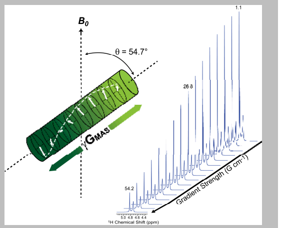
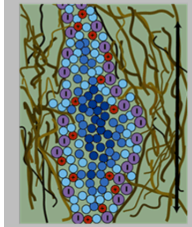
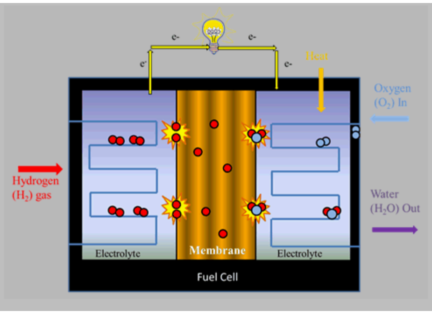
SAND2016-2067PE

NMR Diffusometry of Energy Related Materials: Recent Efforts at Sandia National Laboratories







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3/12/2016

Sandia National Laboratories

Exceptional service in the national interest

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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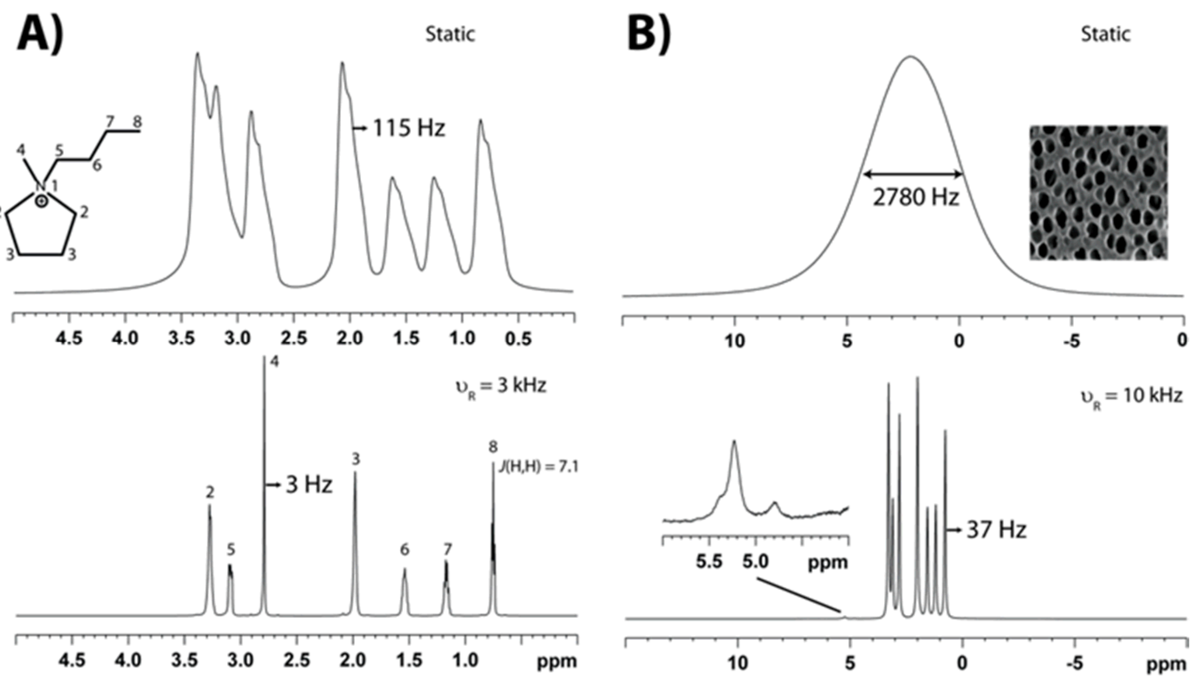
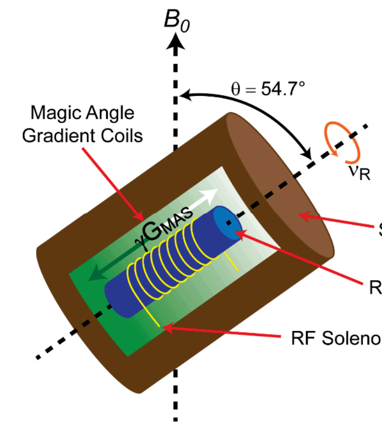
High Resolution Magic Angle Spinning (HRMAS)





“Magic Angle Spinning”

$$\Delta B \sim P_2(\cos\theta) = 3\left(\cos^2\theta - \frac{1}{2}\right)$$

Reduce susceptibility effects in semi-solid materials:

- Combinatorial resins
- Tissues
- Cell dispersions
- Polymer gels

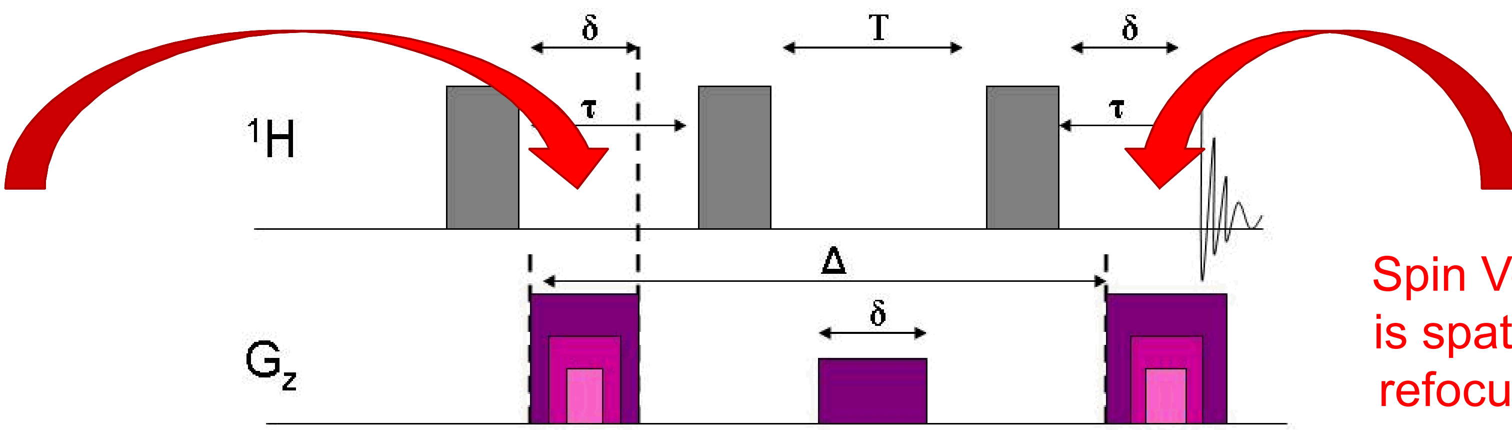
Hamiltonian same form as CSA and dipolar interactions!

Todd M. Alam and Janelle E. Jenkins, “ HR-MAS NMR Spectroscopy in Material Science”, in Advanced Aspects of Spectroscopy, Muhammad Akhyar Farrukh (Ed.), ISBN: 978-953-51-0715-6, InTech, (2012).

Diffusometry NMR

Stimulated Echo (STE)

Spin Voxel is spatially “tagged”



Spin Voxel is spatially refocused

Signal decay is measured by:

$$S(T+2\tau_1)=\frac{M_0}{2}\exp\left(-2\tau_1/T_2-T/T_1\right)\exp\left[-D\gamma^2 g^2\delta^2\left(\Delta-\delta/3\right)\right]$$

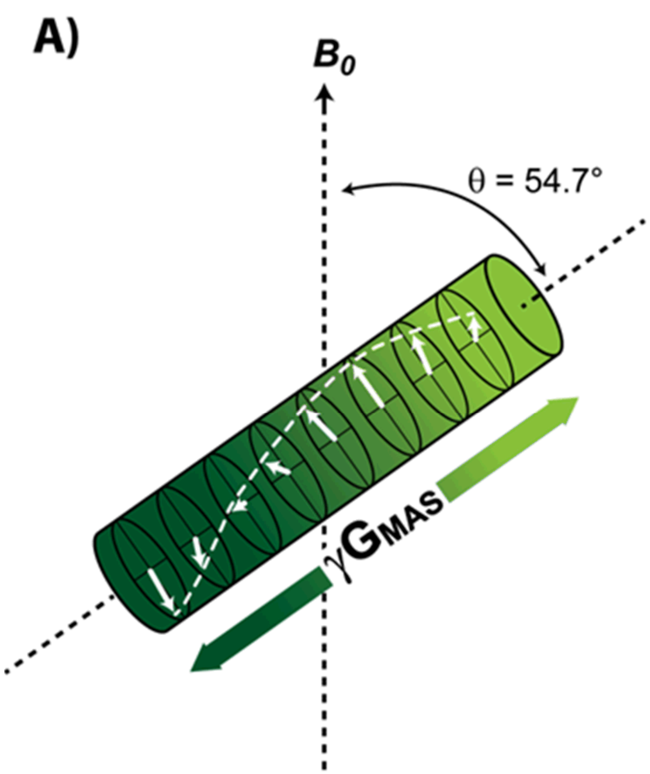
Where:

- **T_1 = spin-lattice relaxation time**
- **δ = length of gradient pulse**
- **g = gradient strength**
- **γ = gyromagnetic ratio**
- **T_2= spin-spin relaxation time**
- **Δ= inter pulse delay**
- **D= diffusion constant**
- **τ, T: inter-pulse spacing**

Pulse Field Gradient (PFG) NMR provides one method for characterizing the self-diffusion transport of species within the membrane.

High Resolution Magic Angle Spinning (HRMAS) Pulse Field Gradient (PFG) Diffusion Experiments

"Diffusometry NMR"



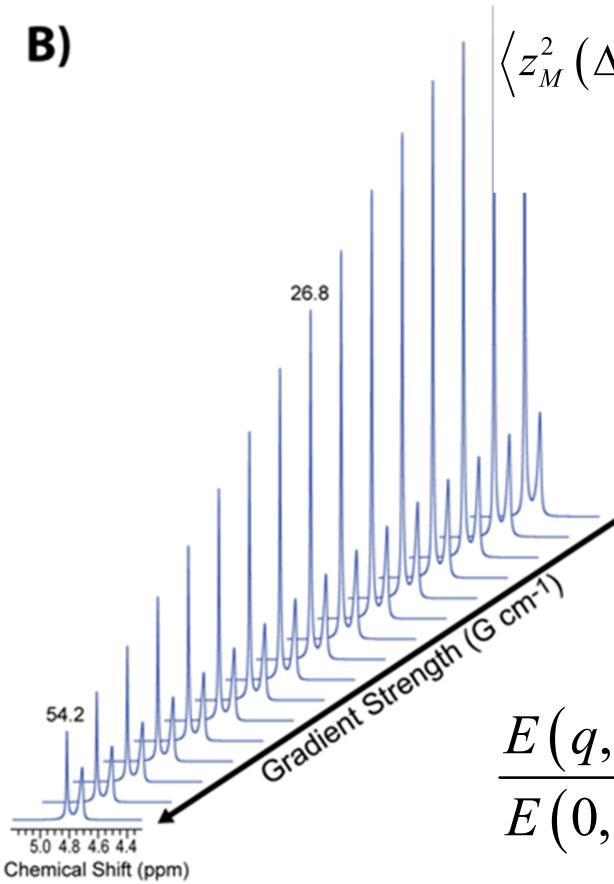


Figure 8: A) Pictorial representation of the gradient produced along the magic angle of the rotor. B) The decay of two different water signals found in a 1N methanol solution of an AEM membrane with increasing gradient strength. Gradient strength values (G/cm) are shown above the stack plot.

$$\left\langle z_M^2(\Delta)\right\rangle = -2\ln\left[E(q,\Delta)/E(0,\Delta)\right]/q^2$$

$$\left\langle z_M^2\right\rangle = 2D_\alpha t^\alpha$$

Diffusion Using Stejskal-Tanner Formula

$$\frac{E(q,\Delta)}{E(0,\Delta)} = \exp\left[-q^2 D\left(\Delta - \frac{\delta}{3}\right)\right]$$

PFG NMR Equipment

Water cooled diffusion probe

Nucleus Specific

^{1}H, ^{2}H, ^{19}F, ^{7}Li, ^{13}C, ^{23}Na, ^{31}P….

Gradient control and B_0 emphasis unit

High power gradient unit

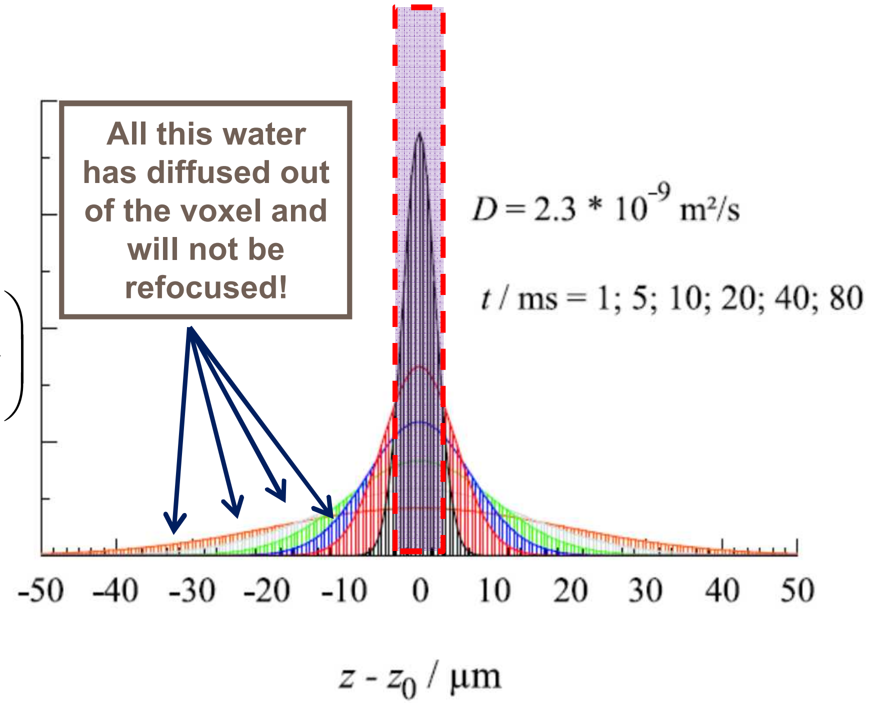
Diffusion Process

Propagator

$$\overline{P}(\vec{r},t) = \int_V P(\vec{r}_1 + \vec{r}, \vec{r}_1, t)\, p_0(\vec{r}_1)\, d\vec{r}_1$$

$$\overline{P}(\vec{r},t) = \frac{1}{\sqrt{(4\pi D t)^3}} \exp\left(-\frac{(\vec{r}(t))^2}{4Dt}\right)$$

$$\left\langle \vec{r}^{\,2}(t) \right\rangle = \int_V P(\vec{r},t)\vec{r}^{\,2}\, d\vec{r}_1 = 6Dt$$

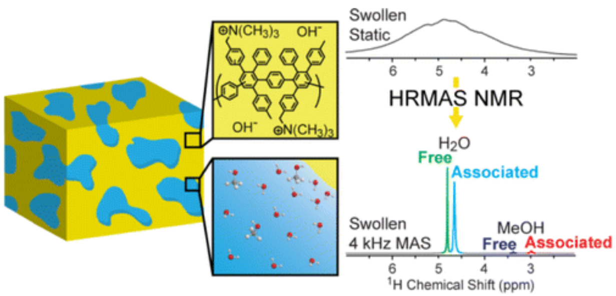


- Will use pulse field gradient (PFG) NMR (described next) to measure this self-diffusion constant (D).
- Signal from the PFG experiment is the FT of the diffusion propagator.

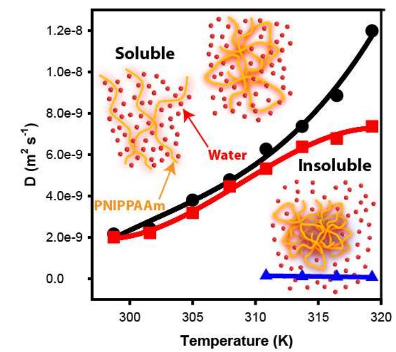
$$\Psi(g,\delta,\Delta) = \int \overline{P}(z,\Delta)\cos(\gamma g \delta z)\, dz$$

HRMAS NMR Diffusometry in Materials

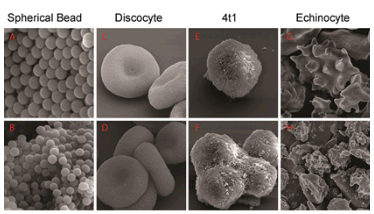
- "Identification of Multiple Diffusion Rates in Mixed Solvent Anion Exchange Membranes Using High Resolution MAS NMR", *ACS Macro Letters*, **1**, 910-914 (2012).
- "Characterization of Heterogeneous Solvent Diffusion Environments in Anion Exchange Membranes", *Macromolecules*, **47**, 1073-1084 (2014)

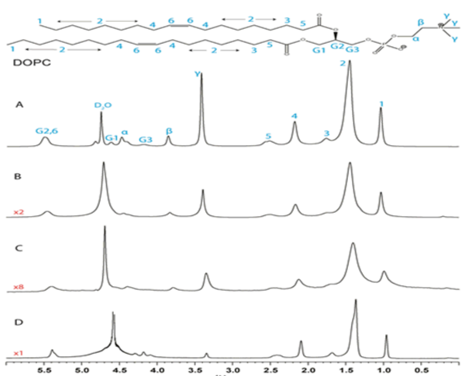


- "Characterization of Free, Restricted and Entrapped Water Environments in Poly(N-Isopropyl Acrylamide) Hydrogels via [1]H HRMAS PFG NMR Spectroscopy", *J. Polymer Science: Polymer Physics*, **52** 1521-1527 (2014).

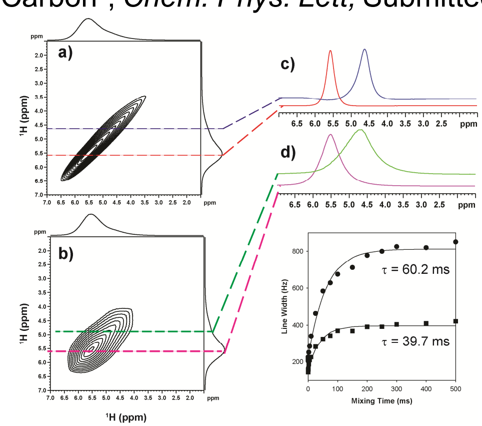


- "The Effect of Curvature on the Dynamic and Diffusional Properties of Phospholipids on Silica Materials using HRMAS NMR", *In Preparation*





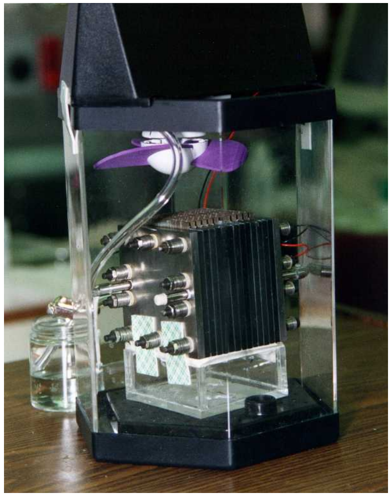
- "Measuring In-Pore Diffusion of Carbonate Solvent Mixtures in Nanoporous Carbon", *Chem. Phys. Lett*, Submitted (2016).

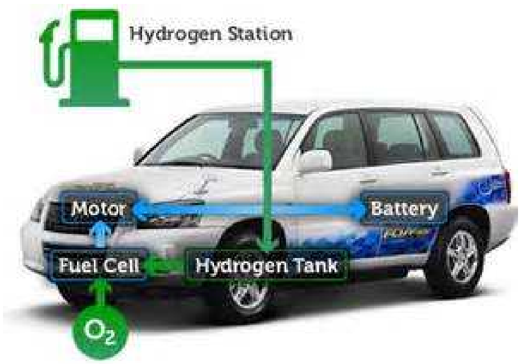


Fuel Cells – Emerging Technology

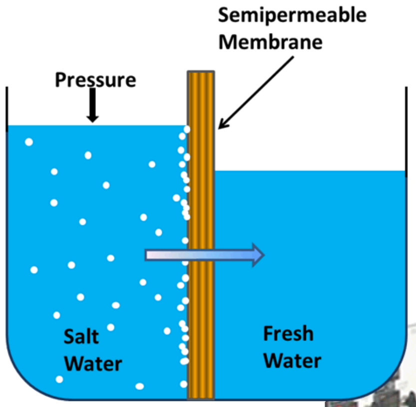
"Old Technology – Material Advances Lead the Way"

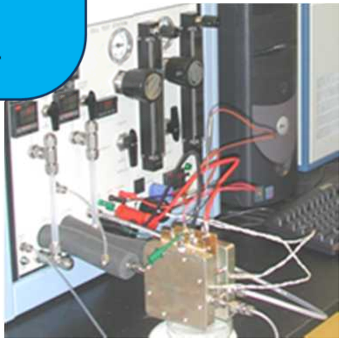
- Convert chemical energy (fuel) to electricity using oxygen.
- Different types of fuels (hydrogen, methanol, ethanol…).
- Can produce electricity as long as there is fuel (unlike batteries).
- Power generation (backup), including remote sites, military, automobile.
- Higher efficiency (60 – 85%) that combustion systems (30%).

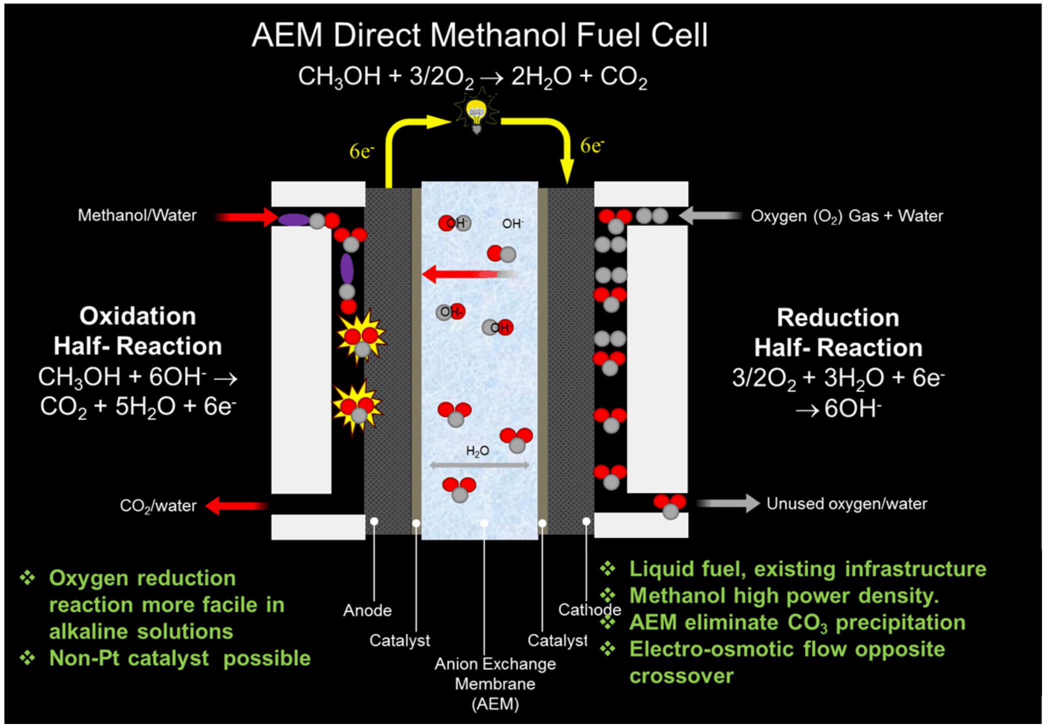




Sandia -Fuel Cell and Desalination Membranes







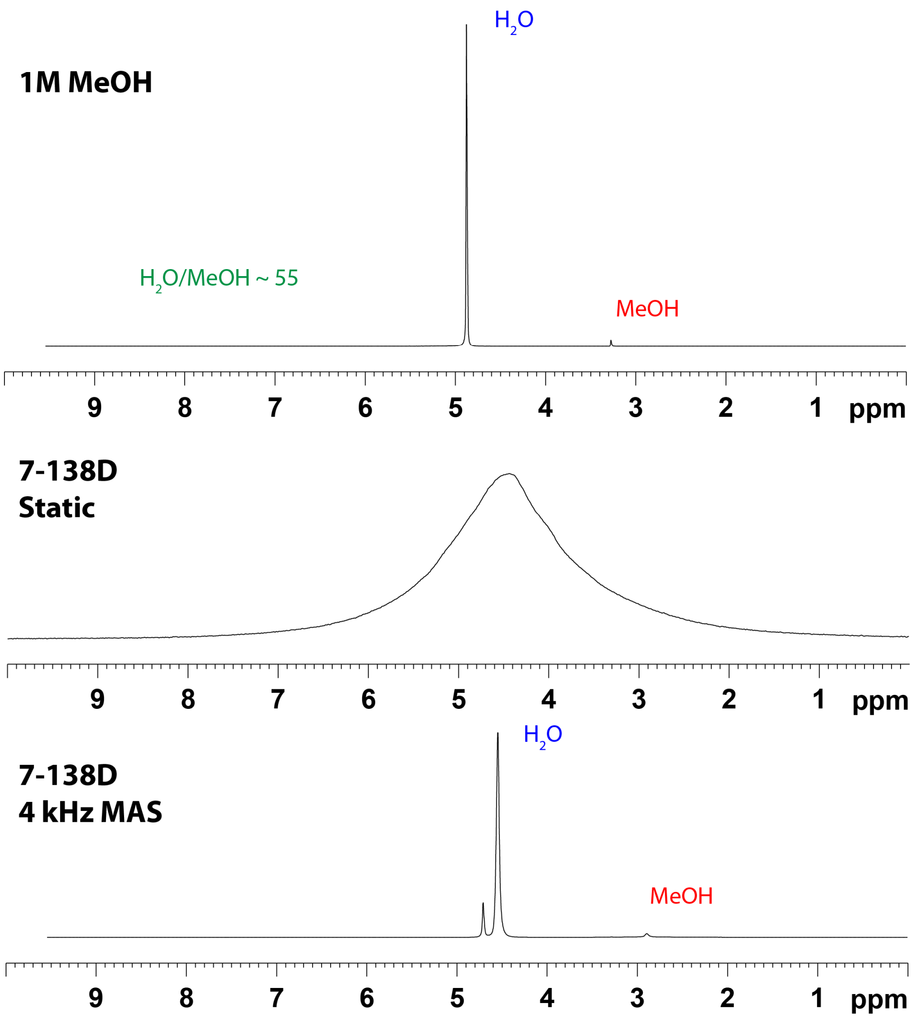
- Desalination
- Reverse Osmosis
- Electrolysis

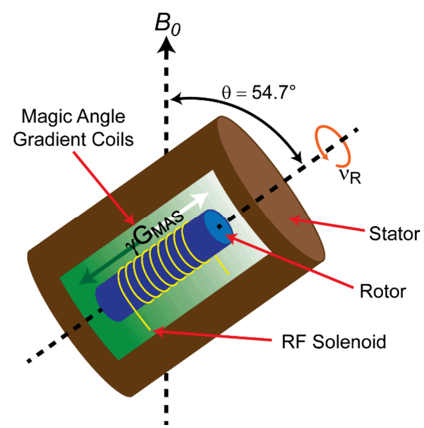
- PEM Fuel Cells
- Alkaline Fuel Cells (AEM)
- Ion Selective Electrodes

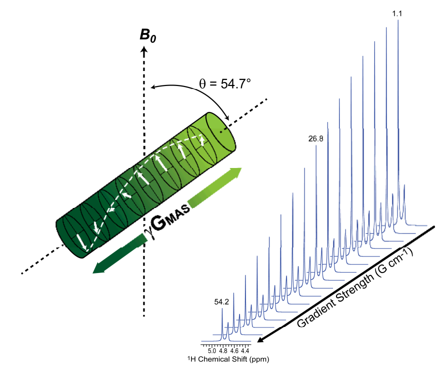
Development of new membranes materials for a wide range of technological applications ultimately based on fundamental understanding of transport.

Site Resolution in MeOH Fuel Cell Membranes

“The Odyssey Begins”



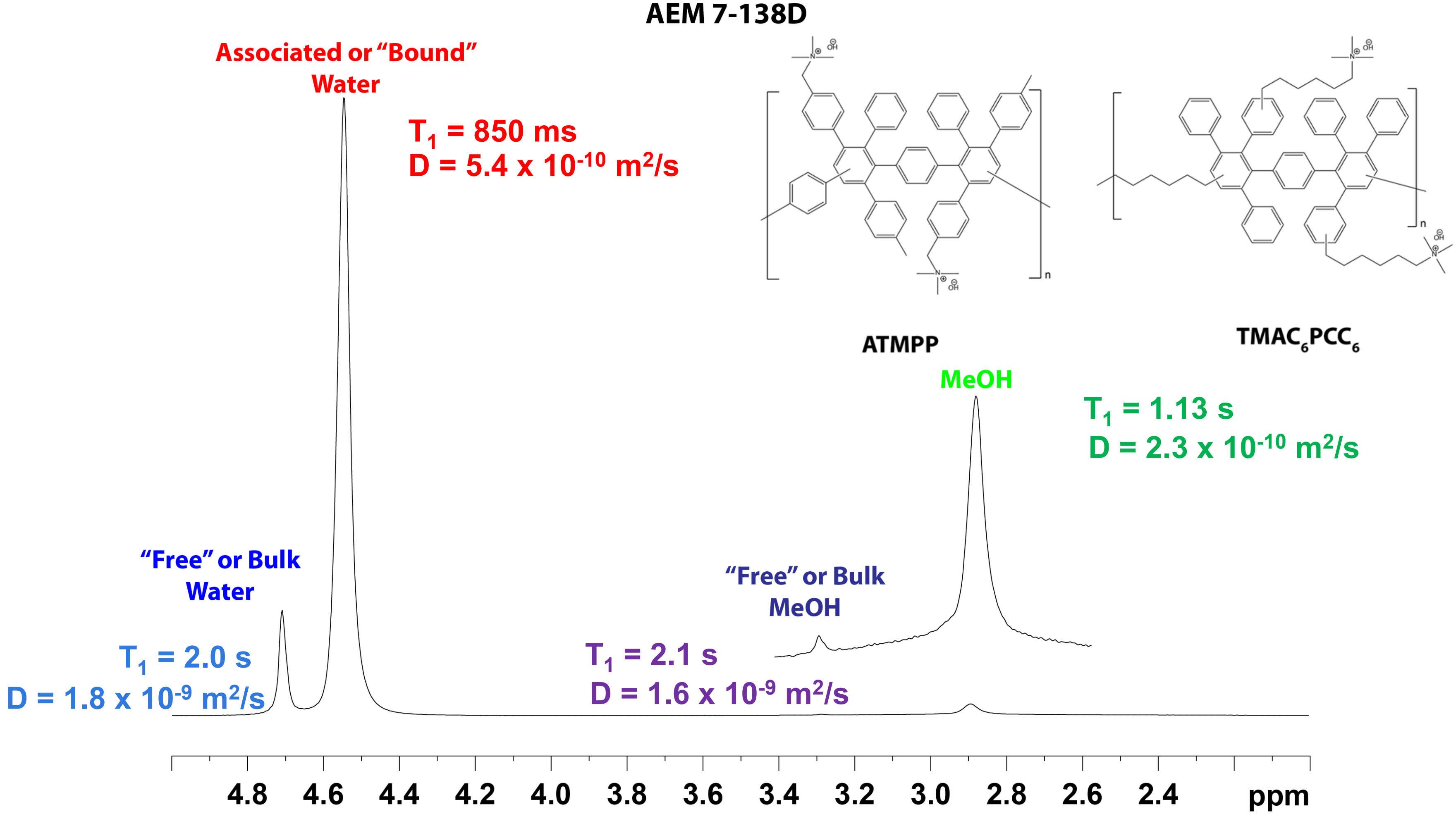




Different water environments in polymers

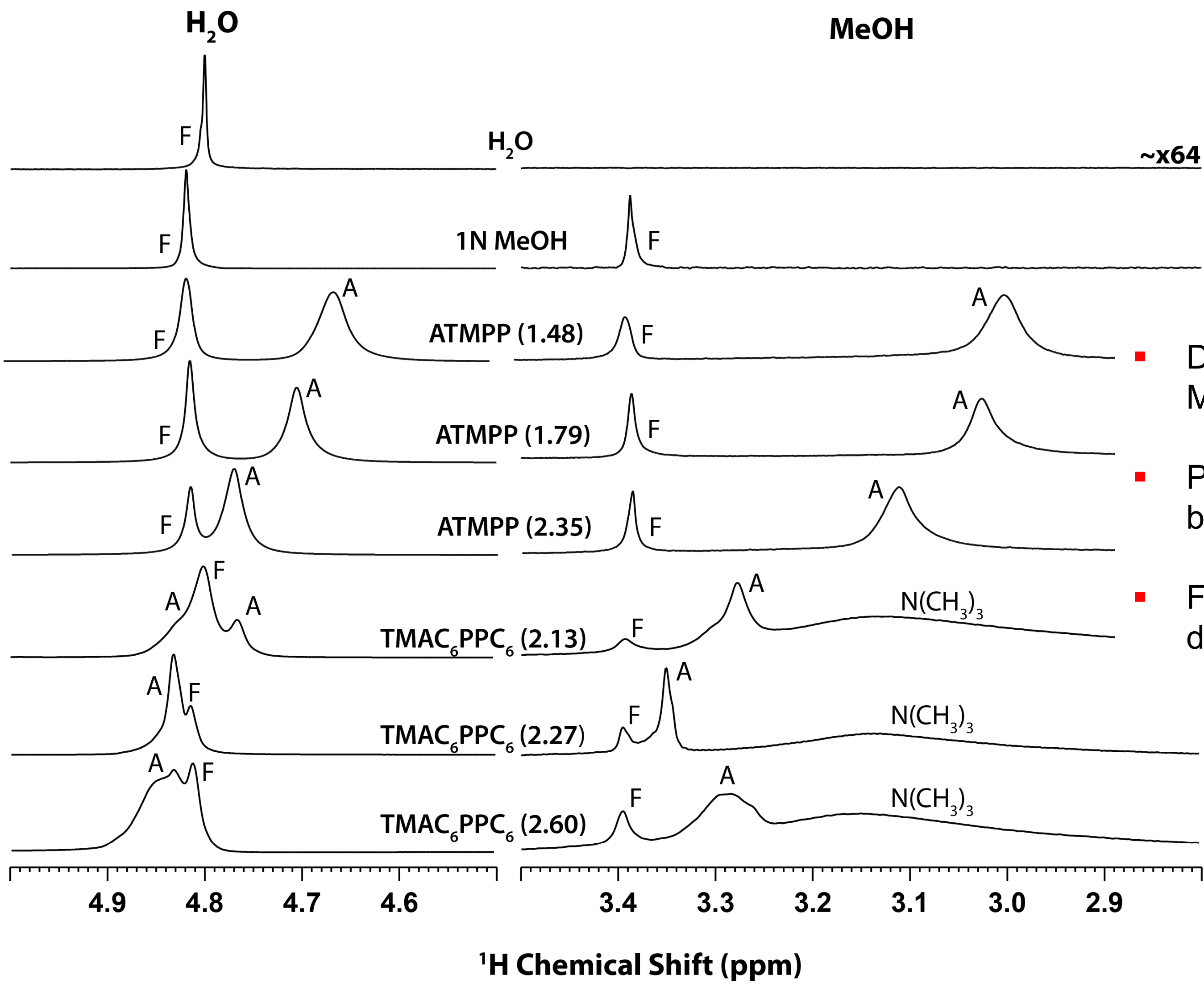
- Water in hot pressed Nafion, Jeong and Han, Bull. Korean Chem. Soc. (2009), 30, 1559.
- Water in PEEK, Baias *et al,* Chem. Phys. Lett. (2008), 456, 227; (2009) 473, 142. MAS with SSB with no chemical shift resolution.
- Mele *et al*., J. Incl. Phenon. Macrocycl. Chem. (2011), 69, 403. HRMAS resolution.

HRMAS PFG NMR and Site Resolution



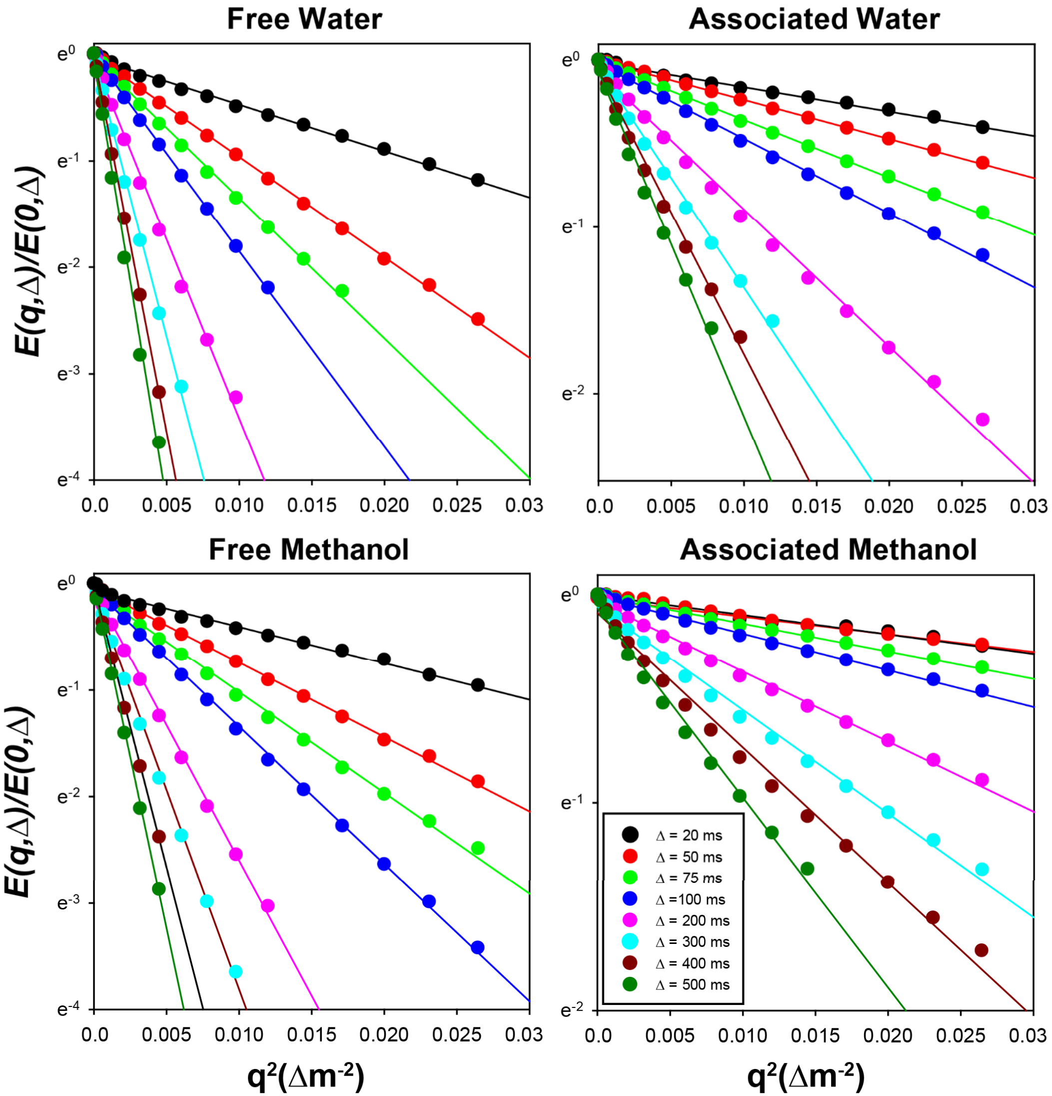
***Resolution is always exciting!* Can ask questions about differences between MeOH and water association with the membrane.**

^1H HRMAS NMR of Different AEM Membranes



- Desired differential impact on MeOH transport.
- Polymer membrane for binding of Pt catalyst.
- Function of both polymer design and IEC.

Diffusion Analysis of Individual Species



$$\langle R^2(\Delta)\rangle = -6\ln\left[E(q,\Delta)/E(0,\Delta)\right]/q^2$$

$$\langle R^2\rangle = 6Dt$$

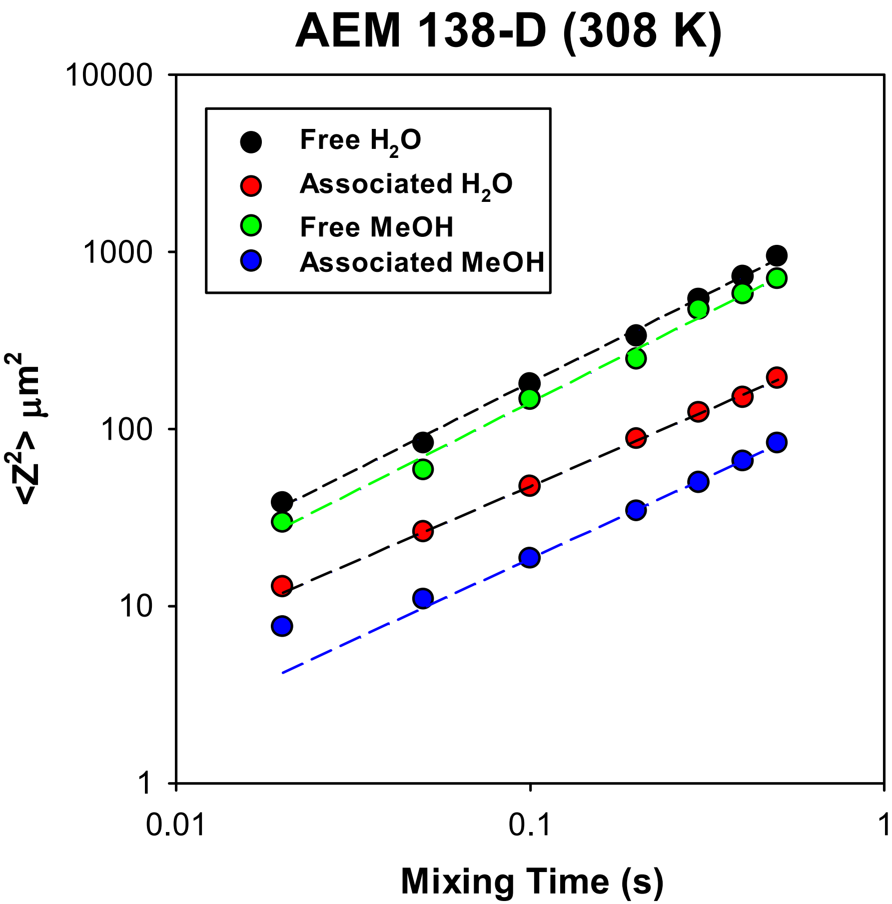
$$\langle z_M^2(\Delta)\rangle = -2\ln\left[E(q,\Delta)/E(0,\Delta)\right]/q^2$$

$$\langle z_M^2\rangle = 2D_\alpha t^\alpha$$

- **Associated diffusion is an order of magnitude slower than free species (Water and MeOH).**
- **MeOH diffusion slower than Water in both environments.**
- **The ratio of D_{assoc}/D_{free} is much smaller for MeOH, suggesting preferential association with membrane.**

Todd M. Alam and Michael R. Hibbs, “Characterization of Heterogeneous Solvent Diffusion Environments in Anion Exchange Membranes”, *Macromolecules*, **47**, 1073-1084 (2014). http://dx.doi.org/10.1021/ma402528v

Anomalous Diffusion?



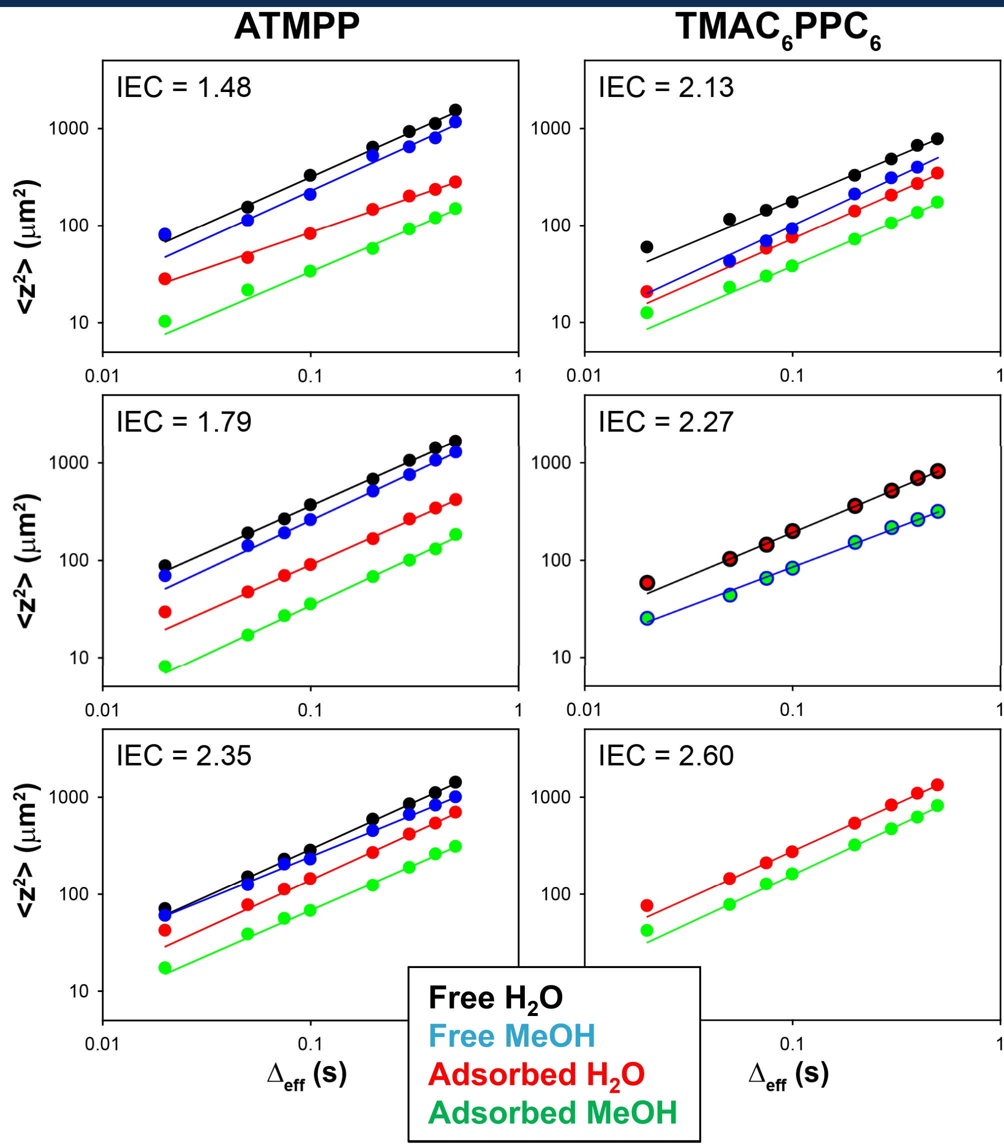
Anomalous diffusion can be expressed can be expressed through the power law.

$$\left\langle z^2 \right\rangle = 2D_\alpha \Delta^\alpha$$

α = 1, normal diffusion
α < 1, sub-diffusive
α ~ 0.7 2D fractal

Disappears with increasing temperature.

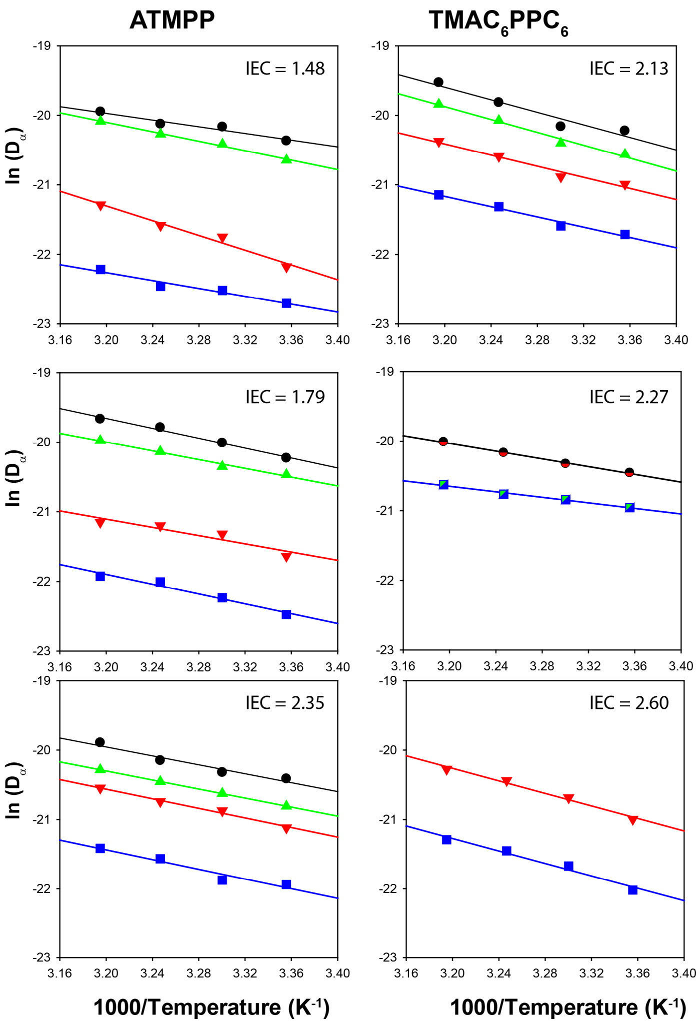
Diffusion Analysis of Individual Species



- Extract $<z^2>$ from multiple different Δ delays in PFG NMR
- Evaluate possibility of anomalous diffusion ($\alpha \neq 1$).
- Most systems show normal diffusion. As expected in these membranes.
- Associated water environment reveal fractal diffusion at lower hydration/temperatures.
- Activation energies (E_a) higher for associated species.

Todd M. Alam and Michael R. Hibbs, "Characterization of Heterogeneous Solvent Diffusion Environments in Anion Exchange Membranes", *Macromolecules,* **47**, 1073-1084 (2014). http://dx.doi.org/10.1021/ma402528v

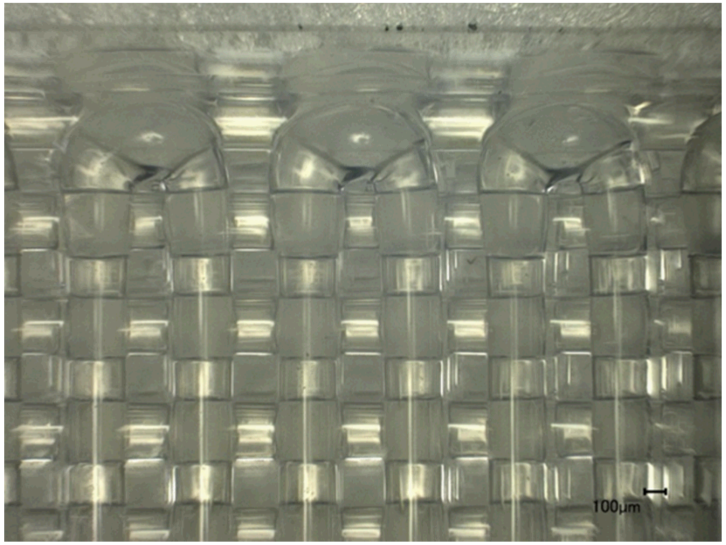
Activation Energies

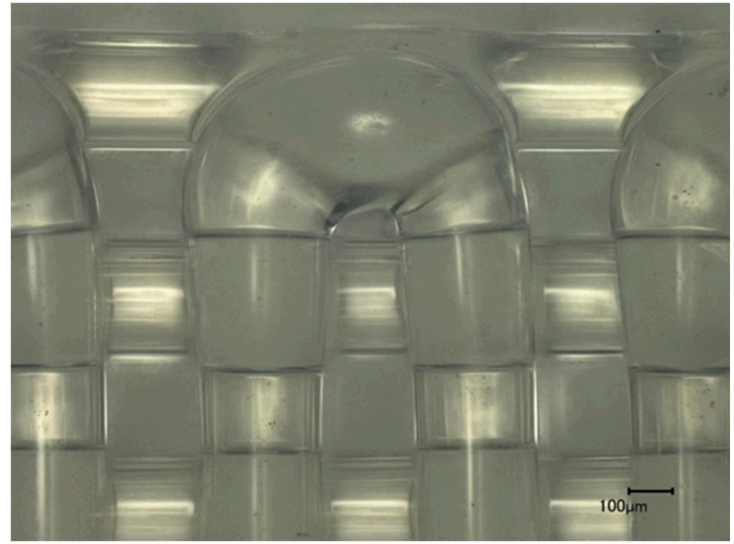


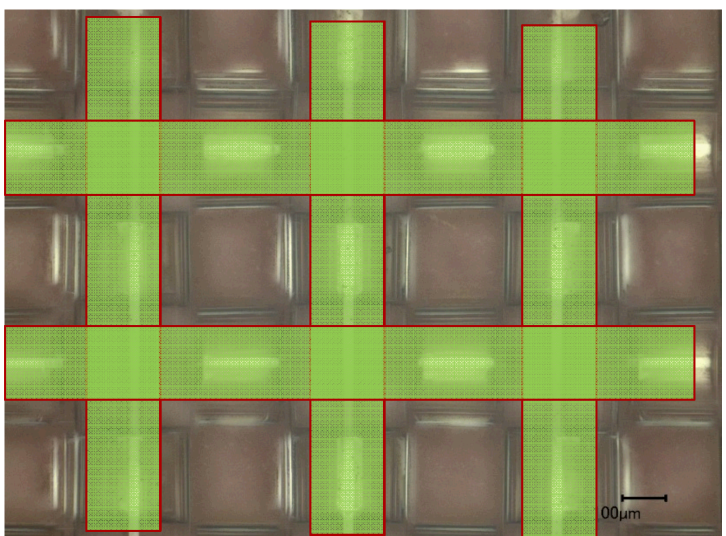
Sample (IEC)	E_a (kJ/Mol)			
	F-H_2O	A-H_2O	F-MeOH	A-MeOH
1N MeOH	26.0	--	27.0	--
ATMPP (1.48)	20.0		28.3	23.6
ATMPP (1.79)	29.7	24.5	26.2	29.4
ATMPP (2.35)	26.7	28.7	27.0	29.2
$TMAC_6PCC_6$ (2.13)	37.6		38.6	30.6
$TMAC_6PCC_6$ (2.27)	--	23.2	--	16.5
$TMAC_6PCC_6$ (2.60)				

- Results similar to Nafion and Nafion composites.
- No direct comparison because individual water environments not investigated.

Solvent Diffusion in 3D Printed Materials

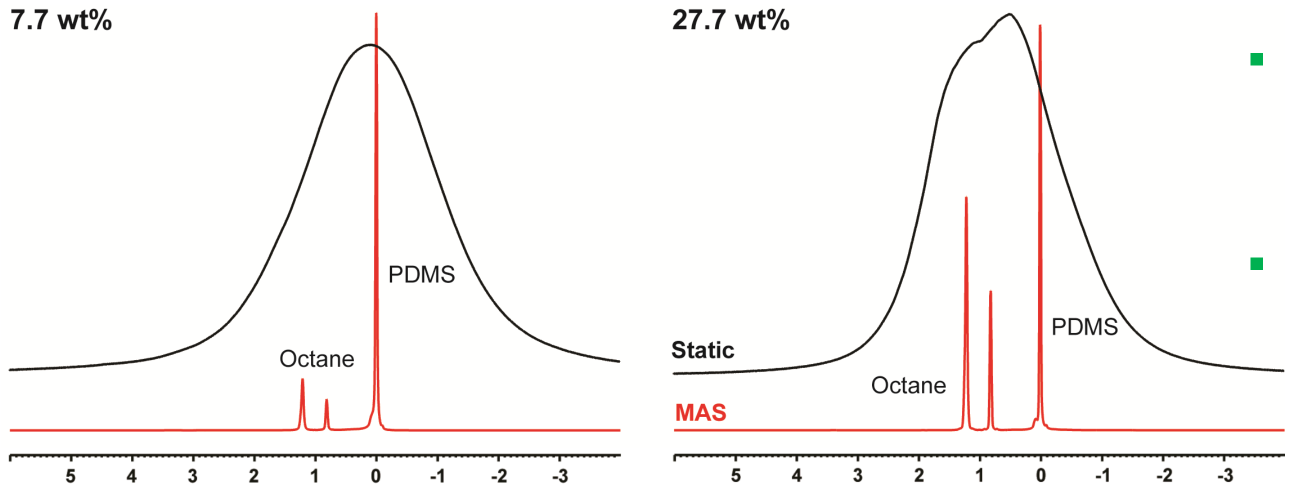






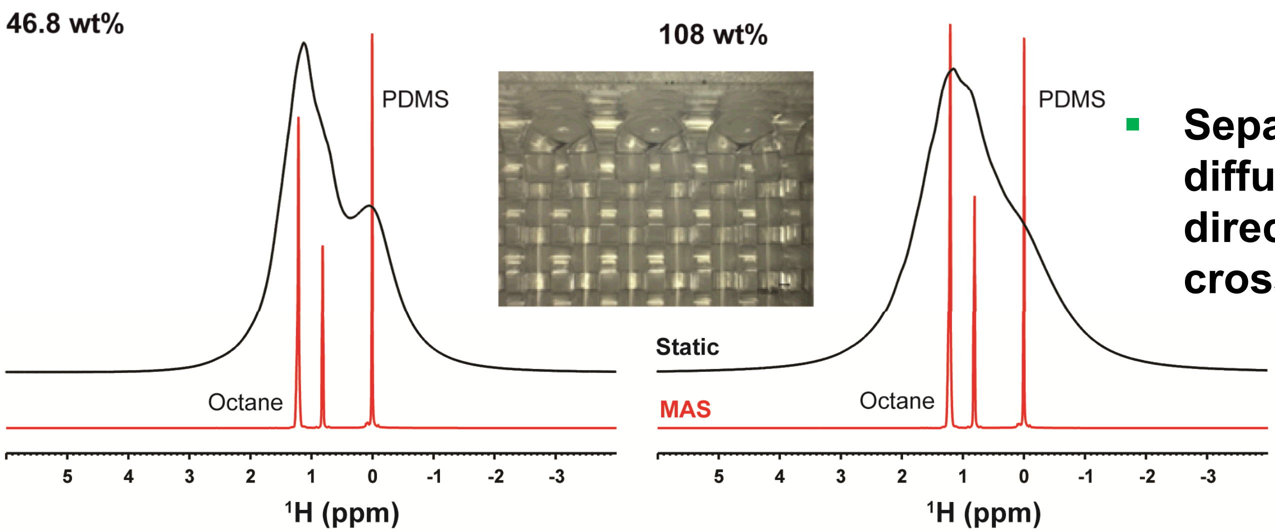
- **Direct-write of Corning SE1700 siloxanes.**
- **Multi-layer (4 to 8 layers).**
- **Variable write and spacing (200 – 400 μm).**
- **Different cure protocol.**
- ***Diffusion of different penetrants?***

Penetrant Diffusion in 3D Printed Silicone Materials



- **HRMAS NMR allows resolution of penetrant diffusion.**
- **Especially at low swelling concentrations (Q).**

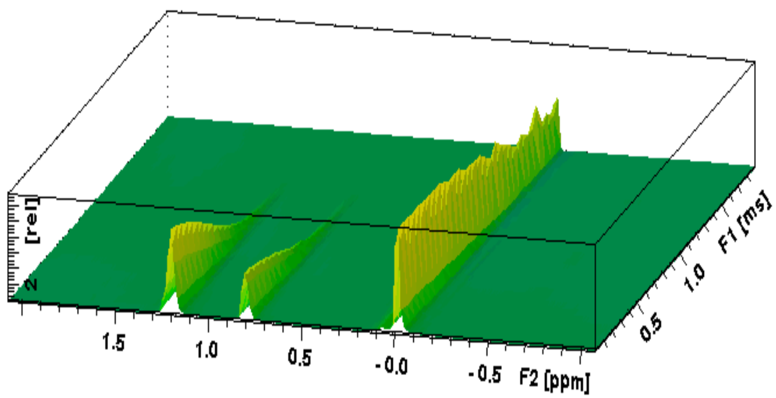
Dow Corning SE1700



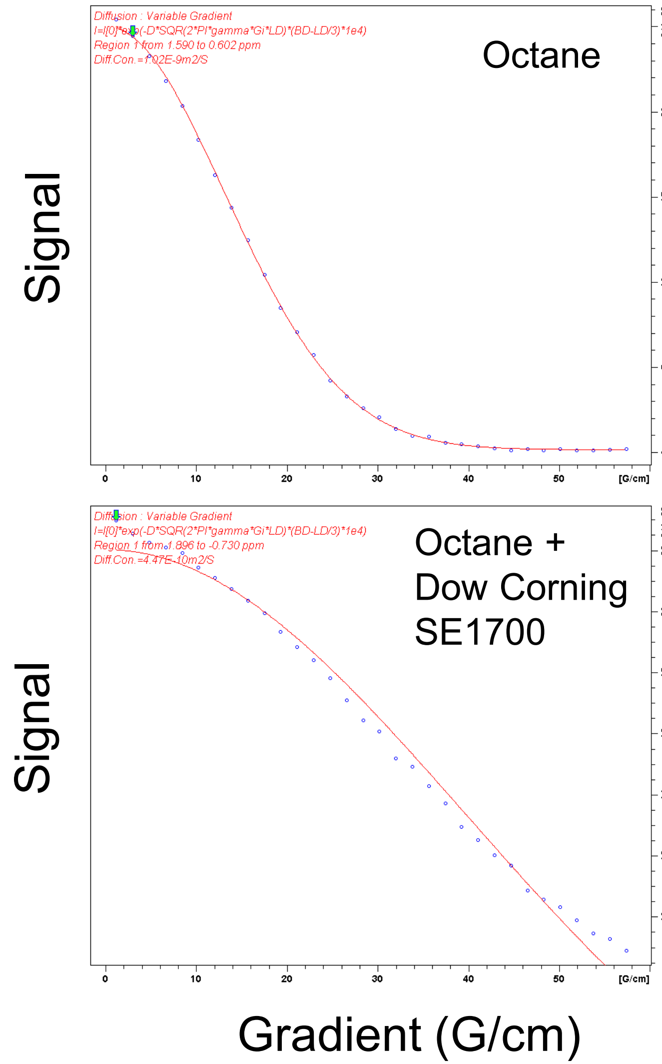
- **Separation in static PFG NMR diffusion experiments impacted directly by degree of PDMS cross-linking.**

Overlap in Diffusion Signal Decay

HRMAS NMR PFG Diffusion

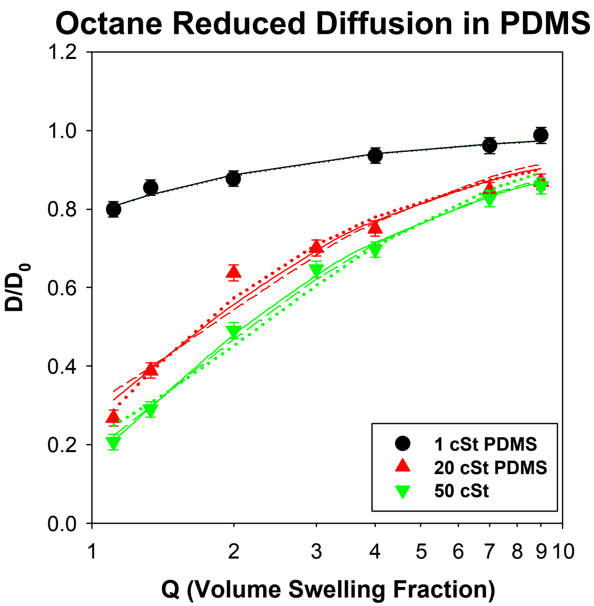


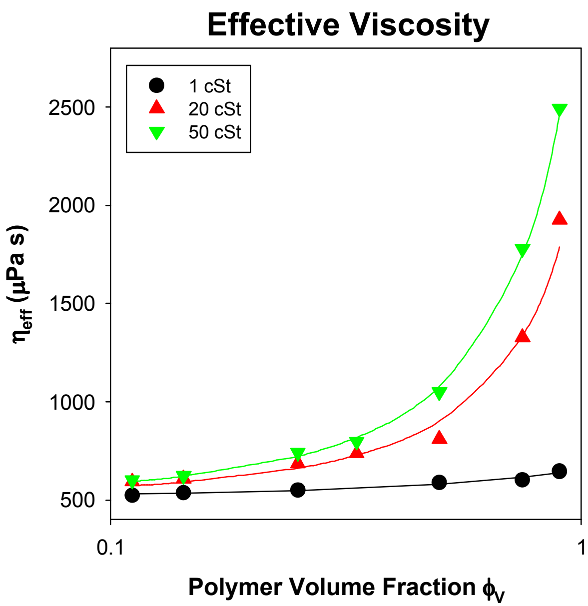
- **No need to separate/extract slowly decaying siloxane signal from mobile octane penetrant.**



Diffusion of Penetrants in Polymers

Linear PDMS





Fujita (Free Volume)

$$\frac{D}{D_0} = \exp\left\{\frac{-B\left(f_s - f_p\right)}{\left(Q-1\right) f_s^2 + f_s f_p}\right\}$$

$$Q = \frac{1}{\varphi_p} = \frac{V}{V_0} = \frac{\left(V_s + V_p\right)}{V_p}$$

Phillies (Stretch Exponential)

$$\frac{D}{D_0} = \exp\left\{-\alpha Q^{-\nu}\right\}$$

Petit (Hydrodynamic)

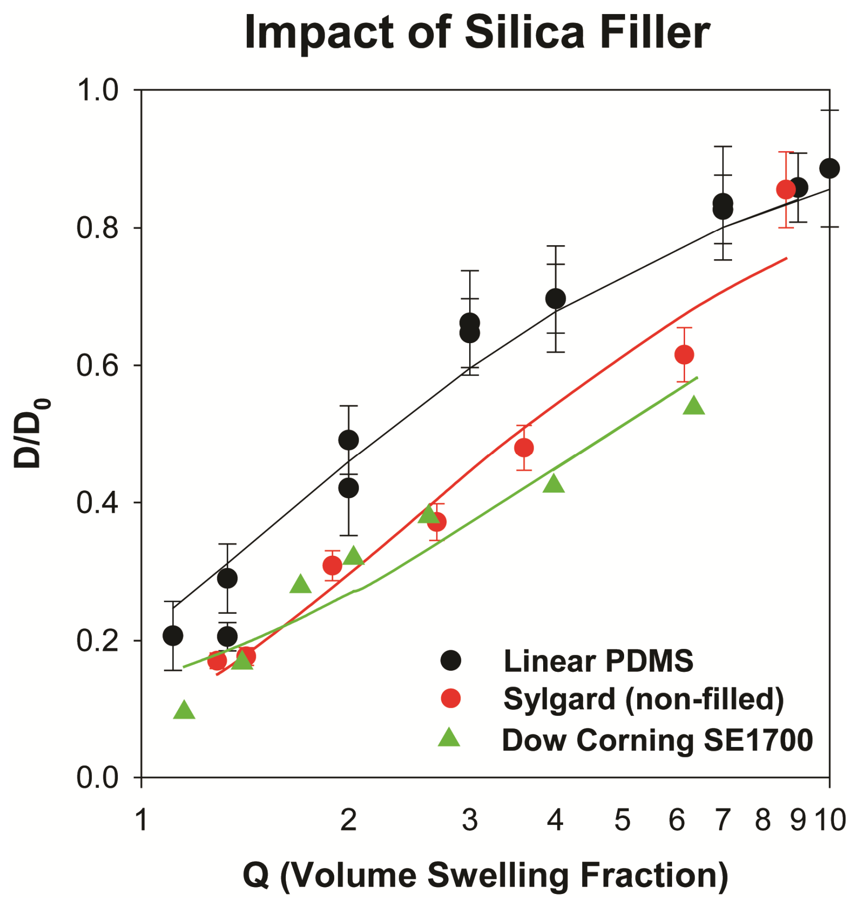
$$\frac{D}{D_0} = \frac{1}{1+\alpha Q^{-2\nu'}}$$

$$D = kT / \zeta$$

- **Diffusion is dependent on concentration of penetrant!**
- **Behavior varies with the polymer/penetrant system.**
- **“Local” effective viscosity can extracted from D/D_0.**

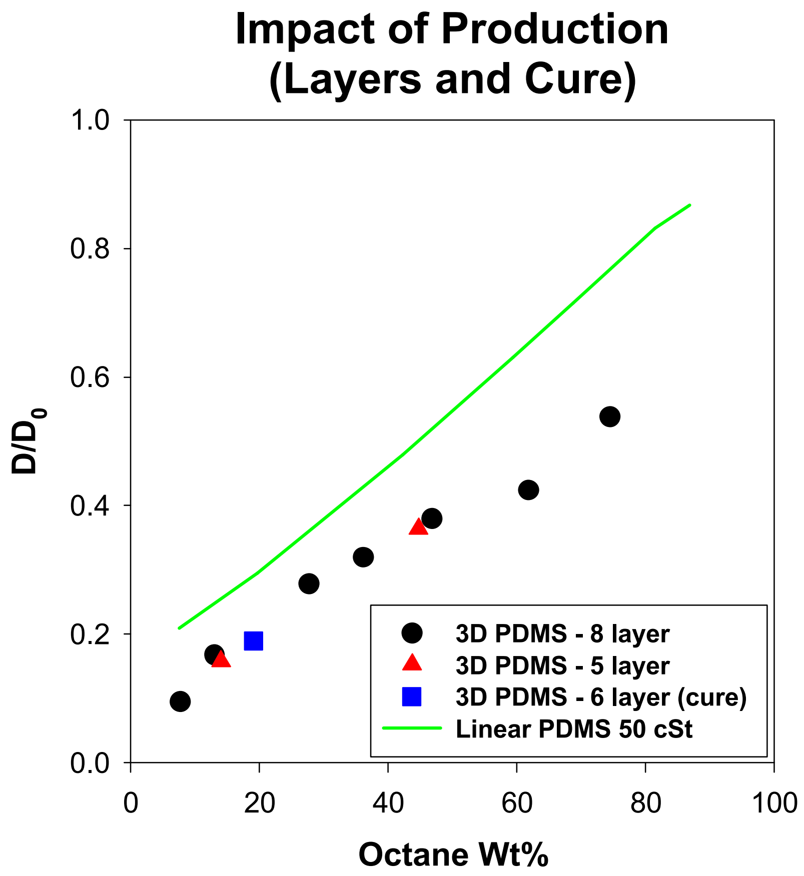
[1] Vrentas, Duba (1977) *J. Polym. Sci.*, **126**, 177-186. [2] Phillies, (1989) *J. Phys. Chem.*, **93**, 5029-5039.
[3] Petit, Roux, Zhu, MacDonald (1996), *Macromolecules*, **29**, 6031-6036.

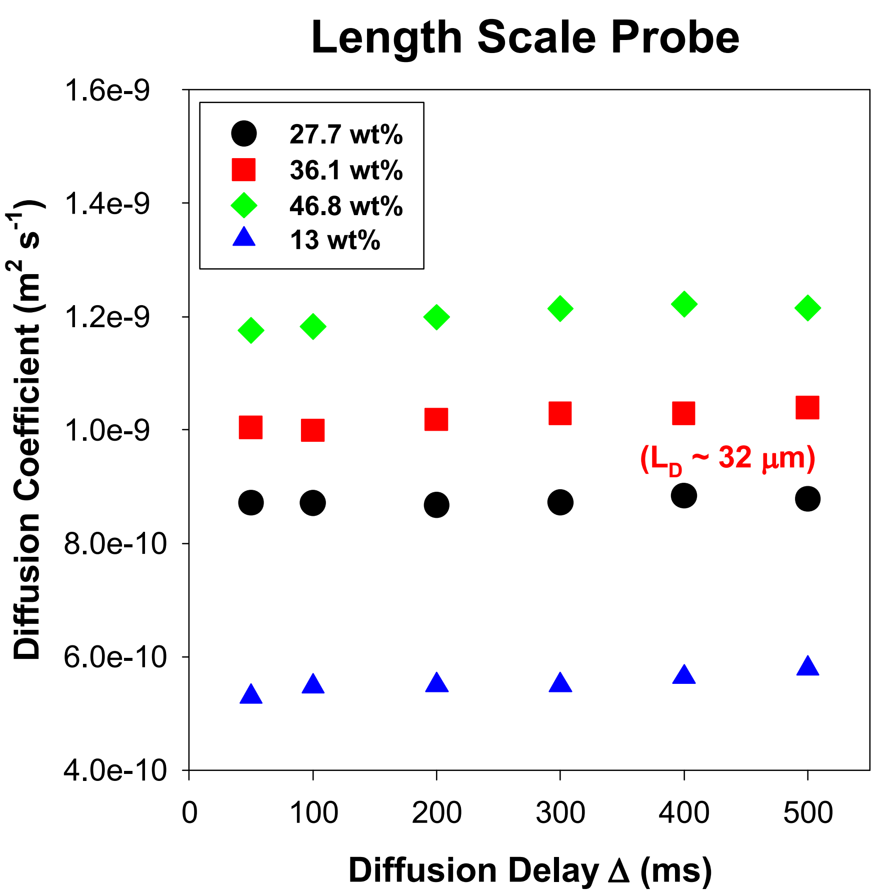
Diffusion of 3D Printed Siloxanes



- **Reduction diffusion in filled PDMS is present.**
- **Differences increase with degree of swelling.**

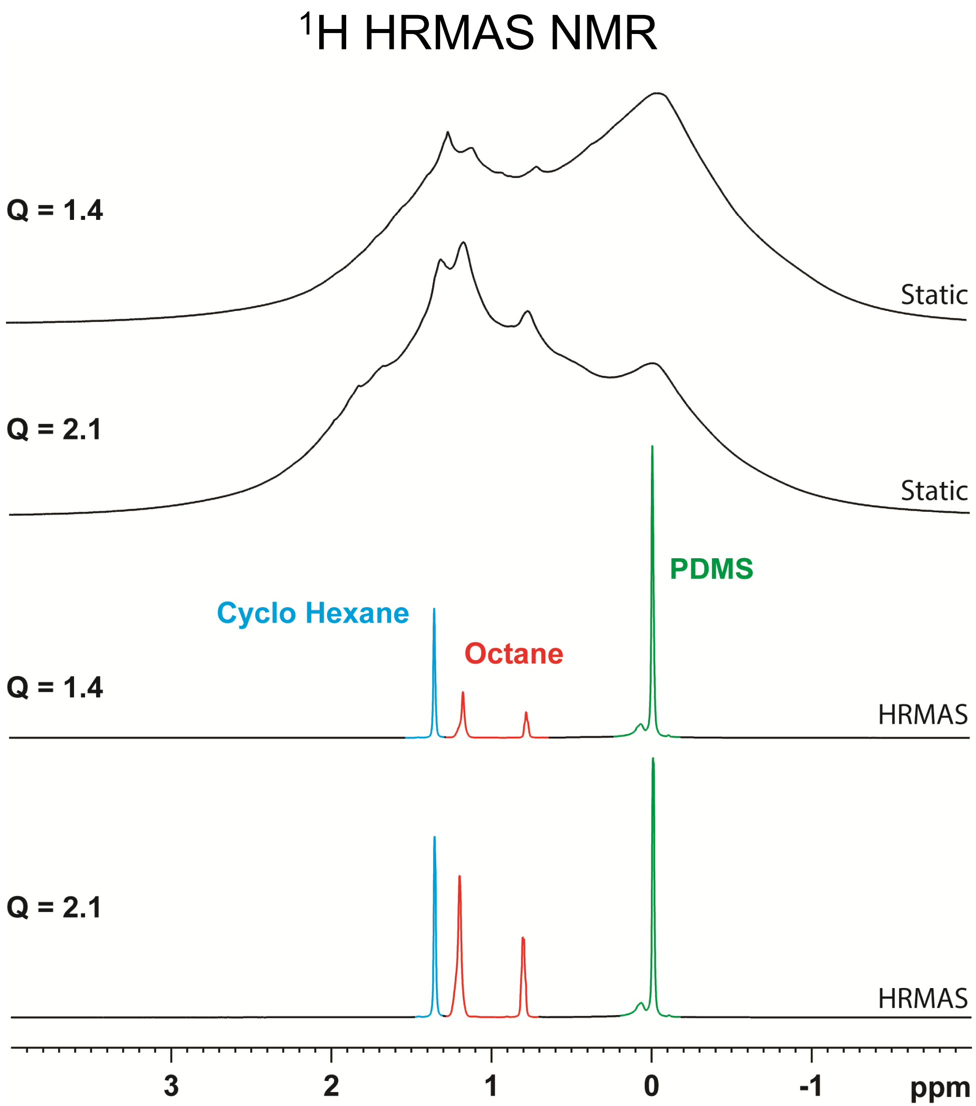
Diffusion of 3D Printed Siloxanes





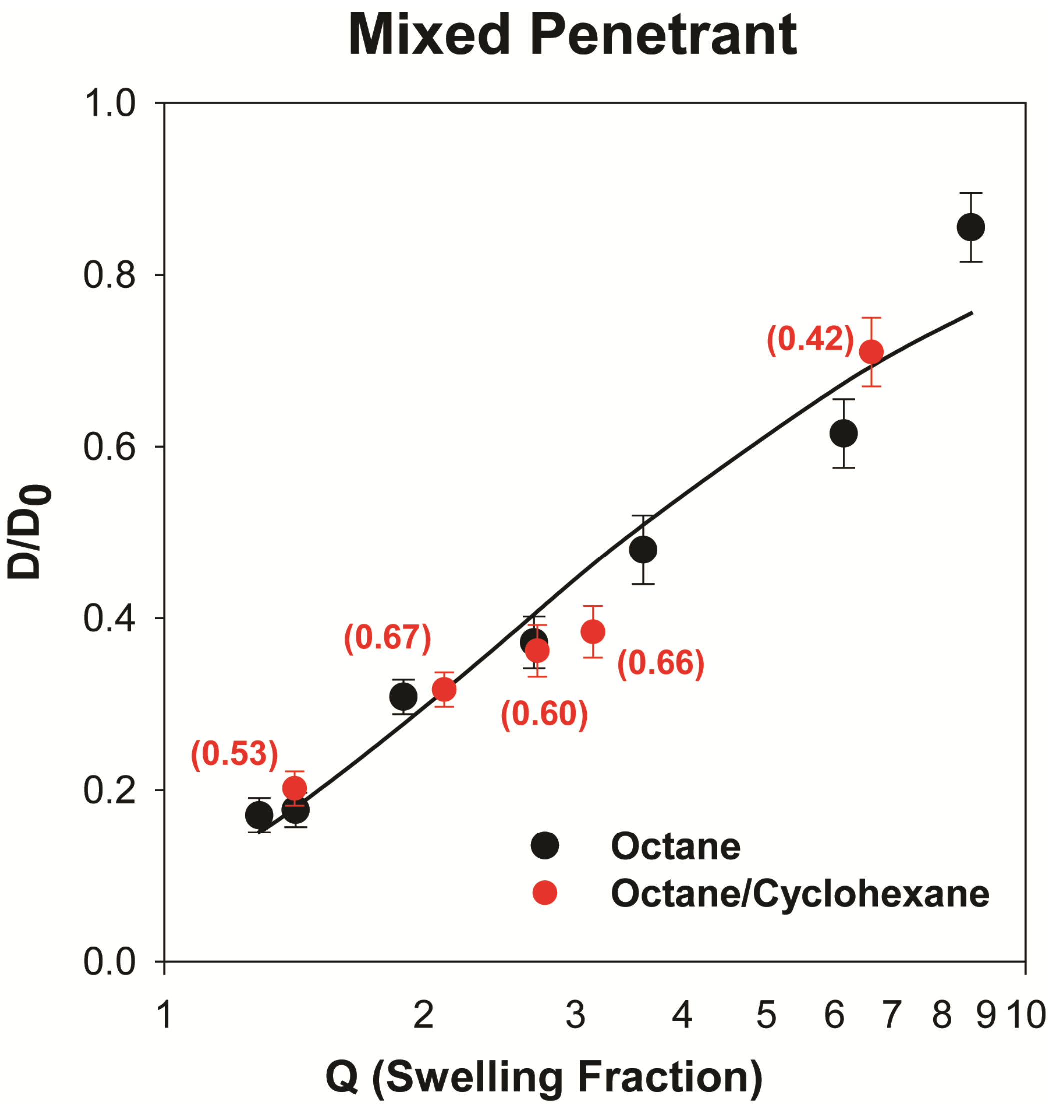
- No impact on number of direct-write layers on overall diffusion.
- No restricted diffusion on 10-50 μm length scale (homogeneous diffusion).
- Diffusion is not the answer to the residual stress effects (….layer gradient….)

Penetrant Mixtures in Swollen Siloxanes

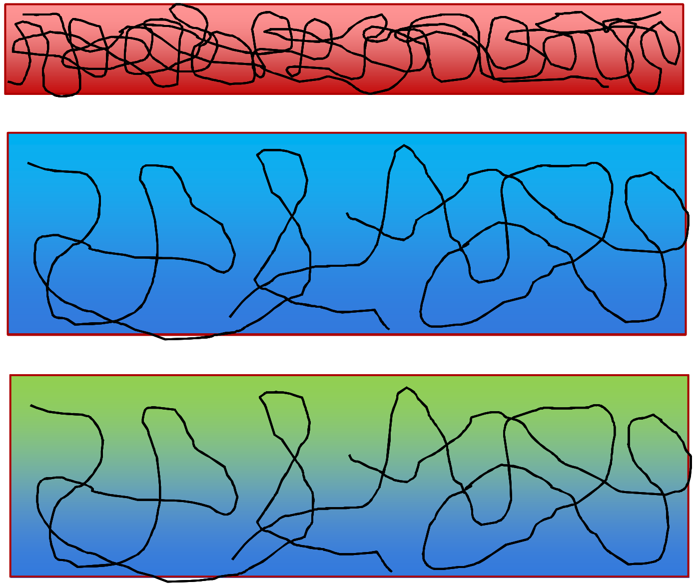


- **Different penetrants are unresolved under static conditions.**
- **Well resolved under HRMAS allowing individual diffusion constants to be measures.**
- **Also reveals differential PDMS species in swollen material.**

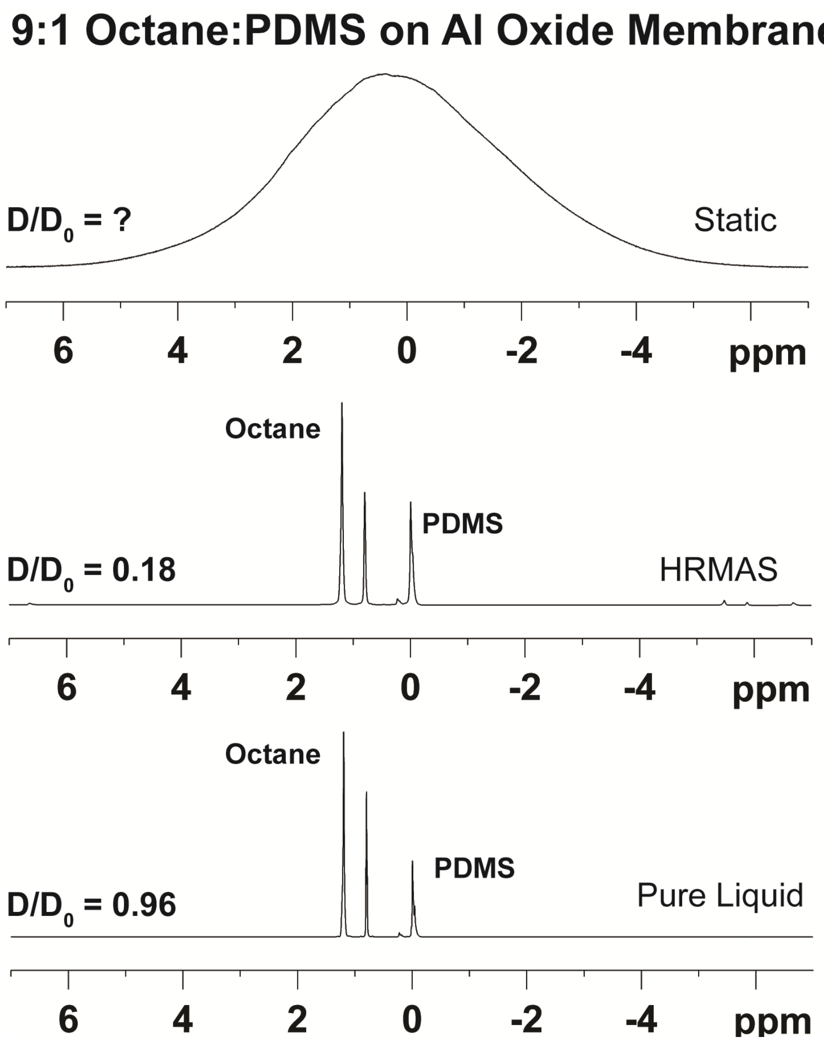
Diffusion for Penetrant Mixtures

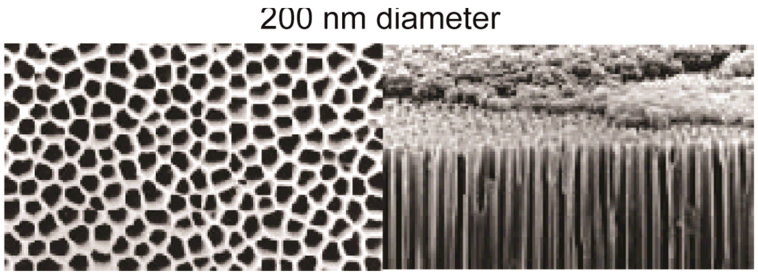


- Diffusion of penetrants not strongly impact by solvent fraction [octane/(octane+cyclohexane).
- Diffusion well described by simple free volume description.
- ***Need to investigate non-ideal solvent mixtures to identify preferential surface interactions.***



Resolution in Nanoporous Membrane Polymer Composites





- Example of surface interactions and confinement impacting diffusion.
- Adsorption into Al oxide membrane reduces diffusion of octane by a factor 5.
- Not a simple free volume effect!

Diffusion in Nanoporous Membrane Polymer Composites (20 nm)

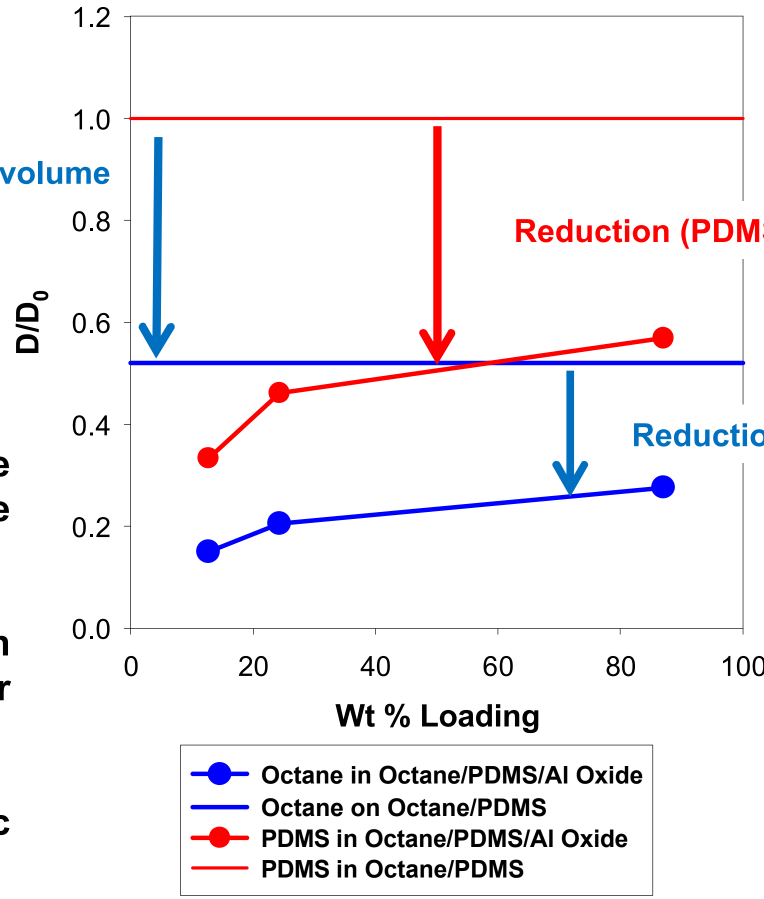
Reduced Diffusion in Aluminum Oxide Membranes

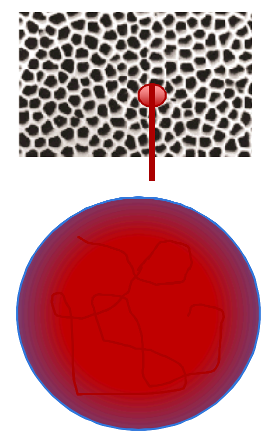
$$\zeta_{avg} = \frac{V_{surf}\zeta_{surf} + V_{free}\zeta_{free}}{\left(V_{surf} + V_{free}\right)}$$

Reduction due to polymer free volume

Reduction (PDMS) due to surface induced friction

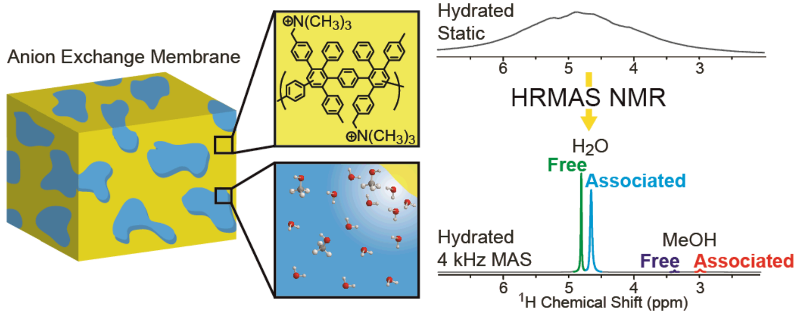
Reduction due to surface induced friction





- **Cleary an impact of the confinement near the surface.**
- **Ratio of surface friction reduction similar for PDMS and Octane.**
- **Not resolvable in static PFG experiment.**

Conclusions



- **HRMAS PFG NMR does provide improved spectral resolution and is a novel tool to study diffusion in heterogeneous polymer materials and composites.**
- **Not a "cure all"…many system not amendable to these efforts. Gradient limited: 55 G/cm versus 1250 to 3000 G/cm on standard diffusion instrumentation.**
- **The picture of MeOH fuel cell membrane had evolved from a homogeneous (single diffusion constant) to a description of multiple diffusion environments produced by differential chemical interactions.**
- **Ideal tool to measure diffusion in siloxane materials – especially for mixed solvents!**
- **In the case of 3D printed siloxane concentration dependent diffusion described well by free volume models.**
- **In Al-oxide membrane : Polymer composites surface interactions play an more dominant role.**

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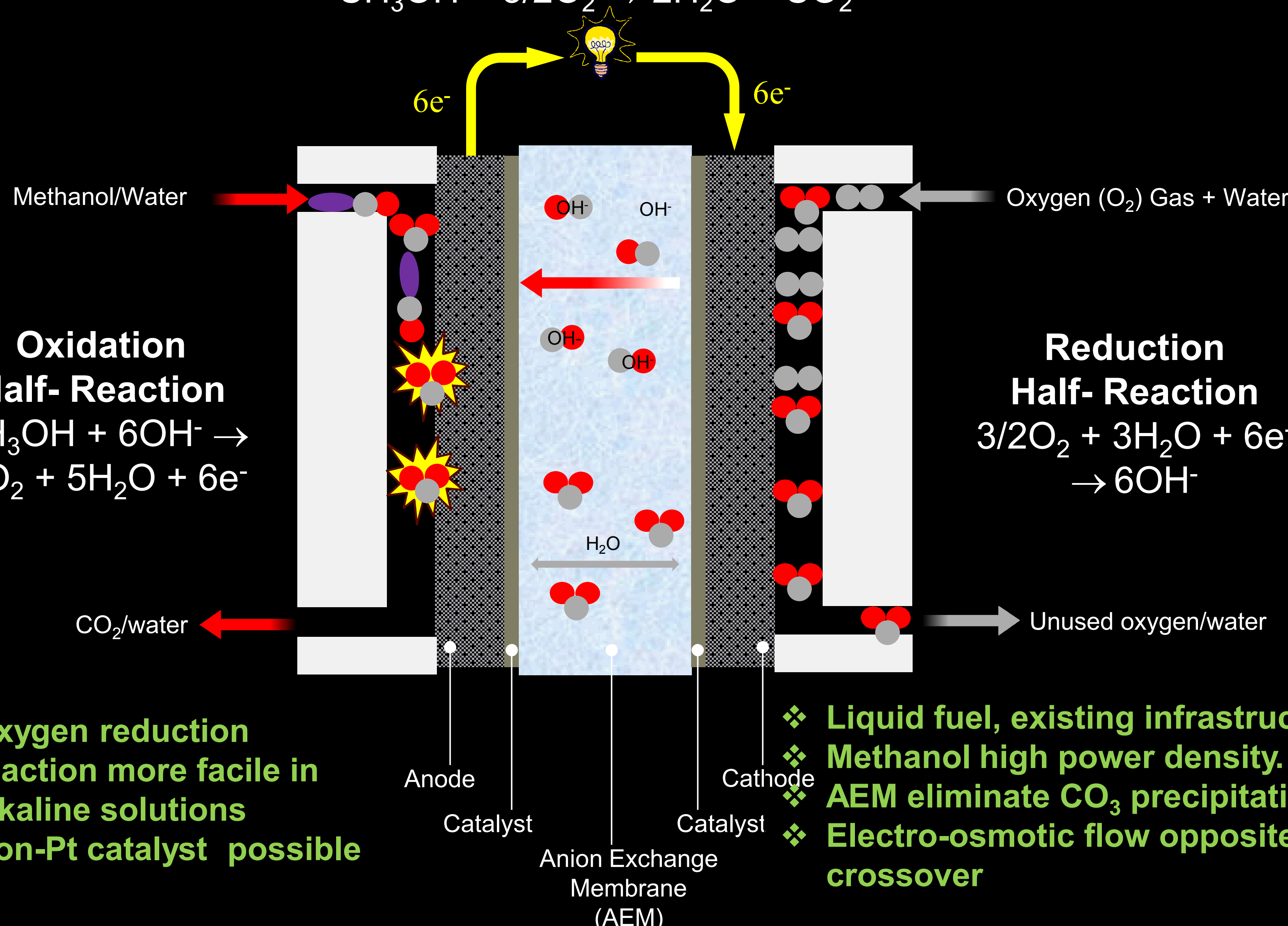
Backup Slides

AEM Direct Methanol Fuel Cell

$$CH_3OH + 3/2O_2 \rightarrow 2H_2O + CO_2$$



Oxidation Half- Reaction

$$CH_3OH + 6OH^- \rightarrow CO_2 + 5H_2O + 6e^-$$

Reduction Half- Reaction

$$3/2O_2 + 3H_2O + 6e^- \rightarrow 6OH^-$$

- **Oxygen reduction reaction more facile in alkaline solutions**
- **Non-Pt catalyst possible**

- **Liquid fuel, existing infrastructure**
- **Methanol high power density.**
- **AEM eliminate CO_3 precipitation**
- **Electro-osmotic flow opposite crossover**

Pulse Field Gradient
PFG NMR

Fuel Cells & Desalination

Theory of Conductivity

Example AEM and PEM

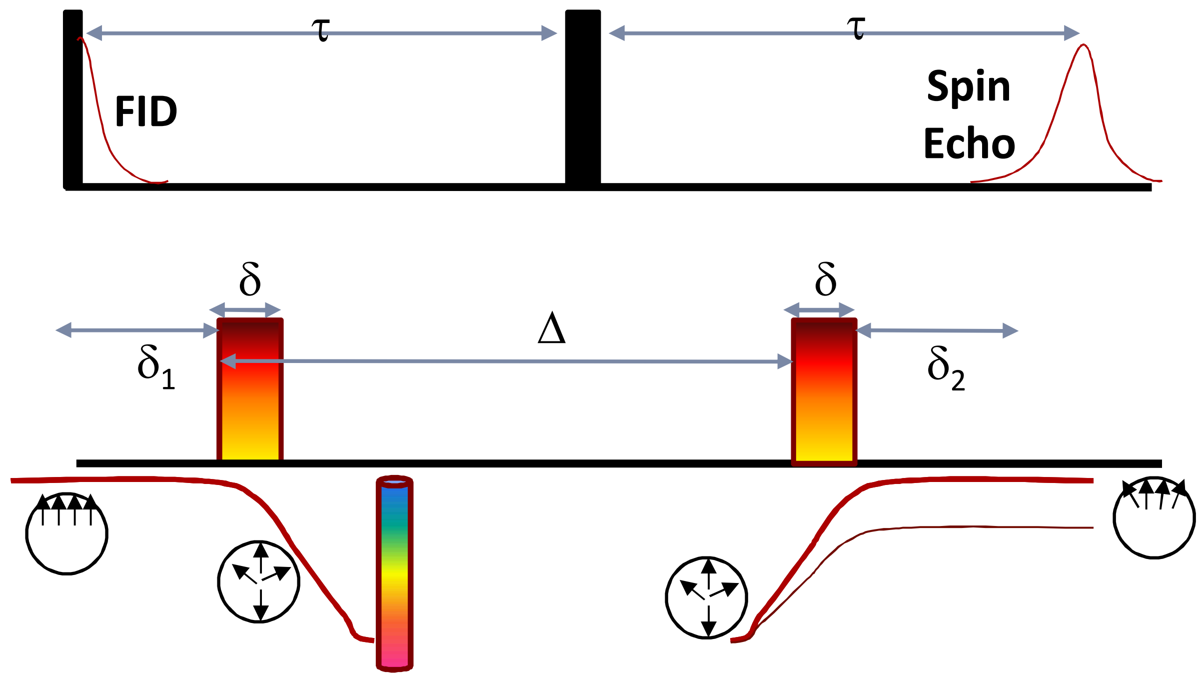
Nanostructure Motivation

Aging Effects

Di-Block Polymers

Tri-Block Polymers

Conclusions



$$B(t,\vec{r}) = (B_0 + B(t,z))$$

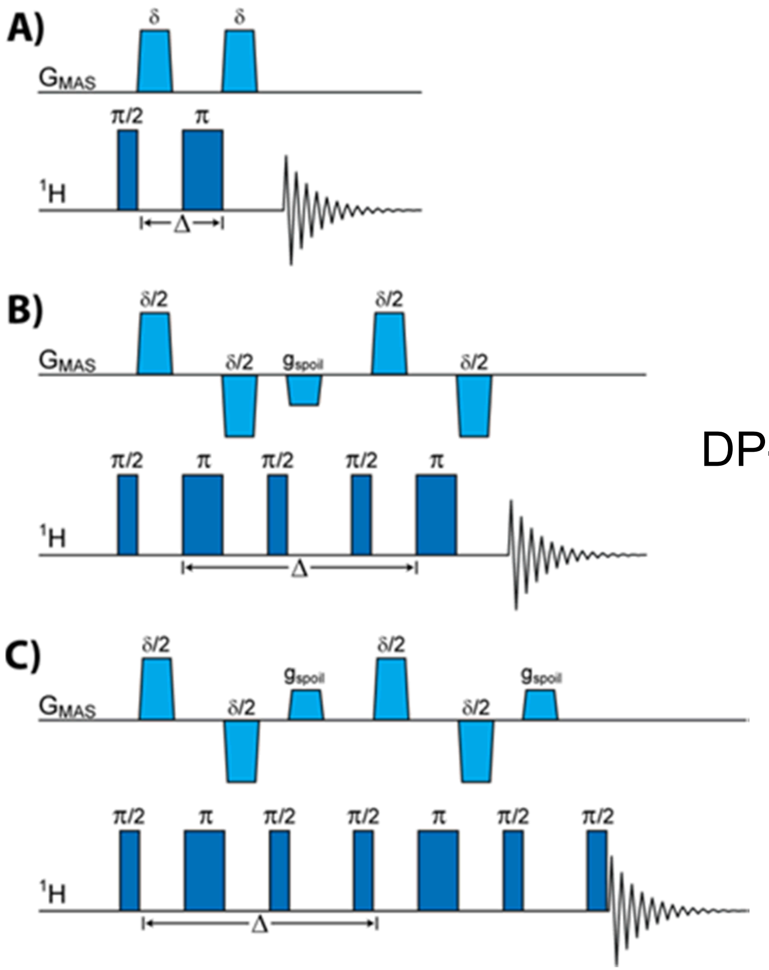
$$B(t,z) = g(t)\cdot z = \frac{\partial B_z(t)}{\partial z}$$

$$\omega(t,z) = \gamma B_0 + \gamma g(t)\cdot z$$

$$\phi(z) = \int \omega(t,z)dt = \gamma\cdot z \int_{\delta_1}^{\delta_1+\delta} g(t)dt$$

- The loss of signal is due to incomplete refocusing as a result of diffusion.
- The ϕ is dependent on position and gradient strength.
- Higher positional resolution requires increased gradient strength.

High Resolution Magic Angle Spinning (HRMAS) Pulse Field Gradient (PFG) Diffusion Experiments



DP-STE

Figure 9: Diffusion pulse sequences. Pulse Field Gradient (PFG) A) Spin-Echo, B) PFG Stimulated Echo with dipolar gradients and spoil gradient based on Cotts *el al.* 13-interval sequence[85], and C) PFG Stimulated Echo with dipolar gradients and spoil gradient with an additional eddy current delay. G_{MAS} indicates that the gradient is applied along the magic angle.

Shimming The Probe Under High Resolution Magic Angle Spinning (HRMAS)

$B_{Z}^{MAS} = \frac{1}{\sqrt{3}} B_{Z}^{Lab} - \frac{\sqrt{2}}{\sqrt{3}} B_{X}^{Lab}$
$B_{Z^2}^{MAS} = B_{(Z^2-Y^2)}^{Lab} - 2\sqrt{2} B_{ZX}^{Lab}$
$B_{Z^3}^{MAS} = -\frac{2}{3\sqrt{3}} B_{Z^3}^{Lab} - \frac{1}{\sqrt{6}} B_{Z^2X}^{Lab} + \frac{5}{\sqrt{3}} B_{Z(X^2-Y^2)}^{Lab} - \frac{5}{3\sqrt{6}} B_{X^3}^{Lab}$
$B_{Z^4}^{MAS} = -\frac{7}{18} B_{Z^4}^{Lab}$
$B_{Z^5}^{MAS} = -\frac{1}{6\sqrt{3}} B_{Z^5}^{Lab}$

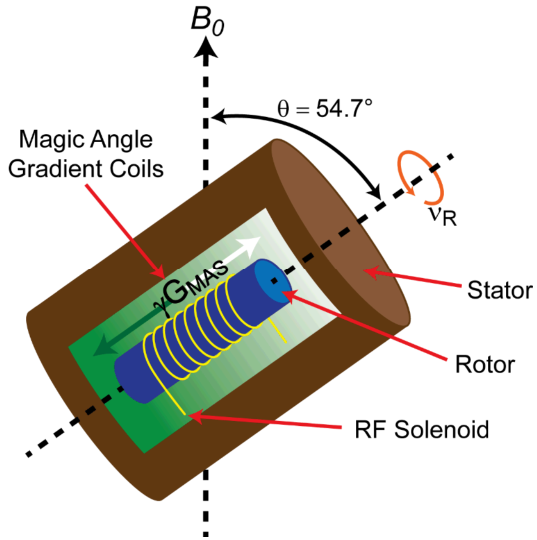
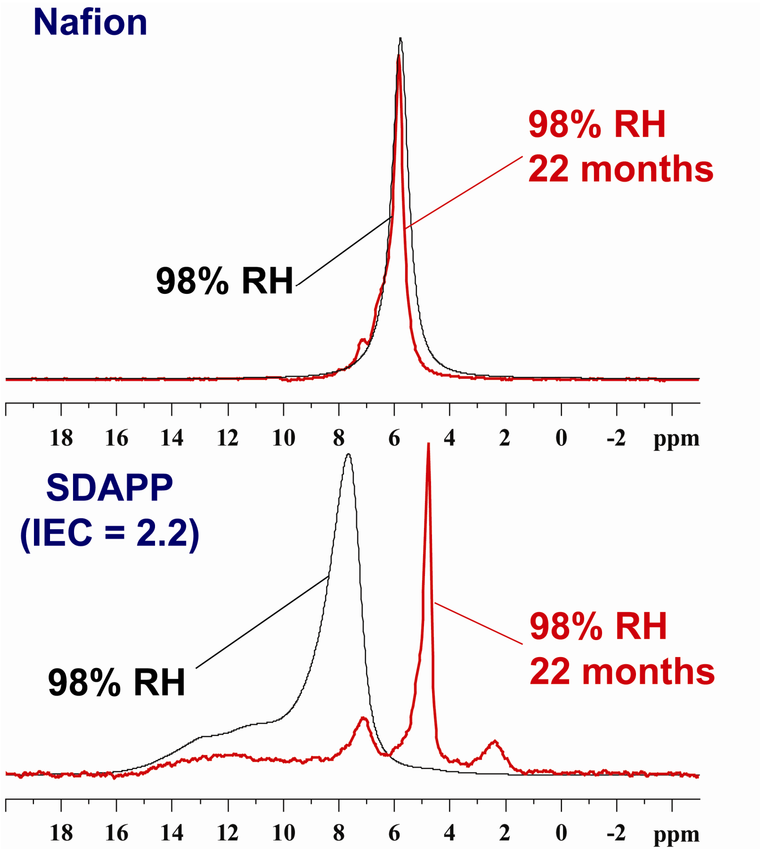
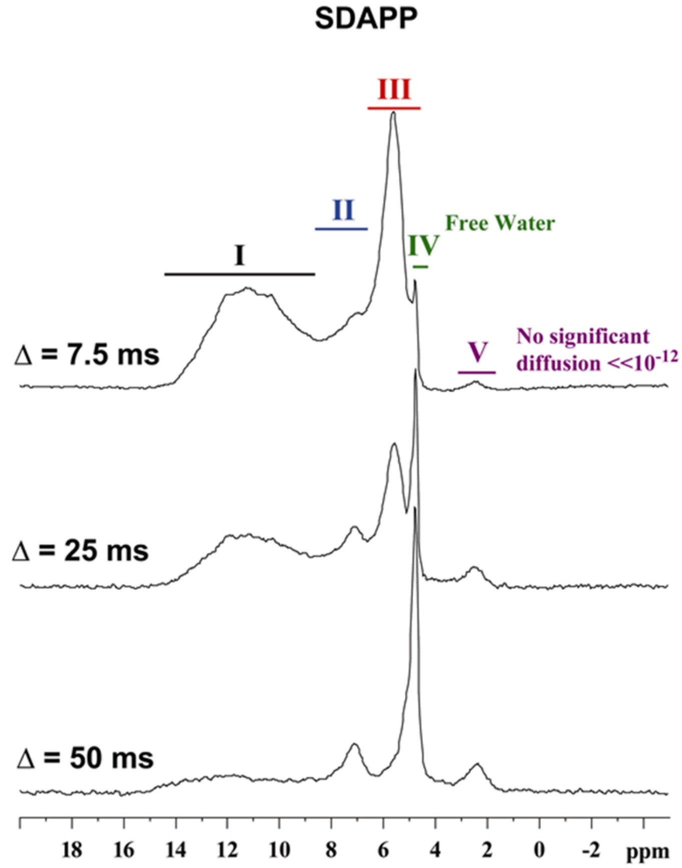


Table 1: MAS shims in terms of laboratory (Lab) frame[25]

PFG NMR and Site Resolution

Pulse Field Gradient (PFG) NMR used to measure diffusion.

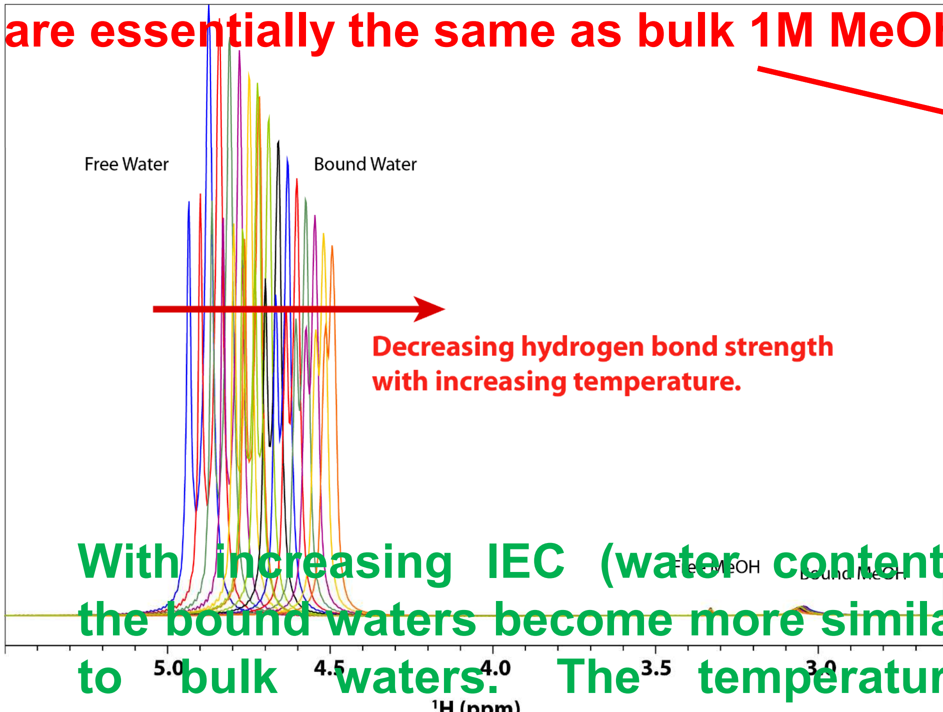




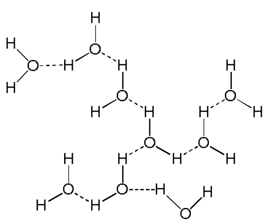
Under static PFG NMR we have occasionally observed different water environments, but the lack of resolution was never considered an issue!

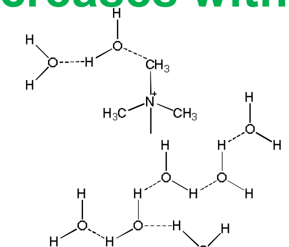
Temperature Effect on Hydrogen Bonding

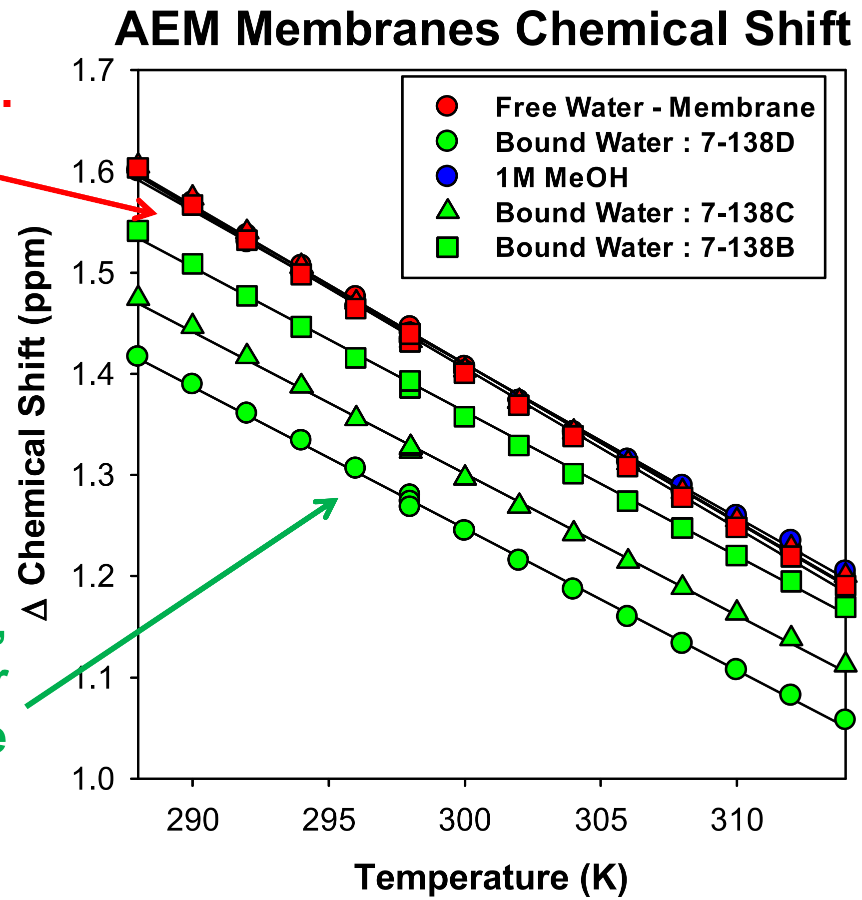
The "free" waters within the membrane are essentially the same as bulk 1M MeOH.



With increasing IEC (water content), the bound waters become more similar to bulk waters. The temperature variation $\Delta\delta/\Delta T$ increases with IEC.

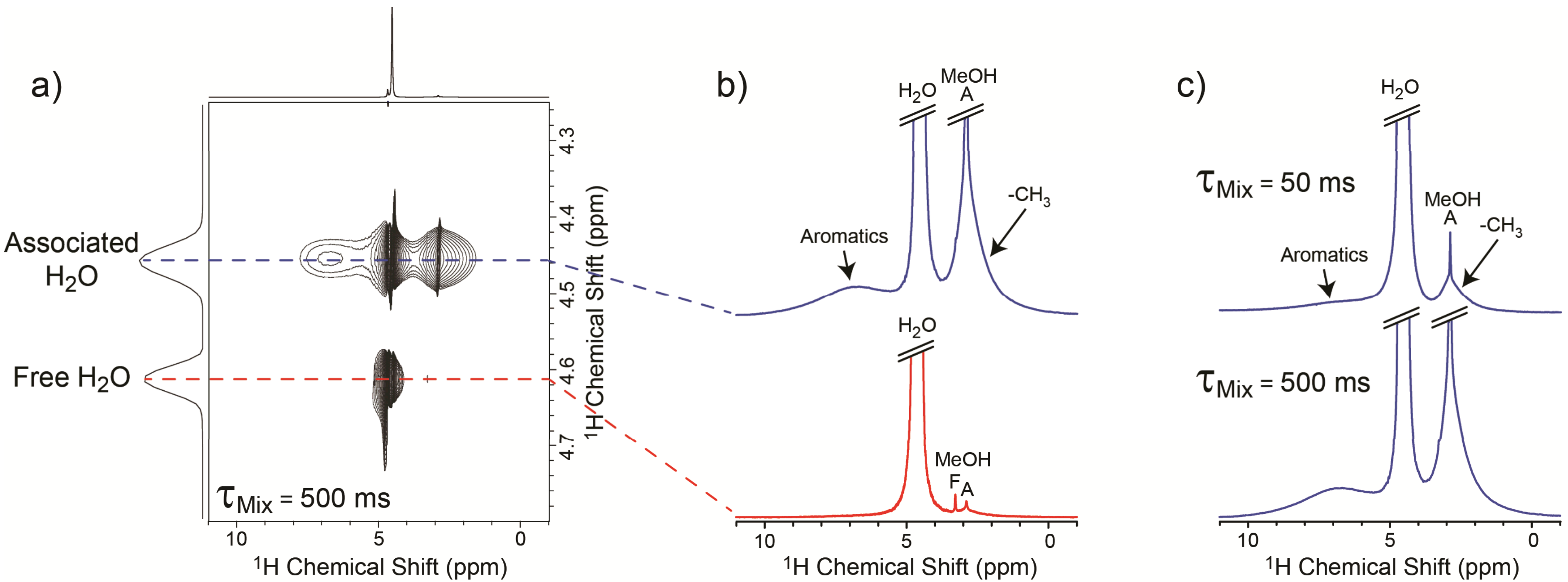






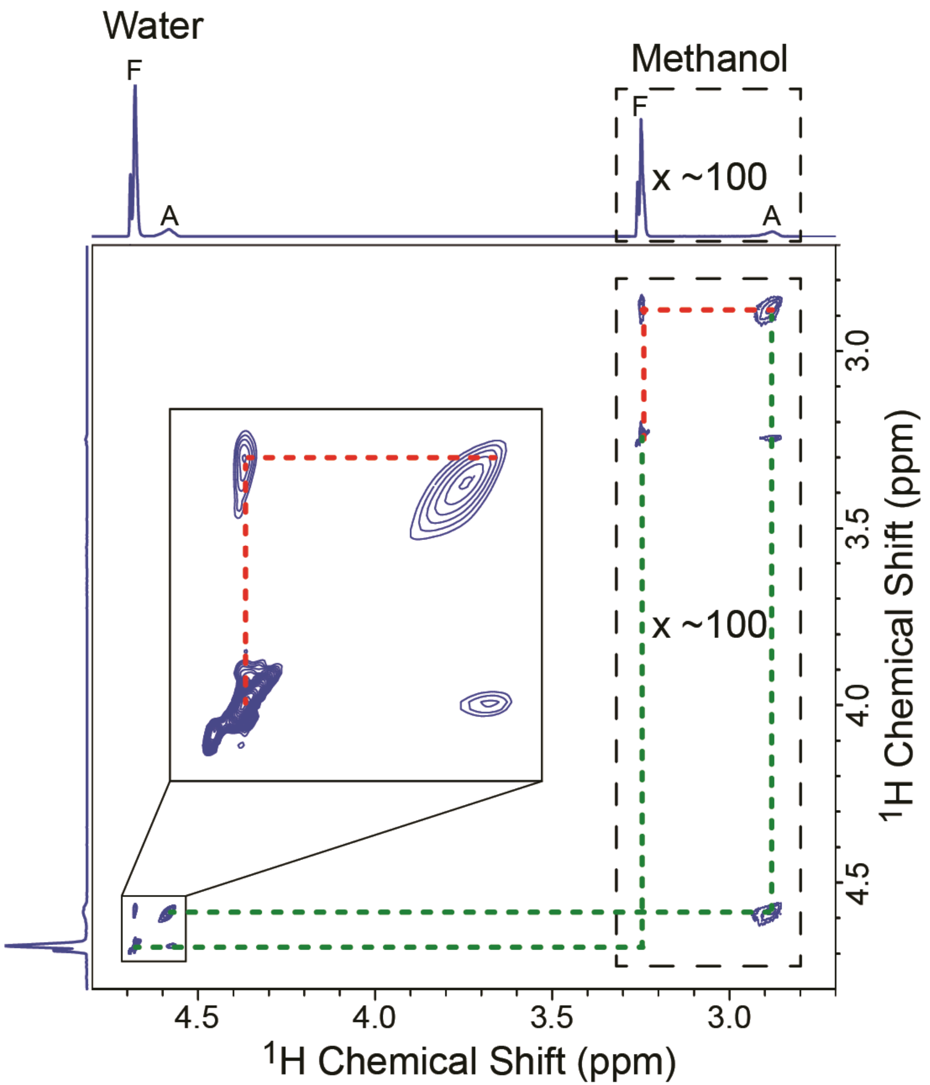
$$\Delta\delta = \delta(H_2O) - \delta(MeOH)$$

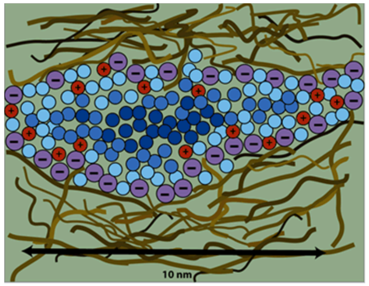
Where are these Associated Species?



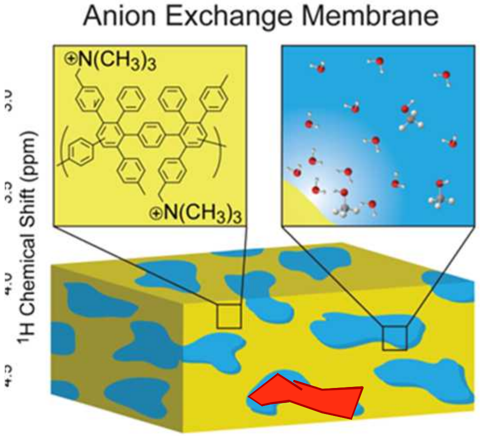
- **The 2D NOESY data (faster spinning speeds) reveal correlation between the associated species (both H_2O and MeOH) and the membrane.**
- **Short mixing times suggest near the cation ($N(CH_3)_3^+$).**
- **Free species do not reveal any strong NOE correlations.**

2D ^1H-^1H Exchange/NOESY Studies

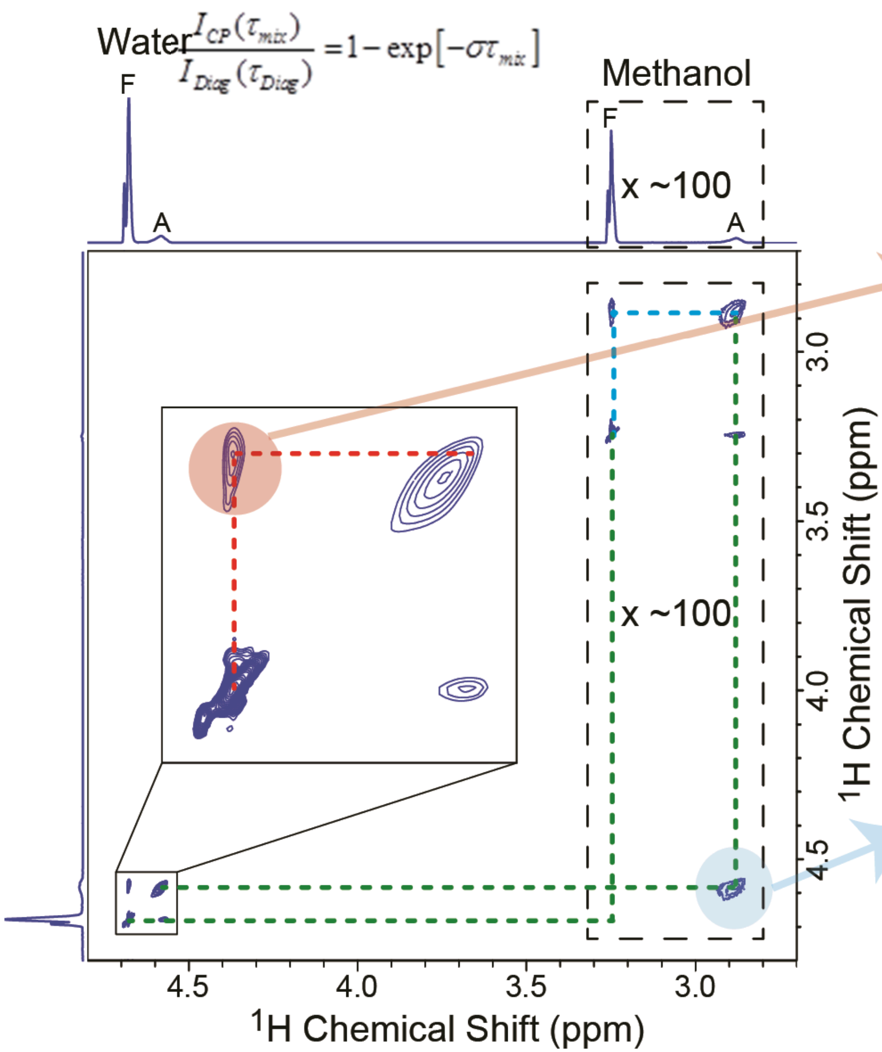


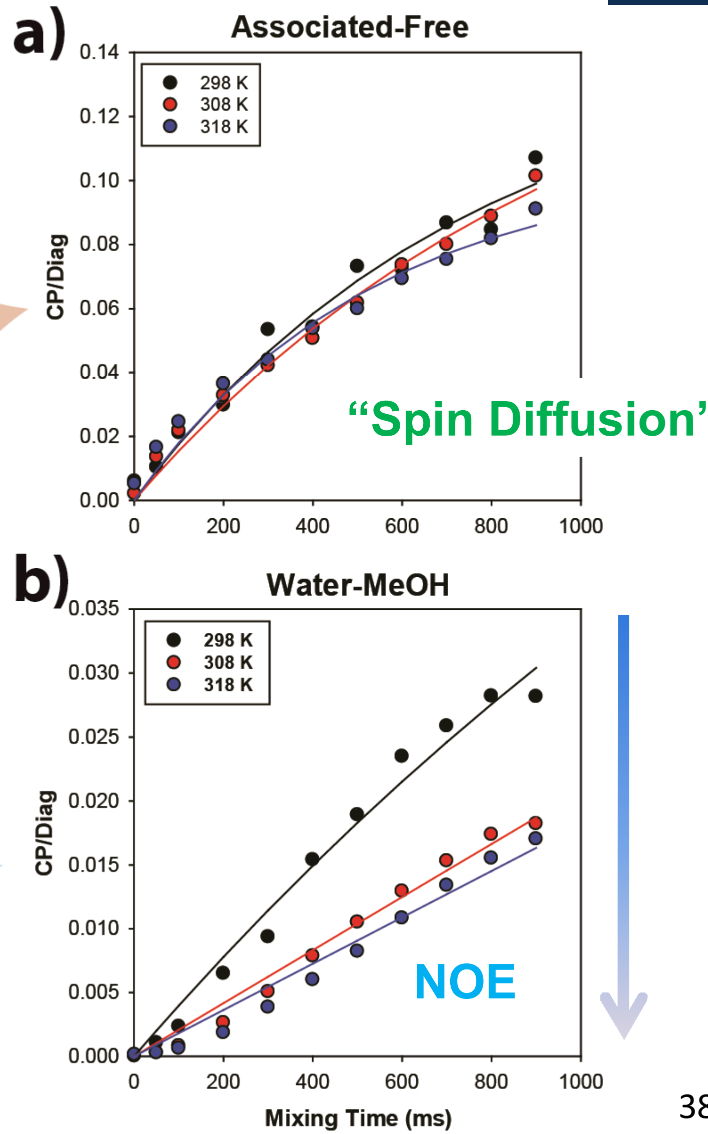


- Free and associated domains exist.
- These domains show some exchange.
- Associated water and MeOH in close contact with membrane.



2D ^{1}H-^{1}H Exchange/NOESY Studies





Sample	F-H_2O		A-H_2O		F-MeOH		A-MeOH	
	D_α (m^2/s)	α	D_α (m^2/s)	α	D_α (m^2/s)	α	D_α (m^2/s)	α
ATMPP (1.48)	$1.43e^{-9}$	0.96	$2.34e^{-10}$	0.74	$1.08e^{-9}$	0.97	$1.38e^{-10}$	0.92
ATMPP (1.79)	$1.64e^{-9}$	0.96	$4.02e^{-10}$	0.95	$1.29e^{-9}$	1.0	$1.73e^{-10}$	1.00
ATMPP (2.35)	$1.37e^{-9}$	0.97	$6.75e^{-10}$	0.98	$9.79e^{-10}$	1.0	$2.97e^{-10}$	0.94
$TMAC_6PCC_6$ (2.13)	$1.73e^{-9}$	1.0	$7.65e^{-10}$	0.95	$1.17e^{-9}$	1.0	$3.72e^{-10}$	0.93
$TMAC_6PCC_6$ (2.27)	$<1.31e^{-9}>$[a]	0.97	--	--	$<7.92e^{-10}>$[a]	1.0	--	--
$TMAC_6PCC_6$ (2.60)			$7.62e^{-10}$	0.90			$2.74e^{-10}$	0.80

High Resolution Magic Angle Spinning (HRMAS)

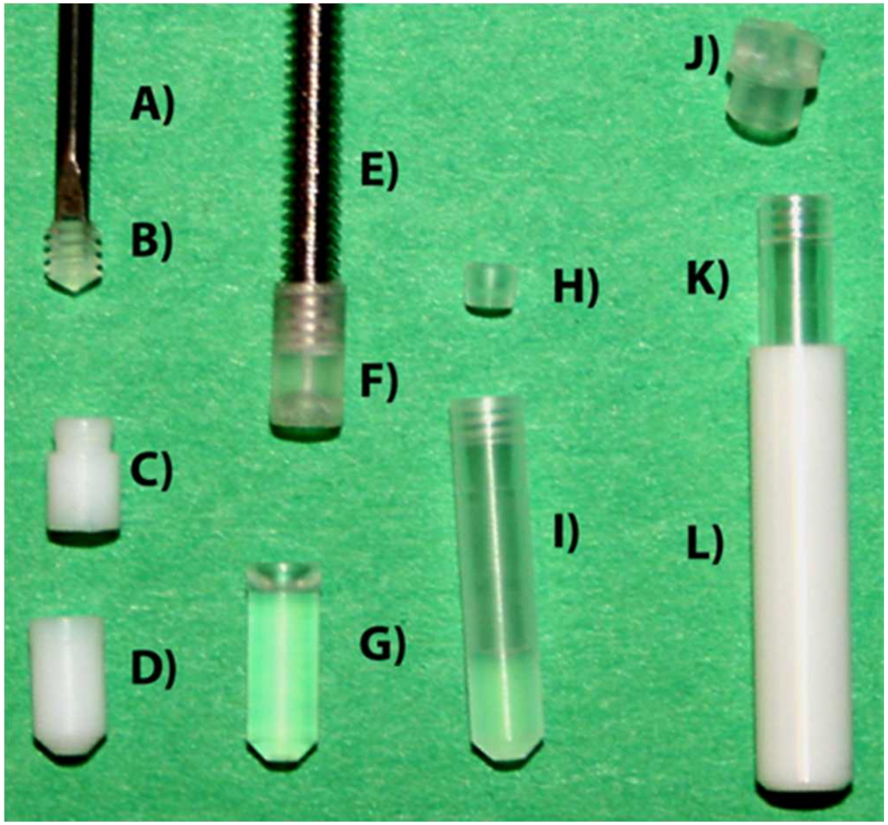
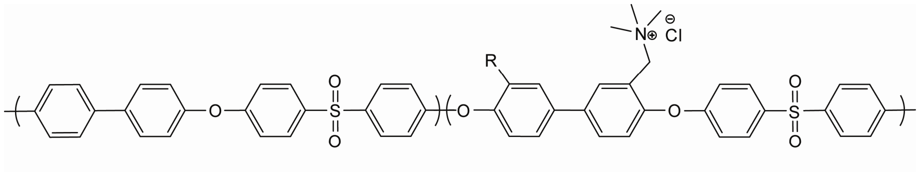


Figure 4: The tools and inserts used for HR-MAS NMR. These include A) the specialized tool for screw cap insertion, B) the sealing screw cap, C) the upper insert (Teflon®), D) lower Teflon® insert for 30 µL volume, E) screw for insertion/extraction of top insert, F) top Kel-F® insert, G) bottom Kel-F® insert for 12 µL sample volume, H) plug for disposable insert, I) disposable 30 uL Kel-F® insert, J) 4 mm rotor cap, K) disposable inserted partially in a 4 mm rotor, L) 4 mm zirconia MAS rotor. All these parts are for the Bruker HR-MAS system, and may vary between vendors.

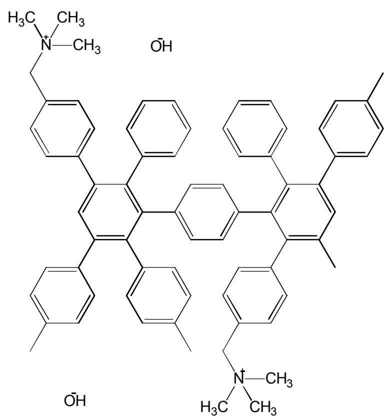
- "Liquid like samples" need to retain liquid under MAS.
- Need to consider centrifugation effects under MAS.

AEM and PEM Membranes

Anion Exchange Membranes (AEM)

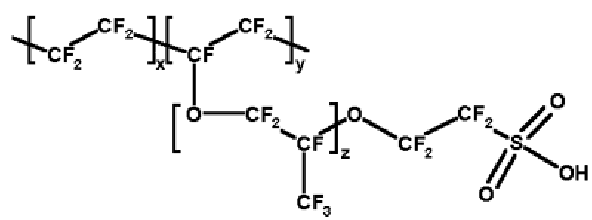


PS-AEM R = H, $CH_2N(CH_3)_3$



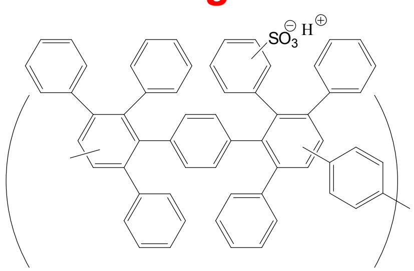
(ATMPP)
aminated trimethyl
polyphenylene

- **High stability at elevated temperatures/pH.**
- **MeOH based fuel cells.**
- **Non-precious metal catalyst at high pH.**
- **MeOH oxidizes easier at high pH**
- **High conductivity and ion selectivity.**



Nafion

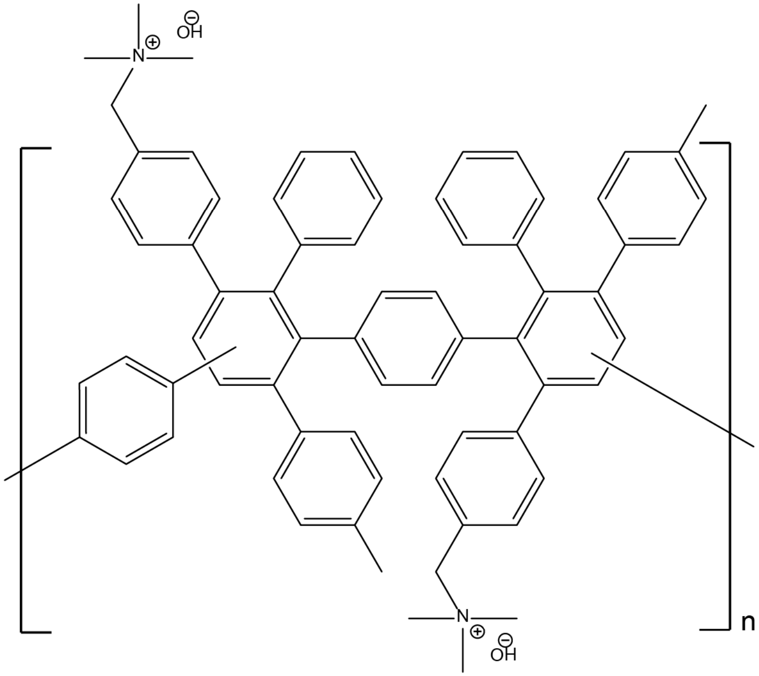
Proton Exchange Membranes (PEM)



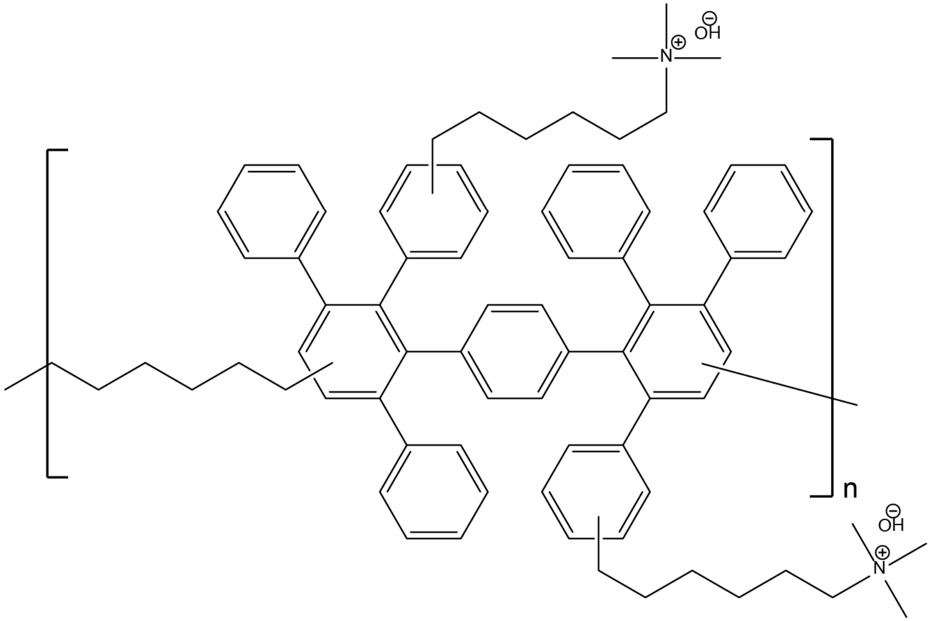
Sulfonated Diels Alder Polyphenylene (SDAPP)

- **High thermal chemical stability.**
- **Easily processed, lower cost.**
- **Wide range of functionalities.**

AEM Membranes Investigated



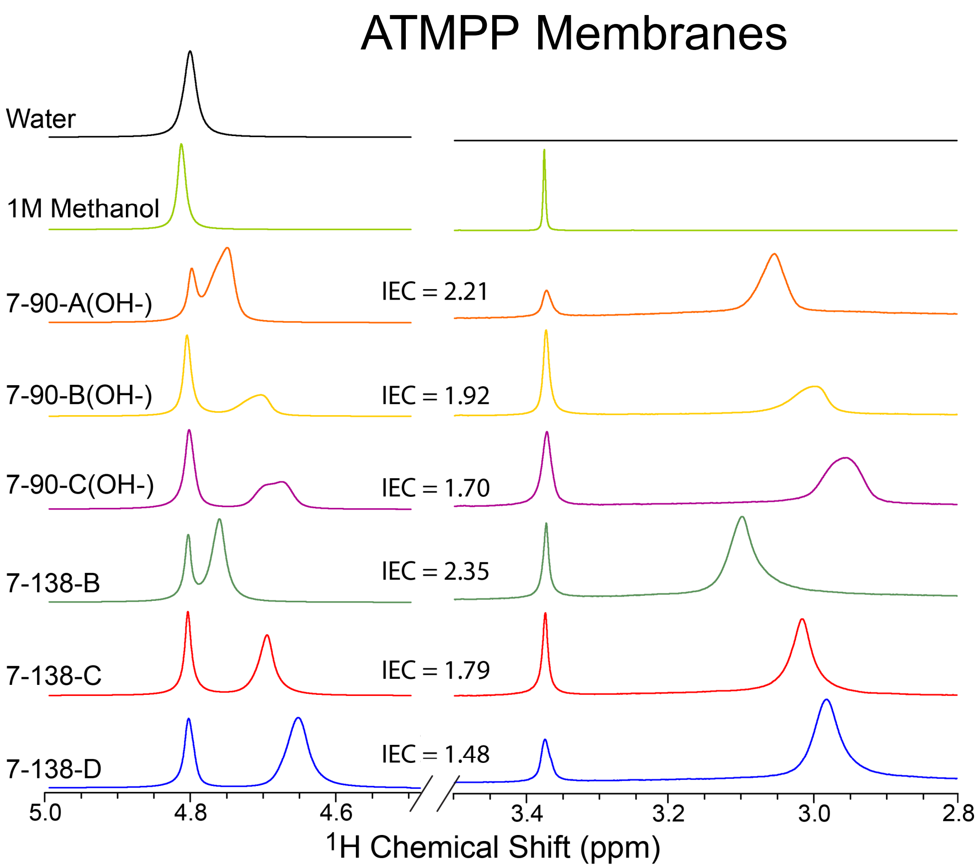
ATMPP

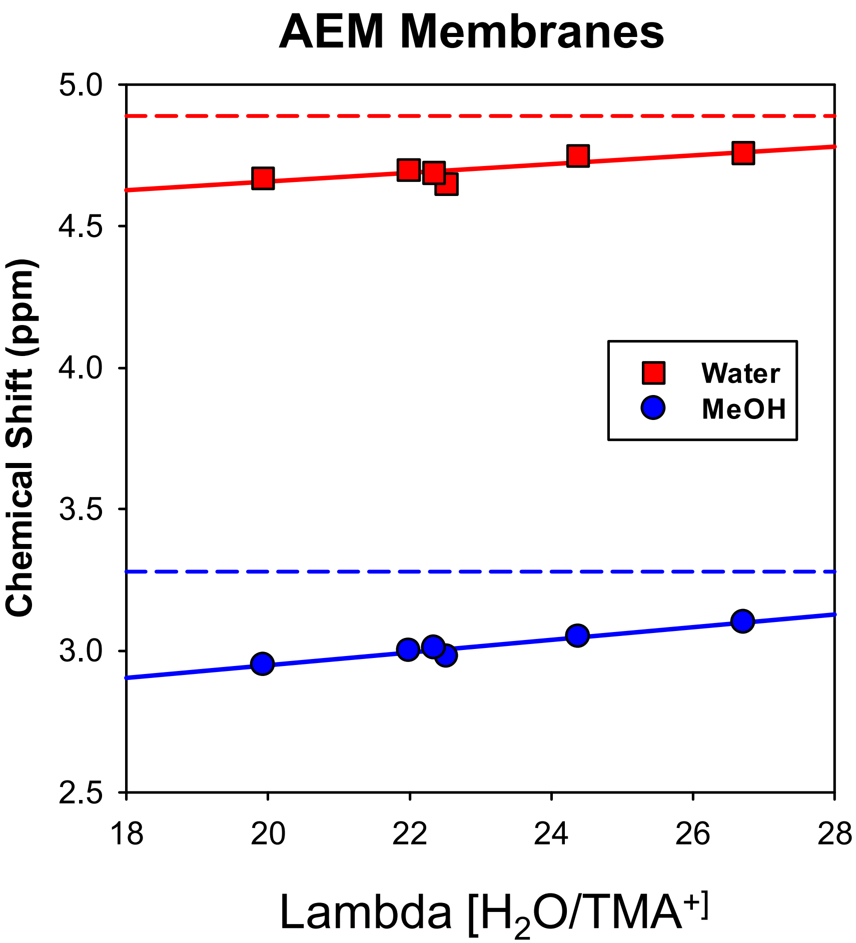


TMAC$_6$PCC$_6$

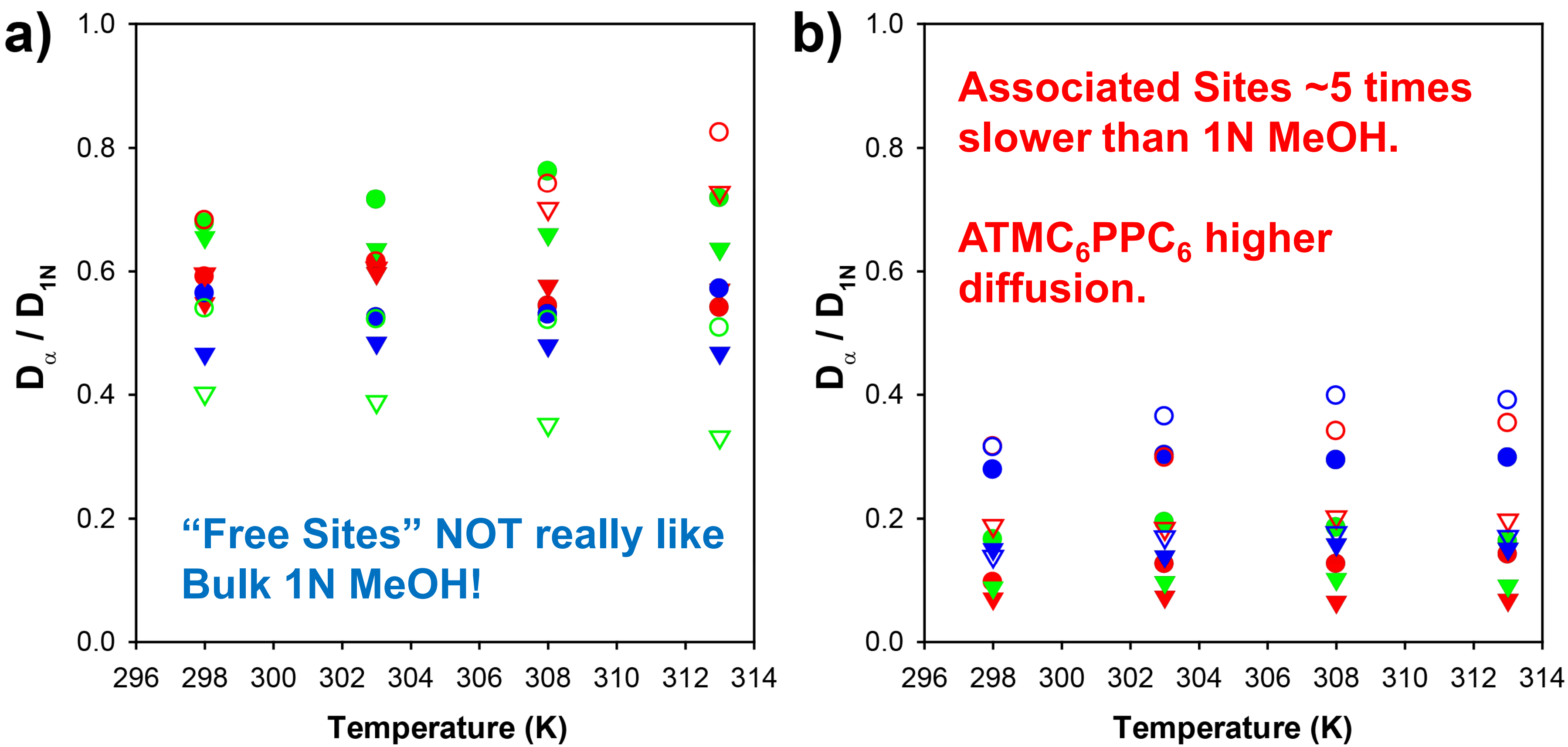
Alkane spacers (C_6) added for higher mobility, increased water content, alkaline stability

Chemical Shifts for Different Membranes

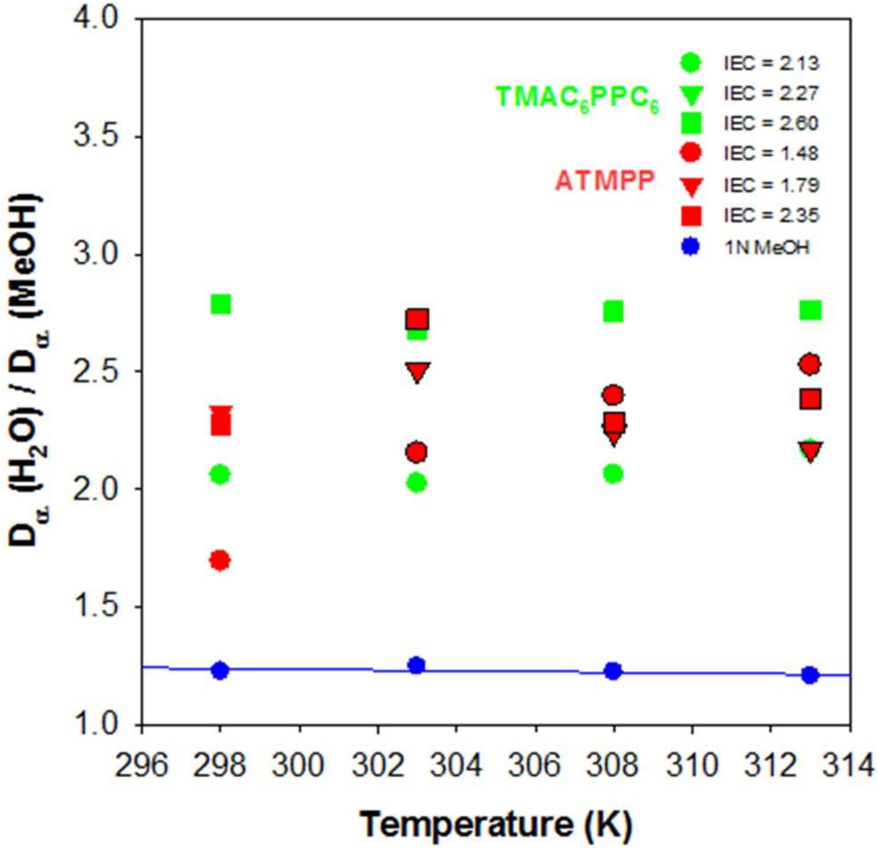




Ratios of Diffusion Rates



Ratios of Diffusion (H_2O/MeOH)



- All of these membranes show a preferential reduction of MeOH.
- Helps reduce MeOH cross-over in membranes.