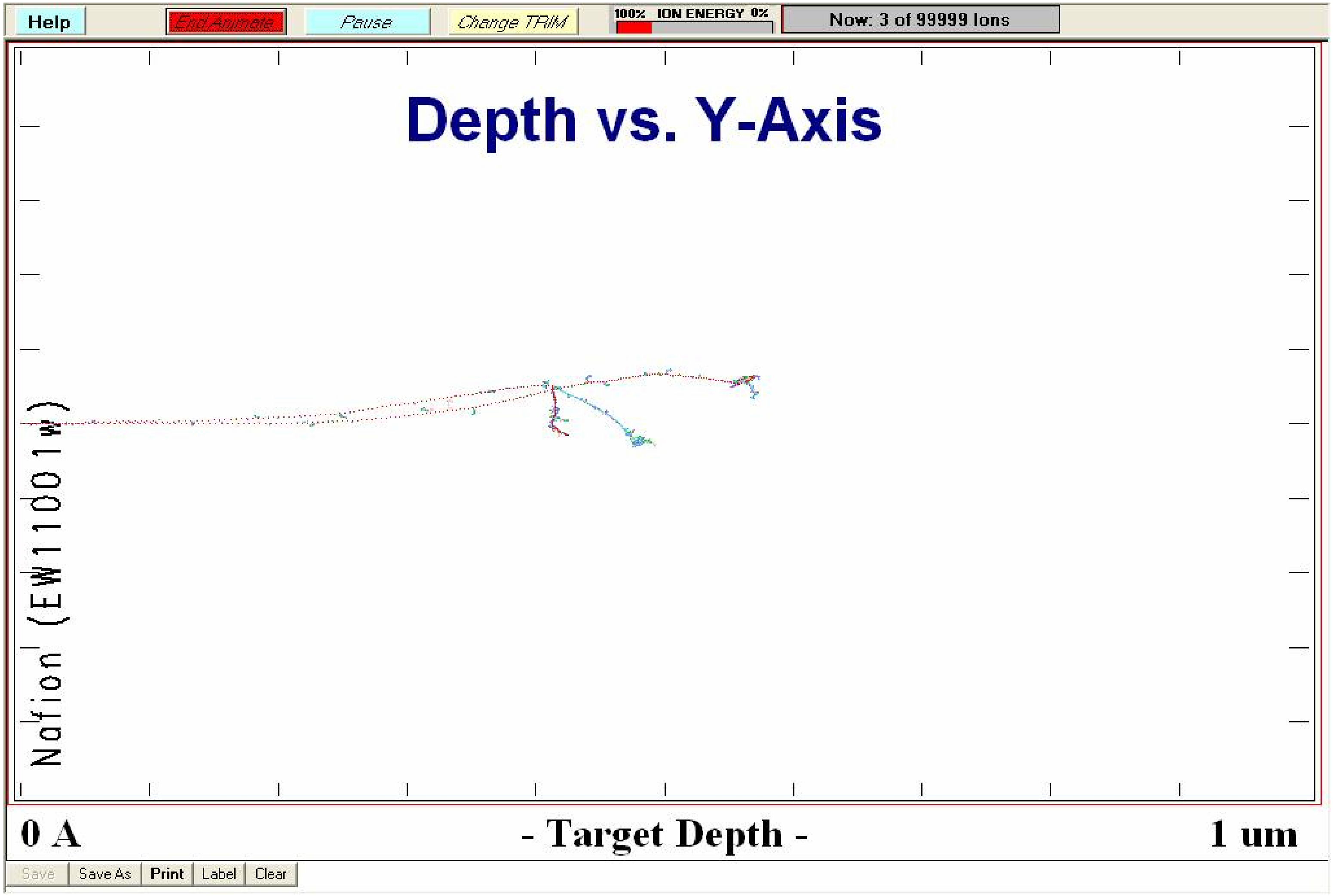
- Correlation between the two efforts will ultimately yield a powerful tool for the development of permselective membranes for CB garments.

Nafion® (du Pont): $[\text{—}(CF_2CF_2)_n\text{-}(CF_2CF(OCF_2CF(CF_3)OCF_2CF_2SO_3H))\text{—}]_x$

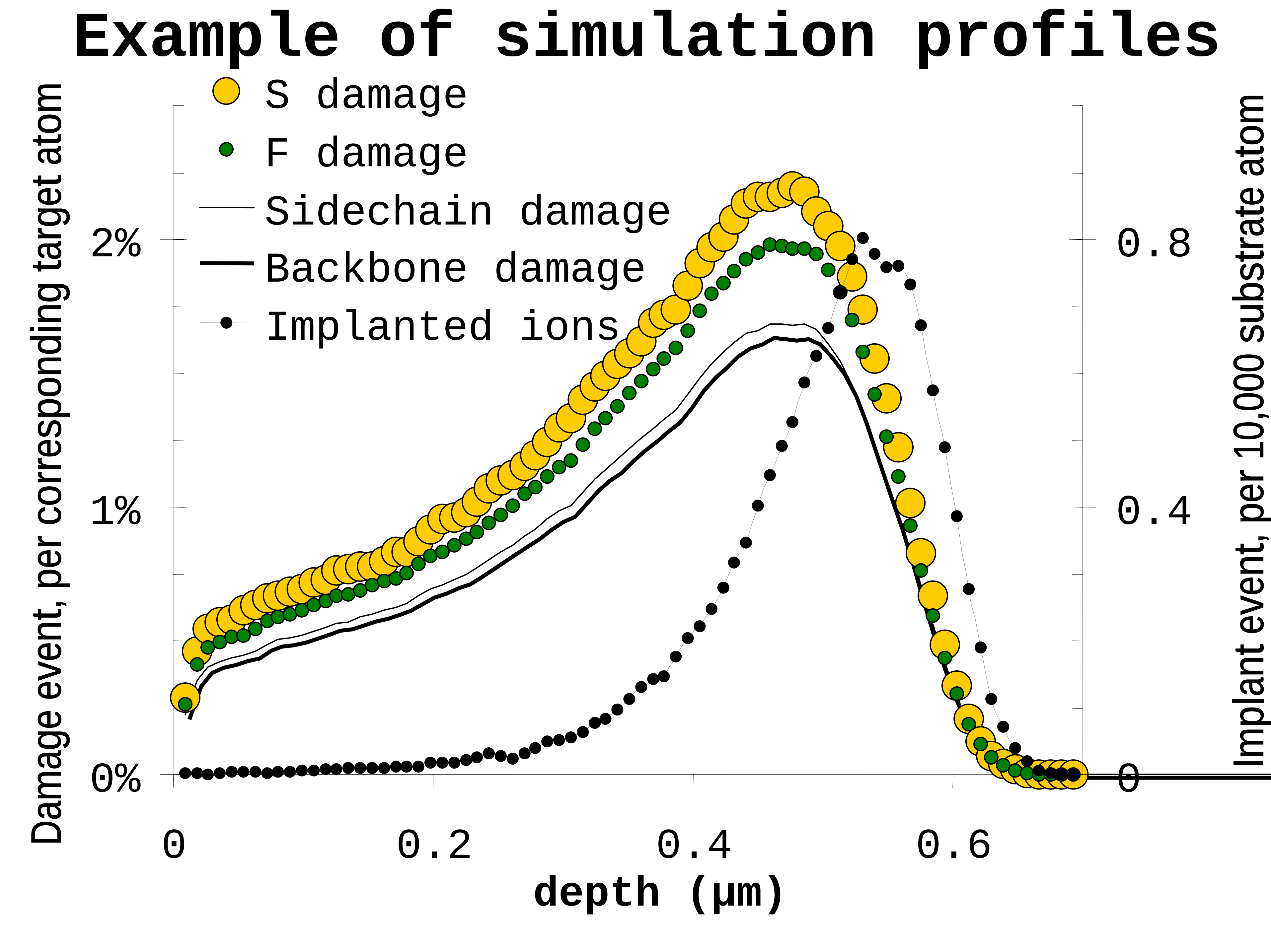


Schematic model of Nafion: hydrophilic, intermediate and hydrophobic phases

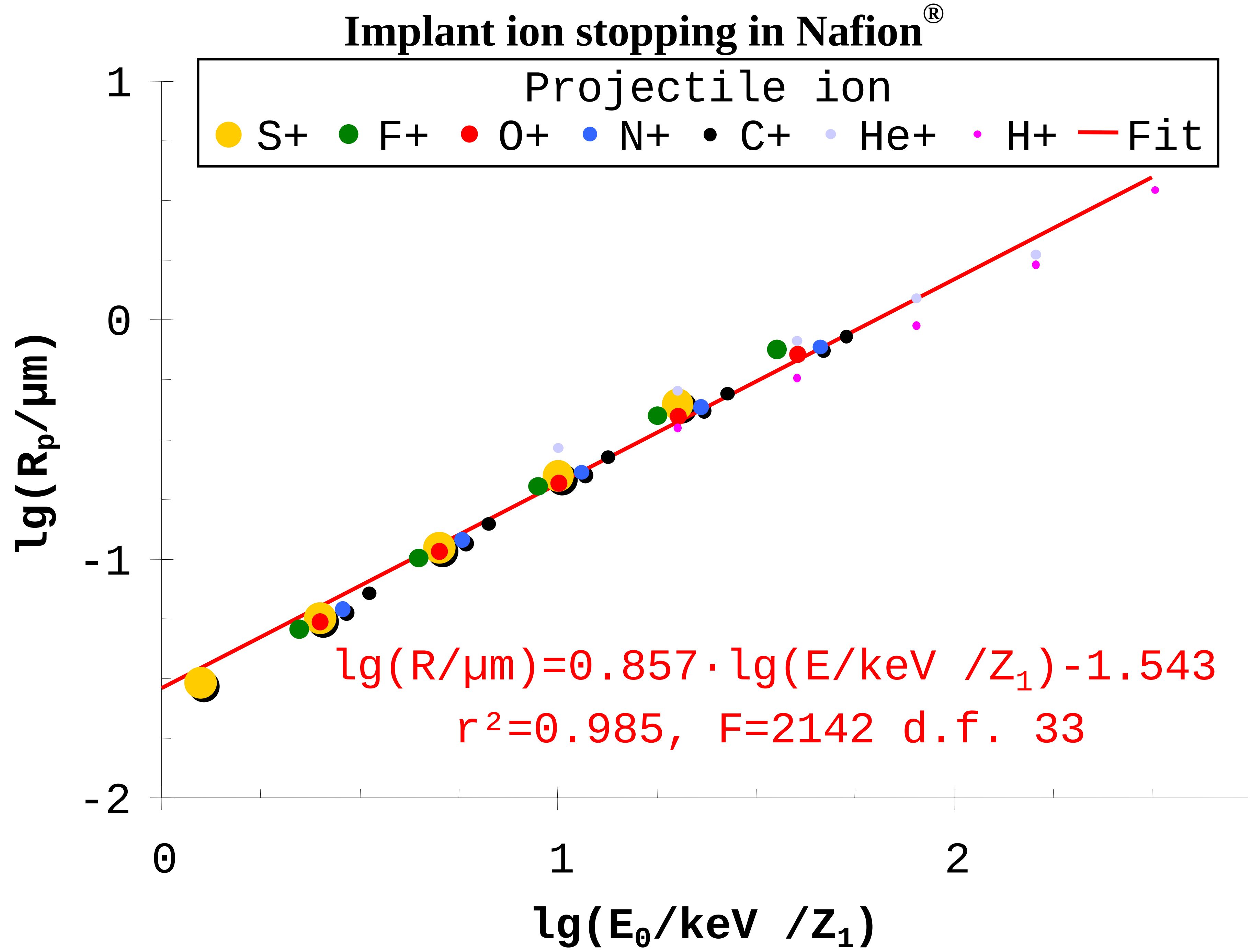
Transport of Ions in Matter (SRIM v.2000.41)[1]



[1]Ziegler, J.F.; Biersack, J.P.; and Littmark, U., The Stopping and Range of Ions in Solids (1985)

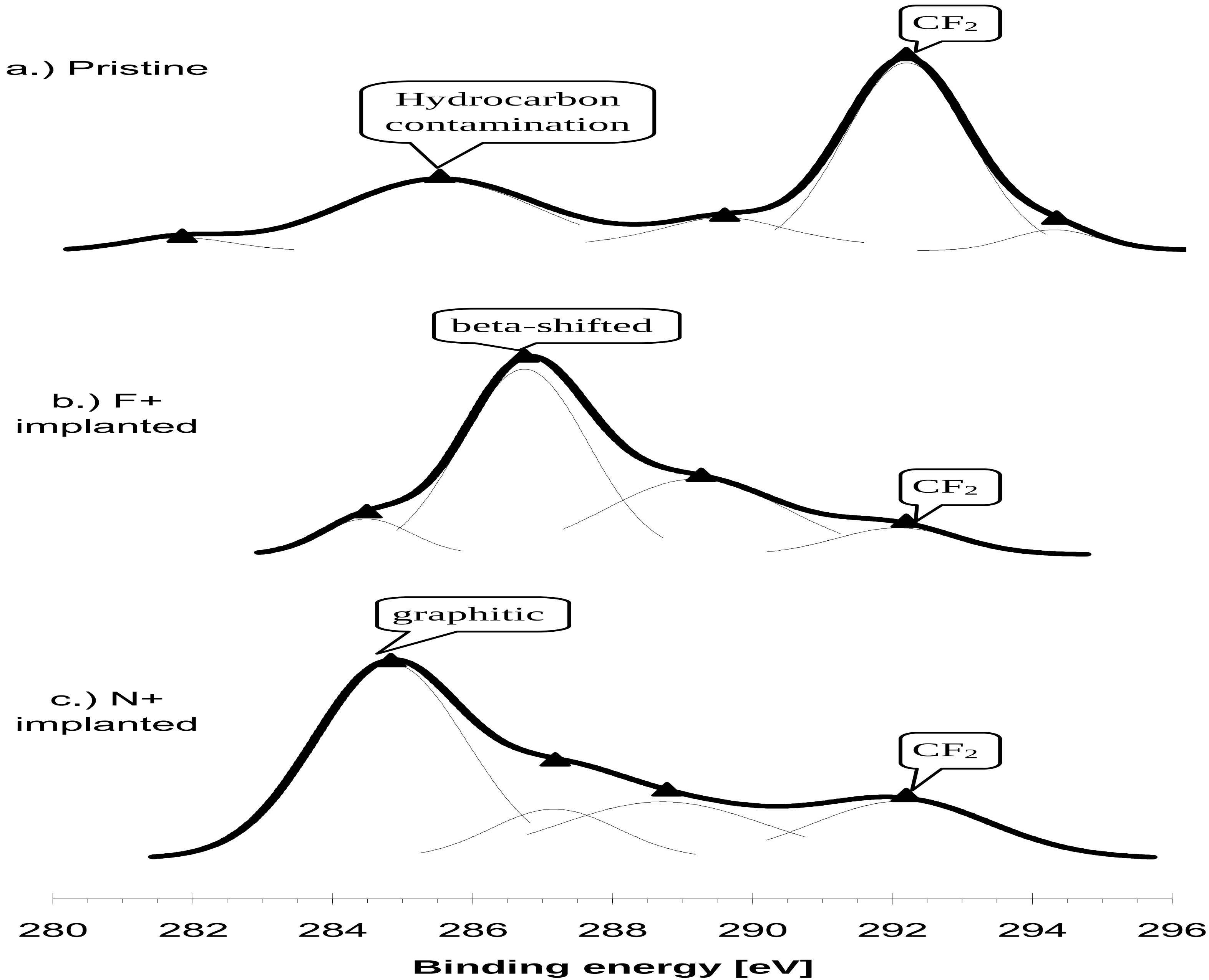


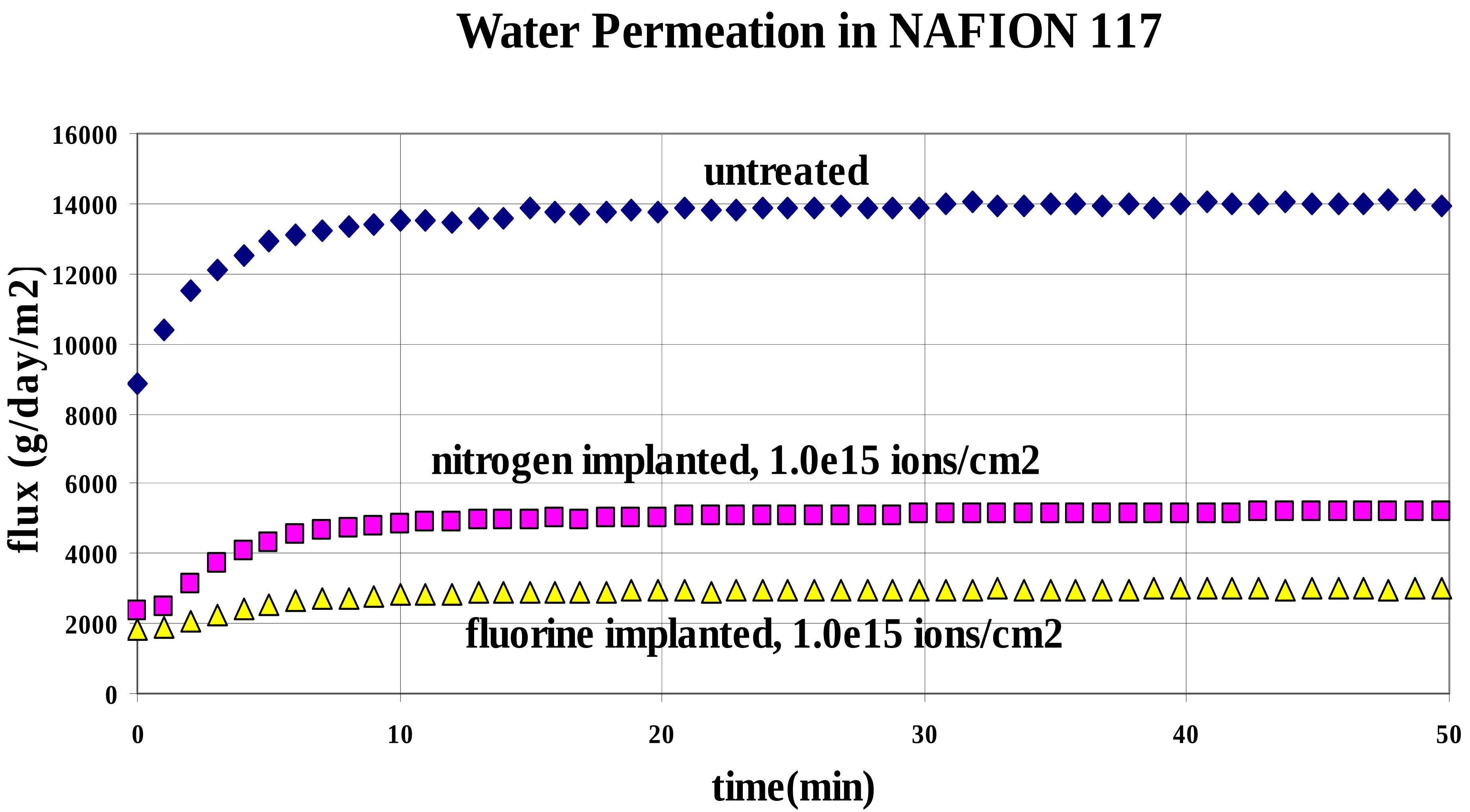
Example of simulation profiles
S damage
F damage
Sidechain damage
Backbone damage
Implanted ions
Damage event, per corresponding target atom
2%
1%
0%
0.8
0.4
0
Implant event, per 10,000 substrate atom
0
0.2
0.4
0.6
depth (μm)

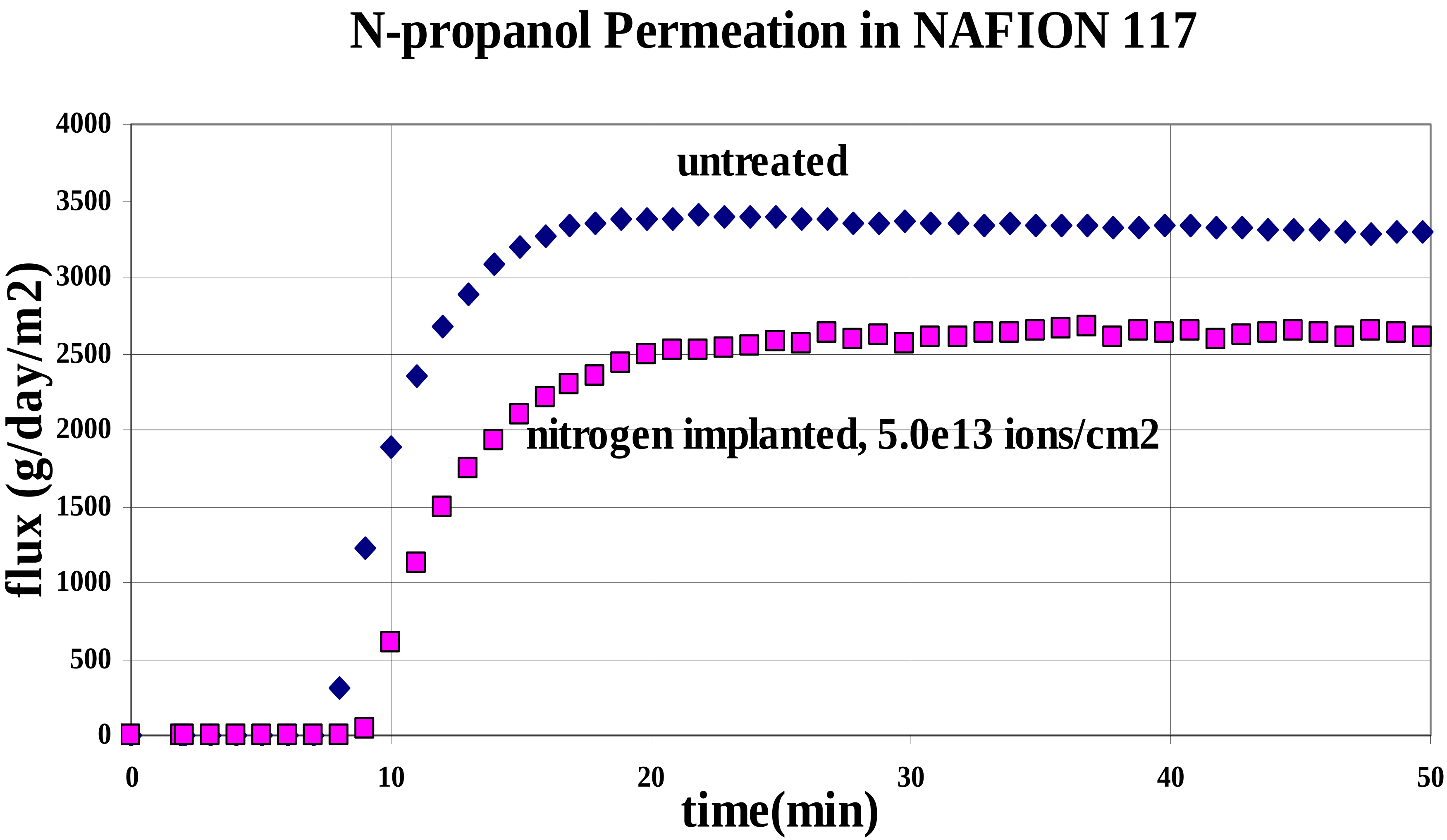


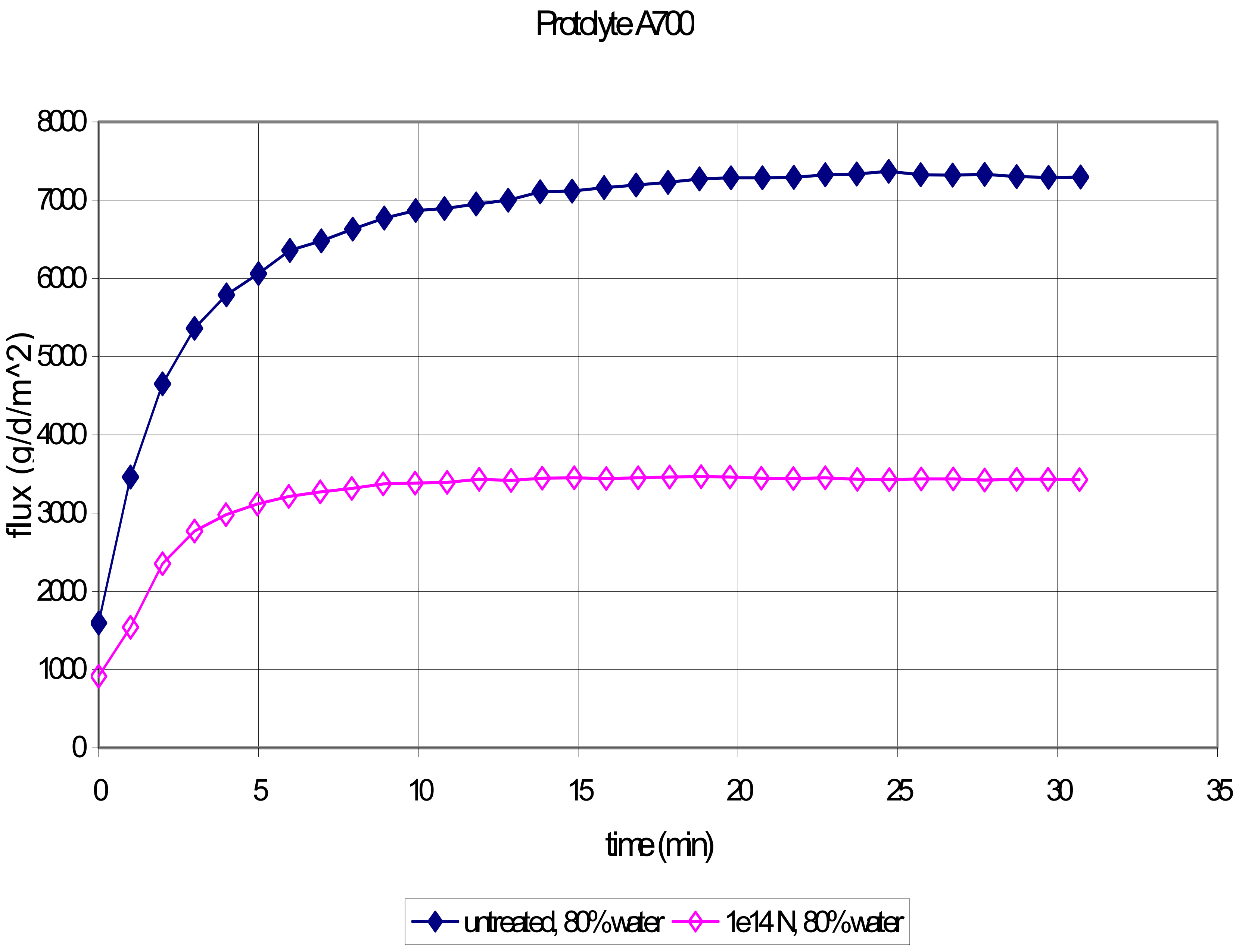
Implant ion stopping in Nafion®
Projectile ion
S+
F+
O+
N+
C+
He+
H+
Fit
lg(R/µm)=0.857·lg(E/keV /Z1)-1.543
r²=0.985, F=2142 d.f. 33
lg(Rp/µm)
lg(E0/keV /Z1)
1
0
-1
-2
0
1
2

Surface analysis: C_{1s} XPS spectra of pristine and ion beam damaged Nafion®

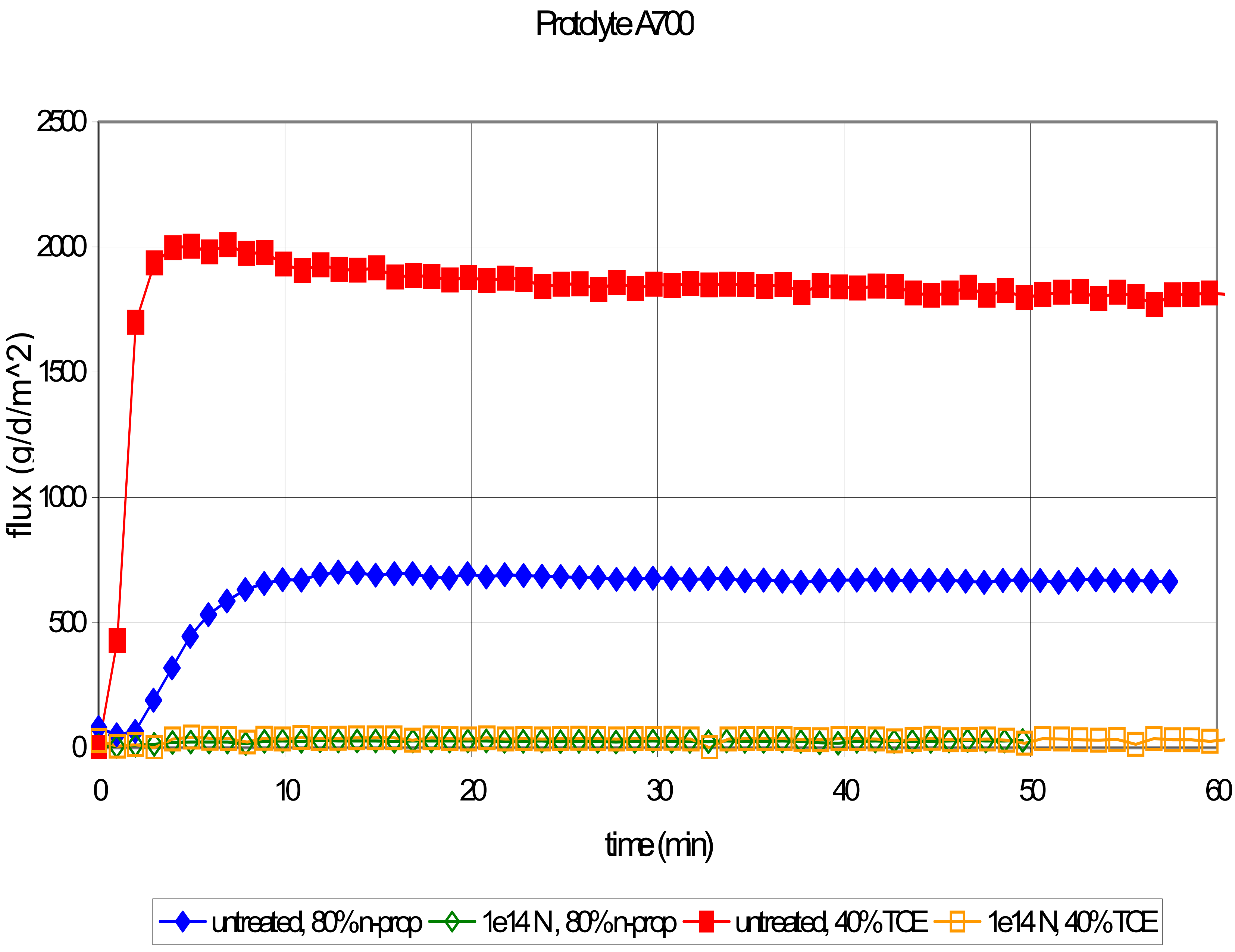



Water Permeation in NAFION 117
untreated
nitrogen implanted, 1.0e15 ions/cm2
fluorine implanted, 1.0e15 ions/cm2
flux (g/day/m2)
time(min)
0
2000
4000
6000
8000
10000
12000
14000
16000
0
10
20
30
40
50


N-propanol Permeation in NAFION 117
untreated
nitrogen implanted, 5.0e13 ions/cm2
flux (g/day/m2)
time(min)
0
500
1000
1500
2000
2500
3000
3500
4000
0
10
20
30
40
50



Protolyte A700
8000
7000
6000
5000
4000
3000
2000
1000
0
flux (g/d/m^2)
0
5
10
15
20
25
30
35
time (min)
untreated, 80% water
1e14 N, 80% water

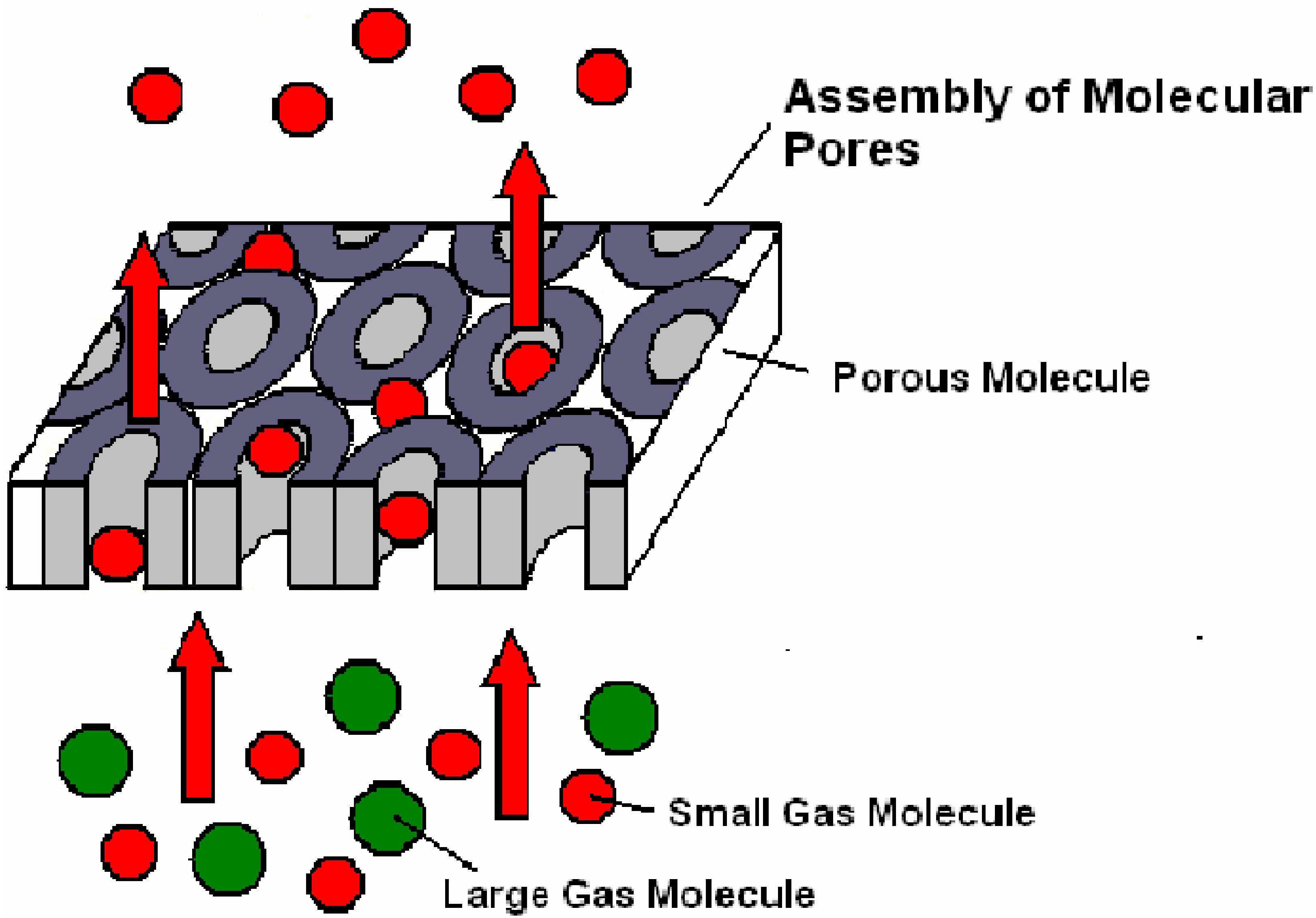


Protolyte A700
flux (g/d/m^2)
2500
2000
1500
1000
500
0
0
10
20
30
40
50
60
time (min)
untreated, 80% n-prop
1e14 N, 80% n-prop
untreated, 40% TCE
1e14 N, 40% TCE

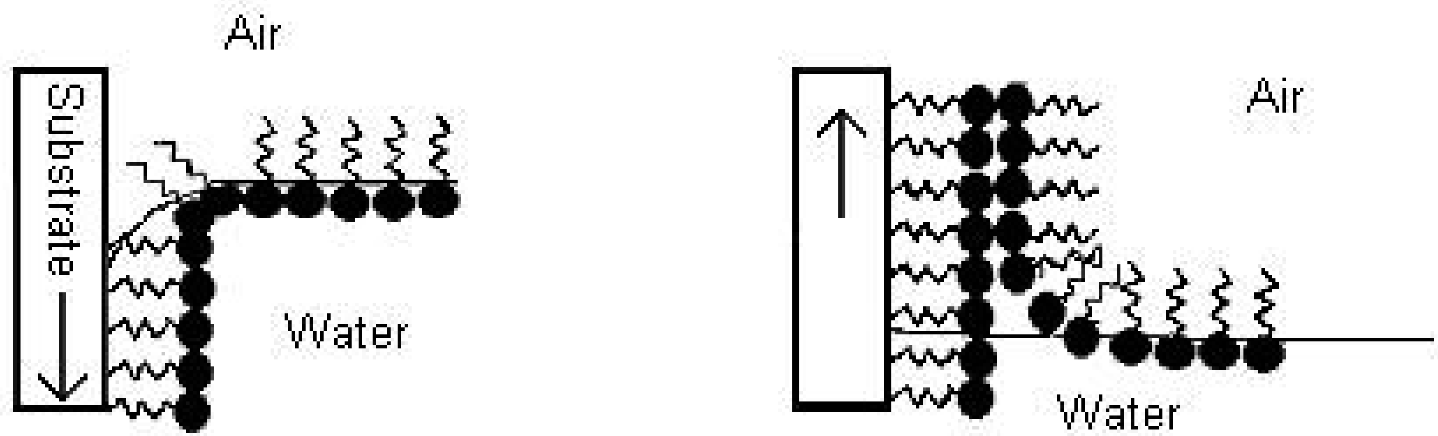
Summary – Ion Implantation

- Medium-energy ion beam treatment is a promising technique for developing barrier membranes selectively permeable to water vapor.
- Theoretical calculations are a useful adjunct for optimizing treatment conditions.
- XPS measurements of the surface reveal that ion bombardment leads to loss of fluorine, with the eventual formation of a carbonized layer.
- This two-pronged approach will ultimately yield a powerful technique for the development of permselective membranes for CB protective garments.

Perforated Monolayer Approach

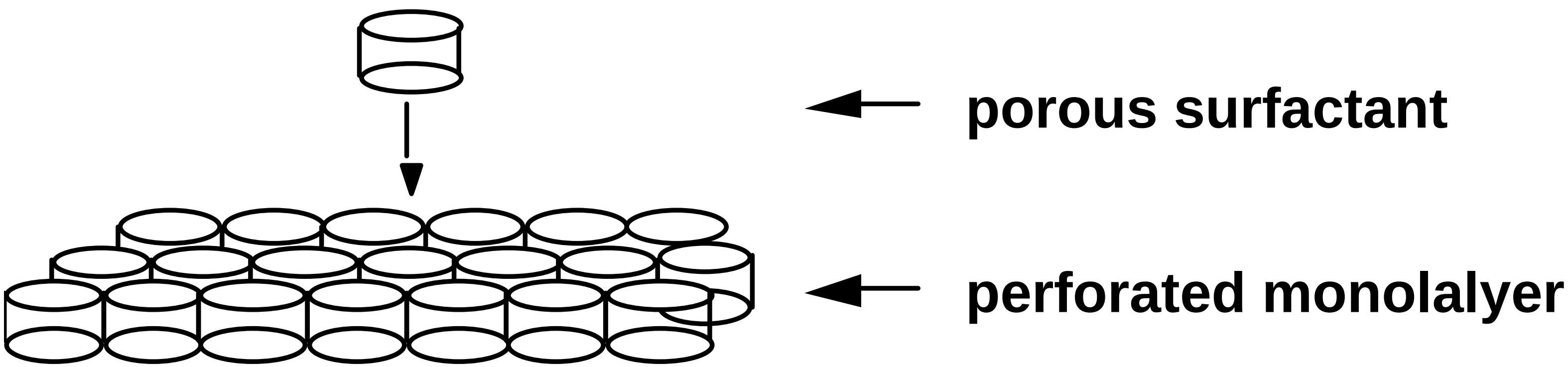


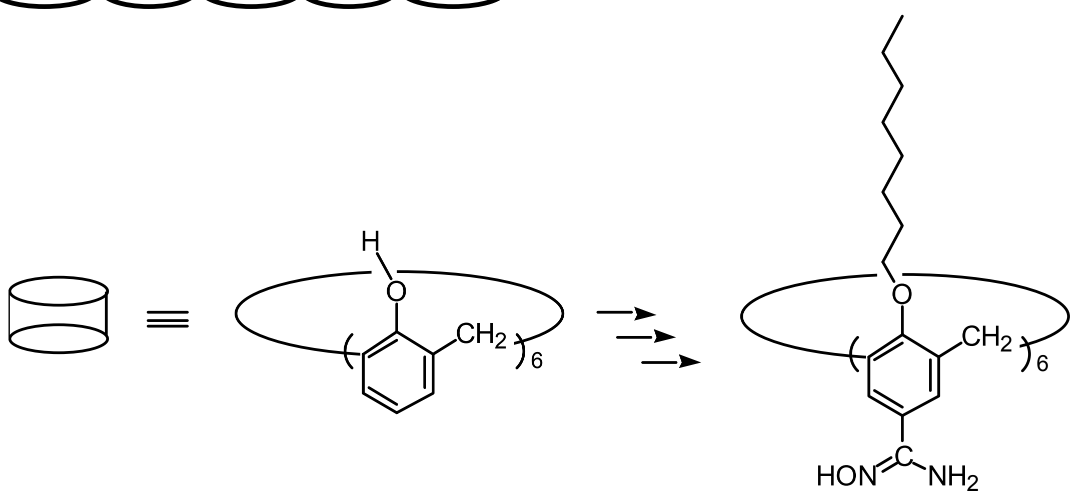
The Langmuir-Blodgett Method



A stylized illustration showing a single surfactant monolayer being transferred to a hydrophobic support on a down-trip, followed by the transfer of a second monolayer on the up-trip, to form a bilayer.

Perforated Monolayers



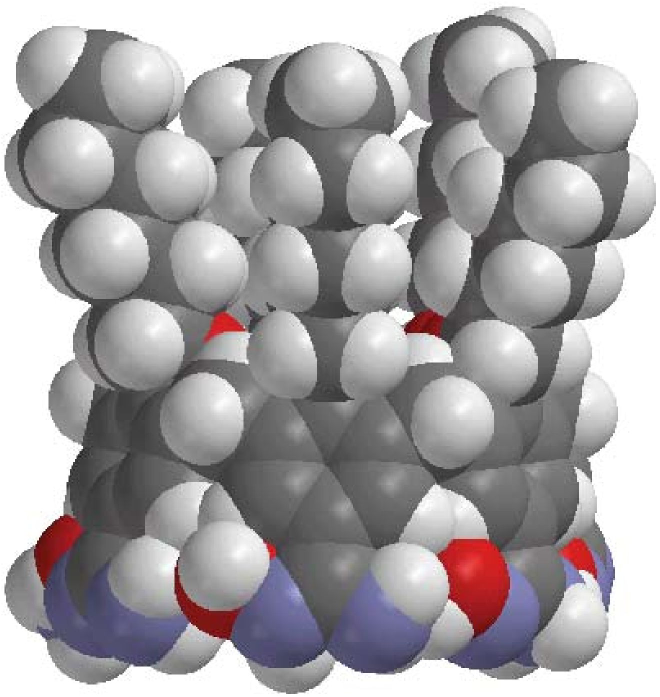


calix[6]arene

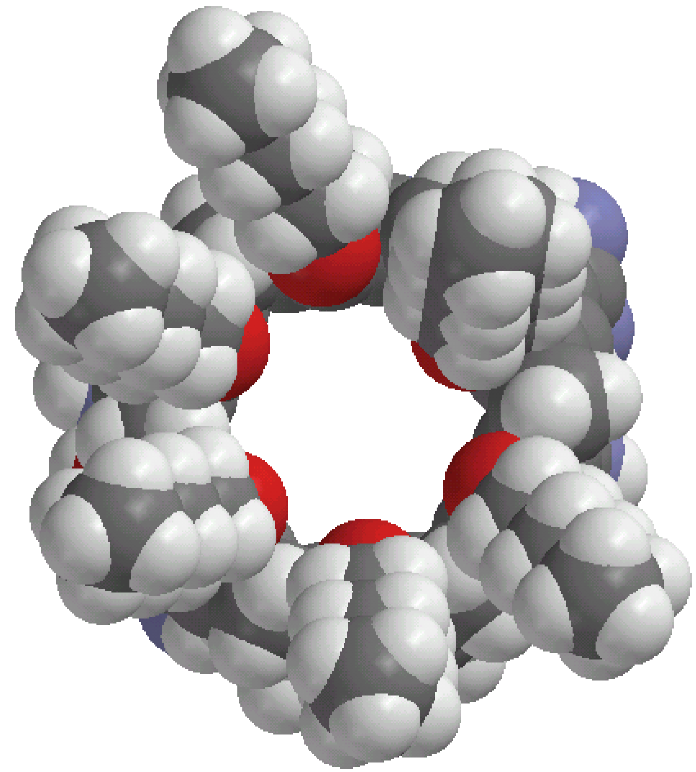
II

An illustration of a perforated monolayer formed from a porous surfactant.

. Space filling models of an analog of **II**

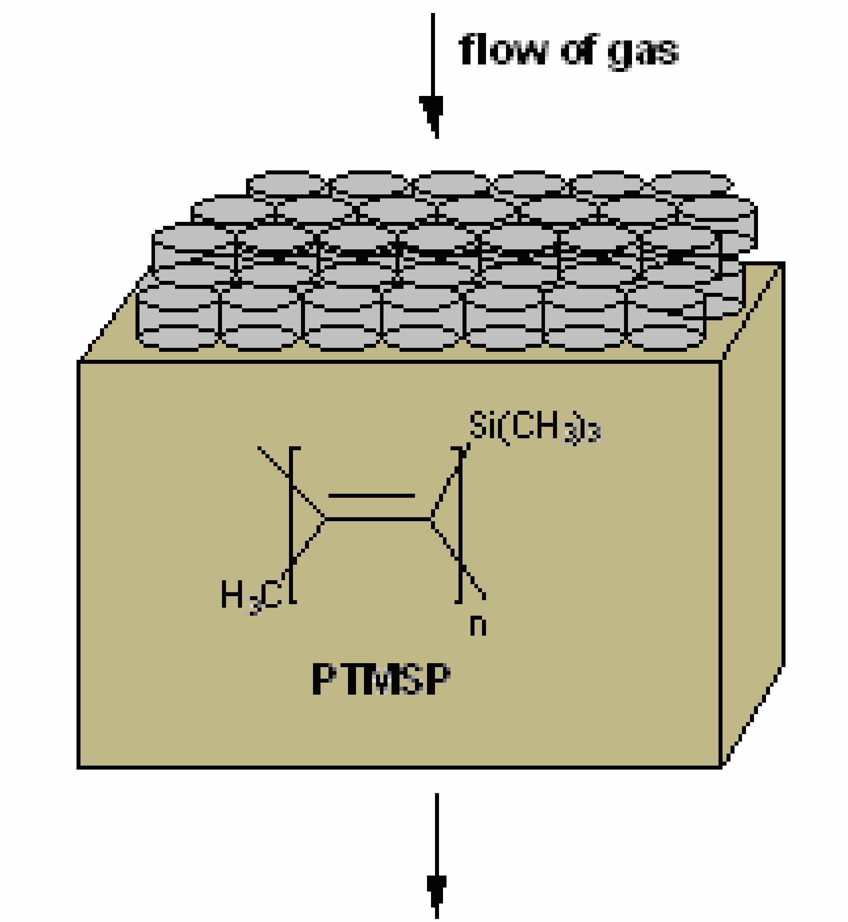


Side View

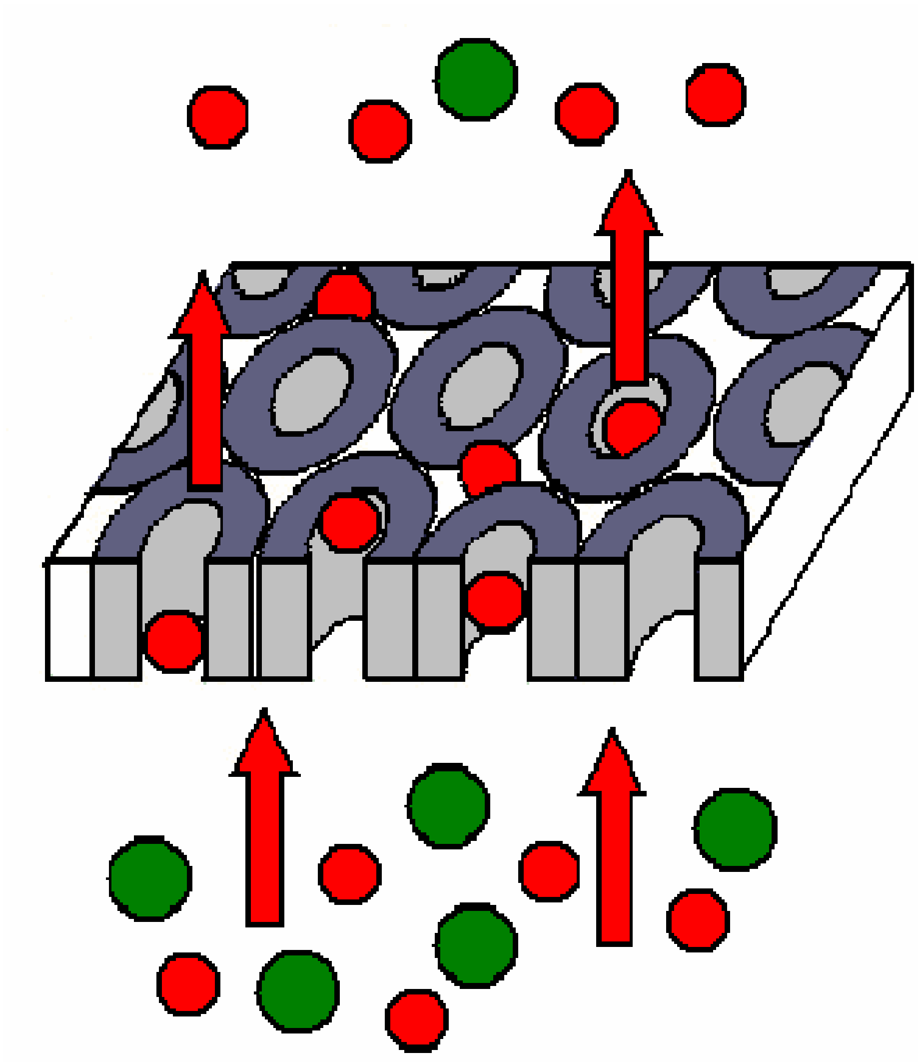


Top View

Composite membrane formed from a bilayer of **II** and poly[1-(trimethylsilyl)-1-propyne] (PTMSP)



Perforated Monolayer of II

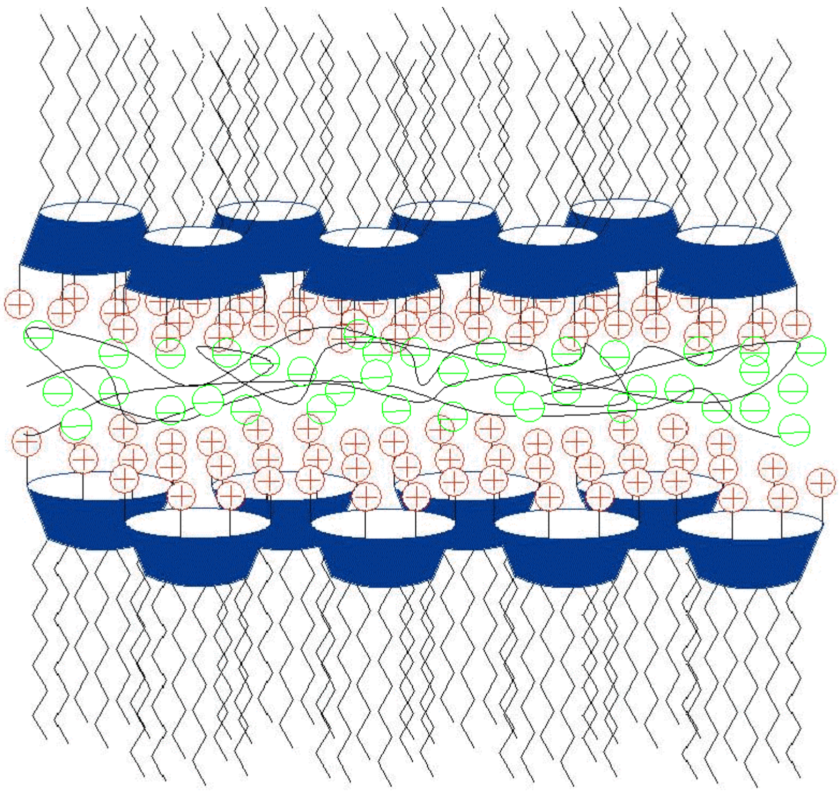


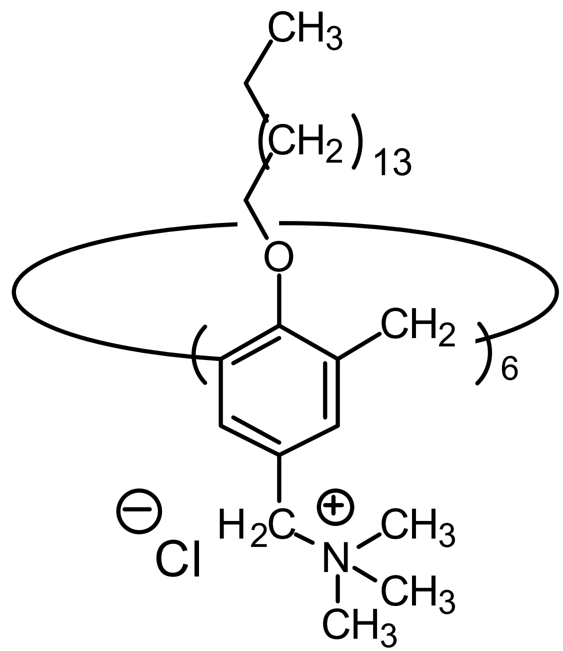
$\alpha_{He/N2} = 18$

Improved Perforated Monolayers through “Gluing”

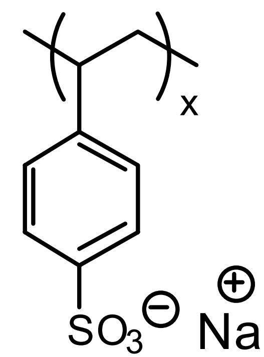
- Ionic cross-linking of a cationic calix[6]arene-based LB film by use of a water-soluble polyanion, would produce a two-dimensional network with enhanced stability
- Filling in void space (defects), the polymeric counterion would result in enhanced permeation selectivity

Glued LB Bilayer





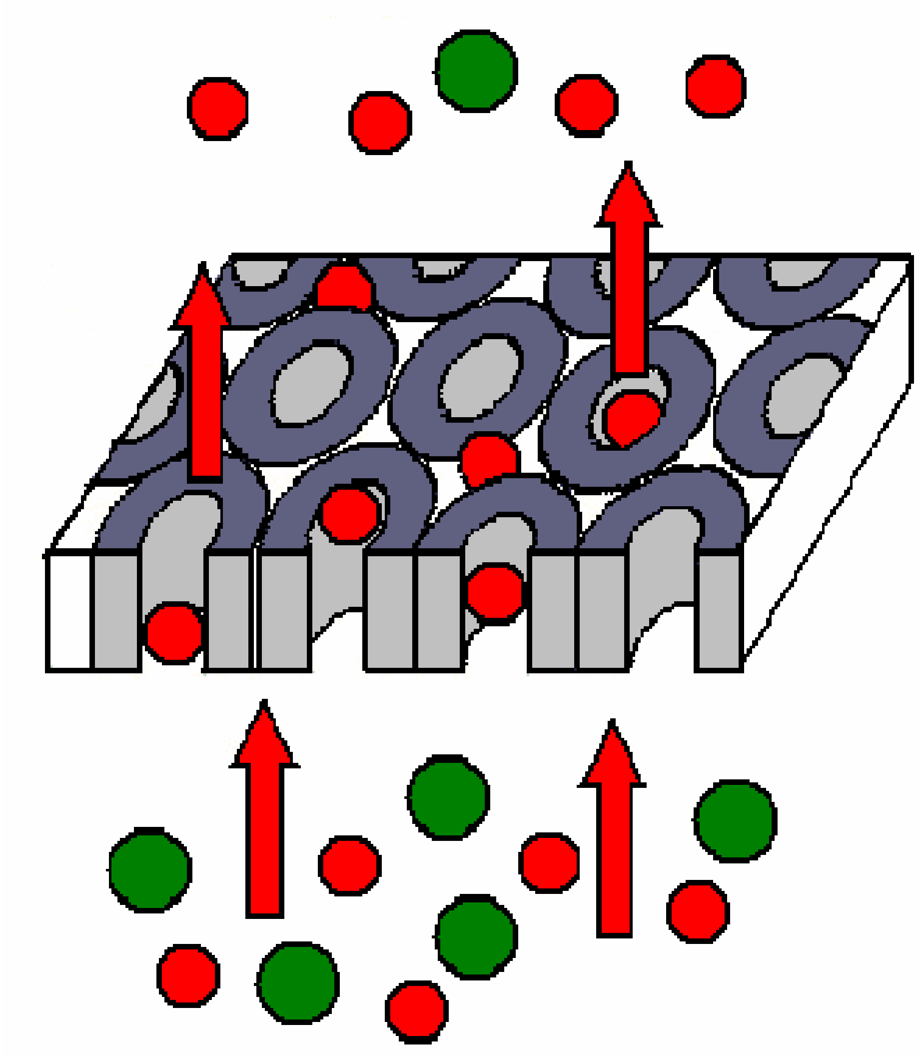
1



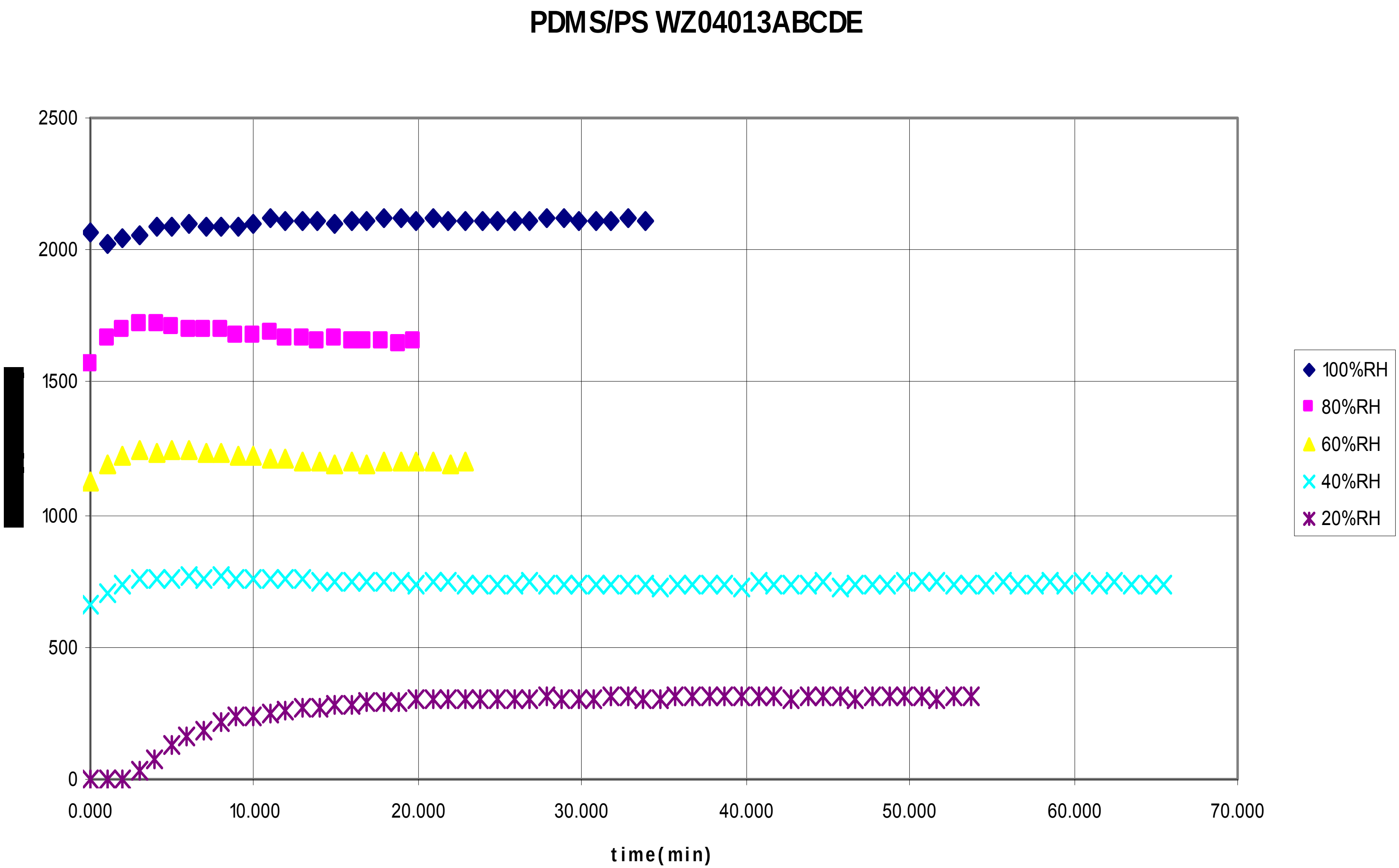
PSS

An illustration of a LB bilayer, made from a multiply charged calix[6]arene that has been glued together through the use of a polymeric counterion.

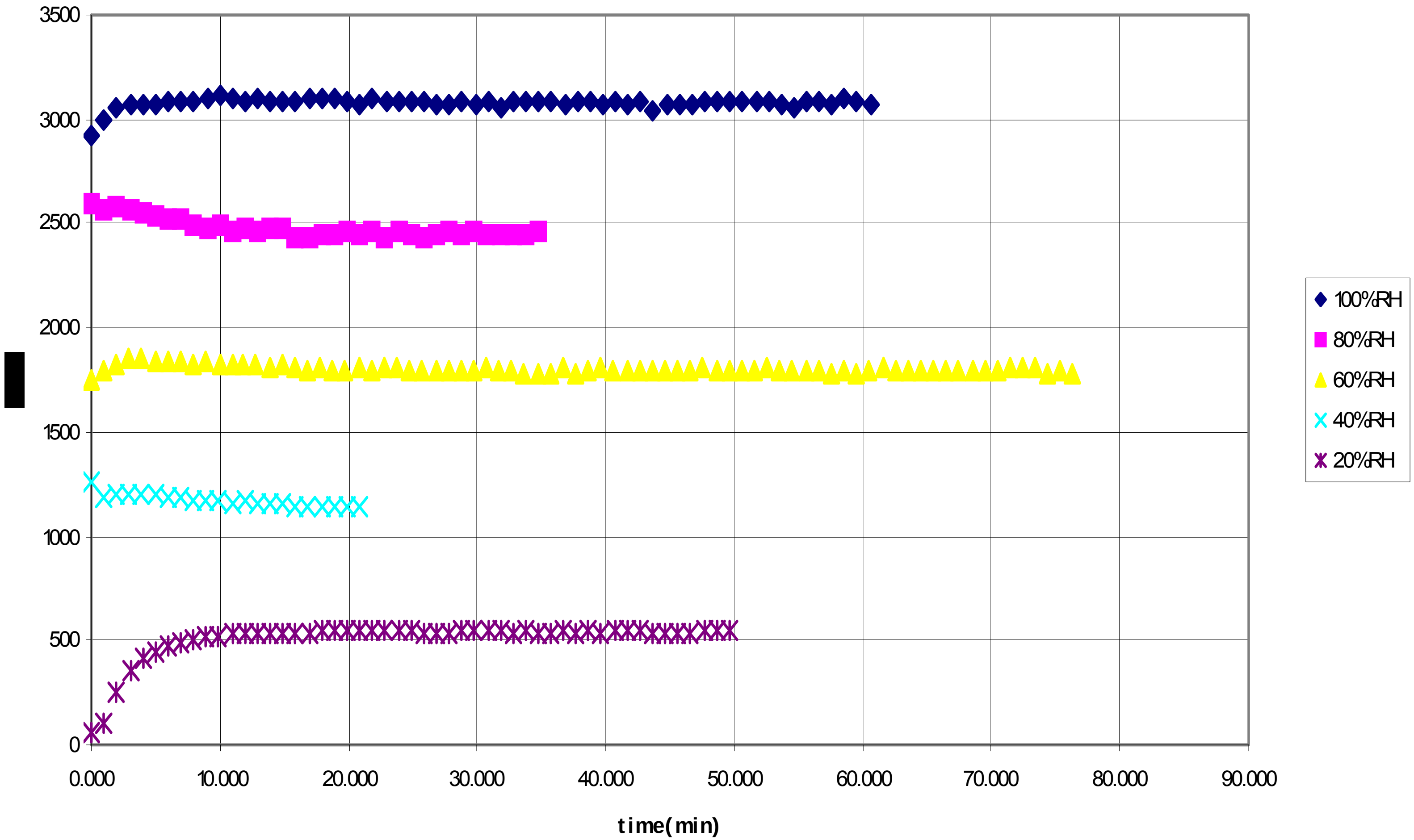
Perforated Monolayer of III & PSS

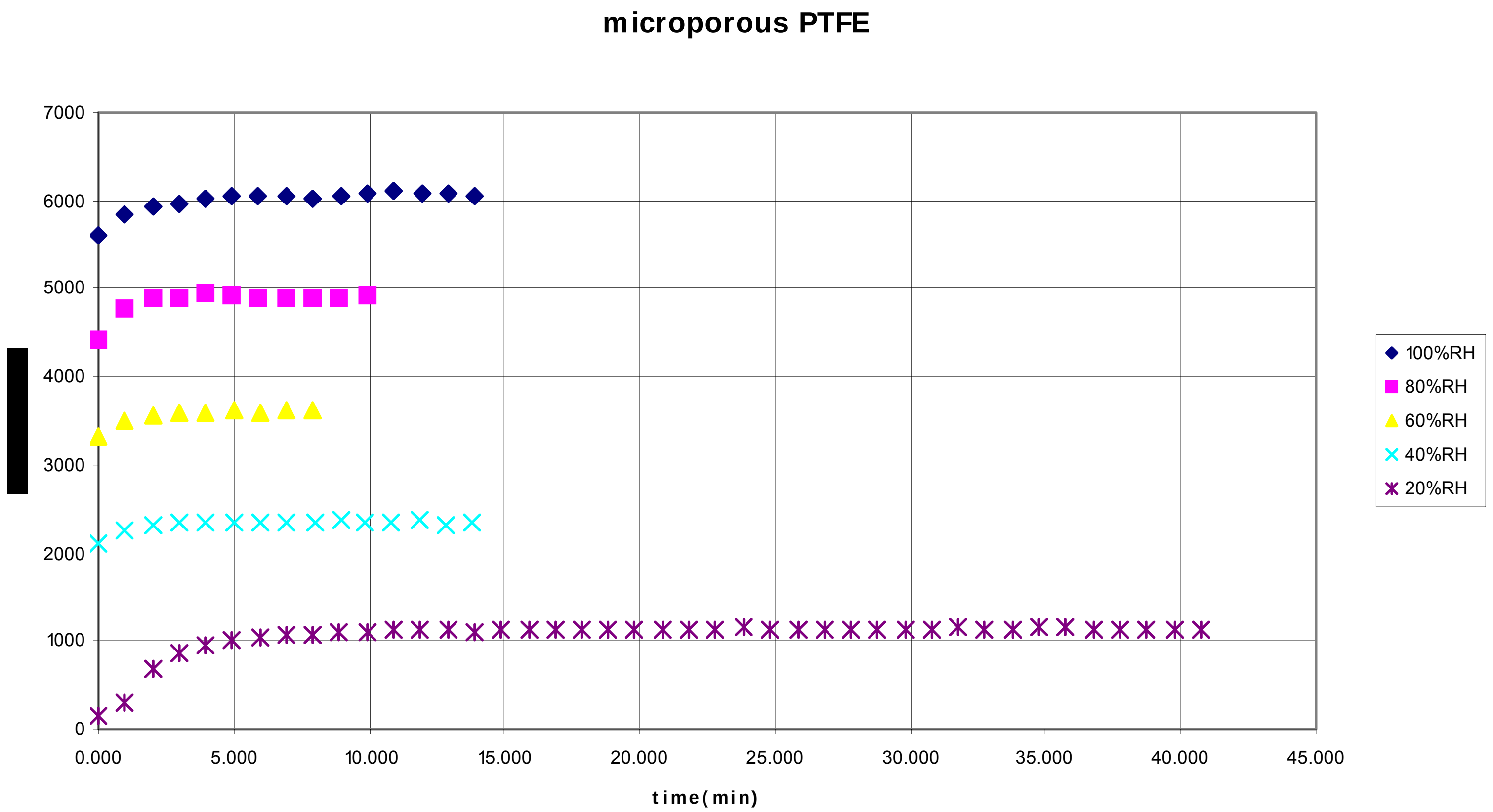


$\alpha_{He/N2} = 240$


PDMS/PS WZ04013ABCDE
2500
2000
1500
1000
500
0
0.000
10.000
20.000
30.000
40.000
50.000
60.000
70.000
time(min)
100%RH
80%RH
60%RH
40%RH
20%RH

PTMSP WZ04023ABCDE




microporous PTFE
[redacted]
7000
6000
5000
4000
3000
2000
1000
0
0.000
5.000
10.000
15.000
20.000
25.000
30.000
35.000
40.000
45.000
time(min)
100%RH
80%RH
60%RH
40%RH
20%RH

Summary – Monolayers

- The surface modification of organic polymers by a tightly packed monolayer of calix[6]arenes or other surfactants could constitute an attractive, selectively permeable barrier, allowing the passage of water vapor (perspiration), while serving as a barrier to chemical warfare agents
- Due to its ultrathin and microporous structure, it is expected that the flux of water across such a membrane would be maximized
- The composite membranes could be used in the protective layer of the next generation of chemical protective clothing
- These novel clothing ensembles would potentially be dramatically lighter weight than current systems

Summary/Challenges
Clothing Operational Context

Improved system integration with suit, mask, helmet, gloves, boots, body armor, weapons, etc. (JSLIST Upgrade)

Cool, lightweight CB duty uniform based on nanofiber or membrane technology with increased mission duration and a reduced logistics burden. (JSLIST Upgrade)

Reactive clothing materials with increased protection, reduced doffing hazard, and reduced logistics burden. (JSLIST Upgrade)