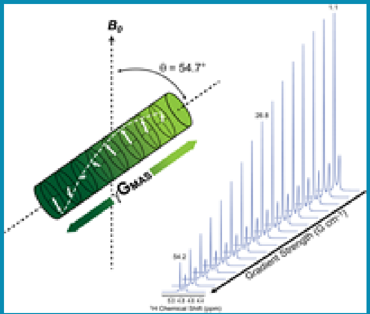
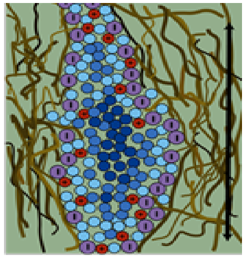
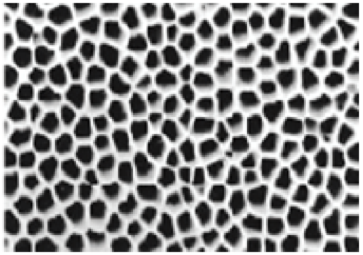
SAND2020-11940PE

Sandia National Laboratories

Exploring High Resolution Magic Angle Spinning (HRMAS) NMR Diffusometry in Swollen Polymers and Gels







Polymer Physics and Polymer Spectroscopy (P3S) Webinar
http://www.physik.uni-halle.de/fachgruppen/nmr
October 29th 2020

PRESENTED BY

Dr. Todd M. Alam

Organic Materials Science Department
Sandia National Laboratories
Albuquerque, NM 87185

LABORATORY DIRECTED RESEARCH & DEVELOPMENT

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SAND2020-XXXX

Outline

Diffusion in DAPP fuel cell membranes

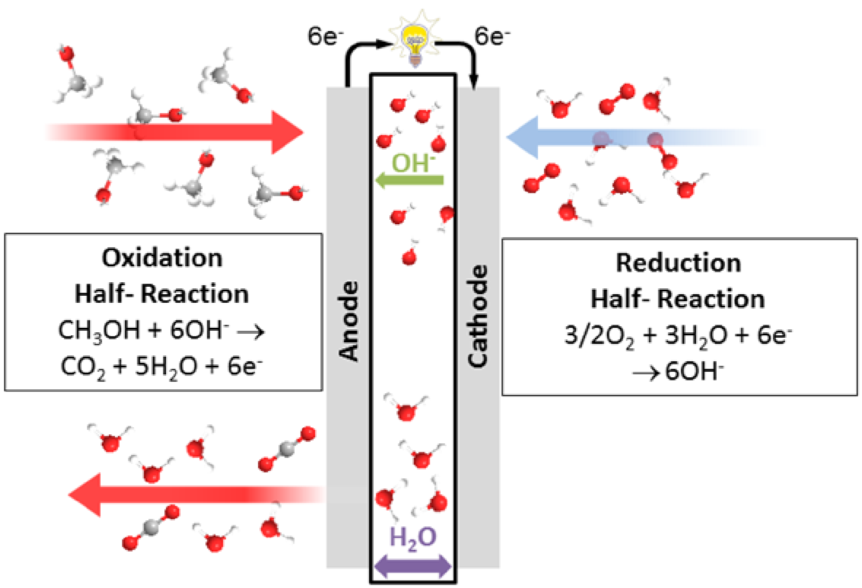
- MeOH fuel cells
- hydrogen fuel cells

Solvent diffusion in swollen PDMS gels

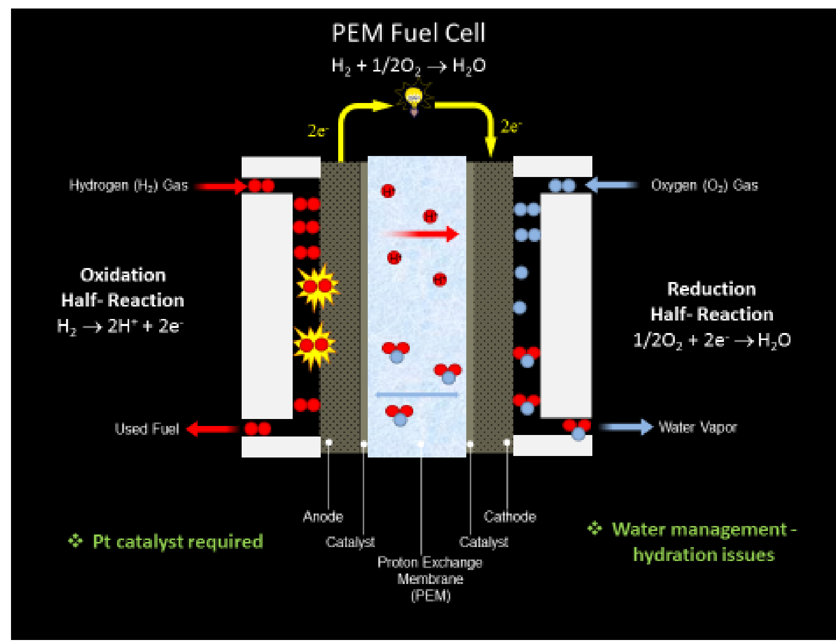
- Additive manufactured (AM) siloxane pads

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)….remote locations.
- Power generation (backup), including remote sites, military, automobile.
- Higher efficiency (60 – 85%) than combustion systems (30%).



AEM = anion exchange membrane

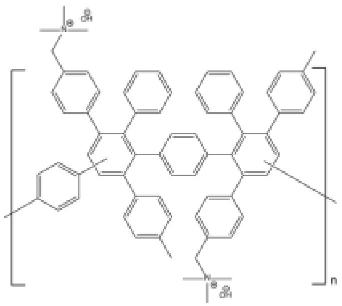


Need to develop fundamental understanding of transport in membranes & binder….

Diels Alder Poly(phenylene) (DAPP) Membranes

ATMPP

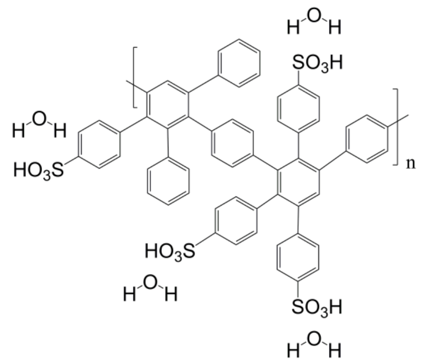
Aminated tetramethyl poly(phenylene)



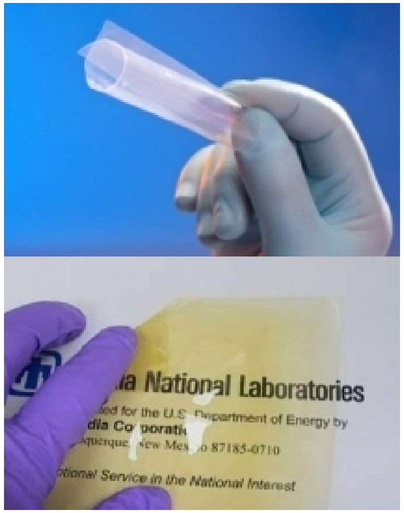
MeOH fuel cell (Hibbs, SNL)

SDAPP

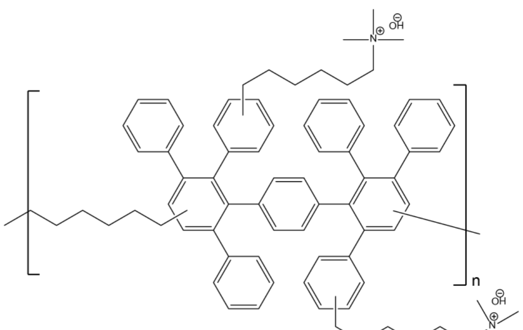
Sulfonated Diels Alder poly(phenylene)



- Stable in alkaline environments.
- High T_g (~350 °C).
- Easily processed.
- Wide range of functionalities.
- Promising alternative to Nafion.
- No F (i.e. HF) during aging
- AEM, PEM
- Vanadium flow batteries

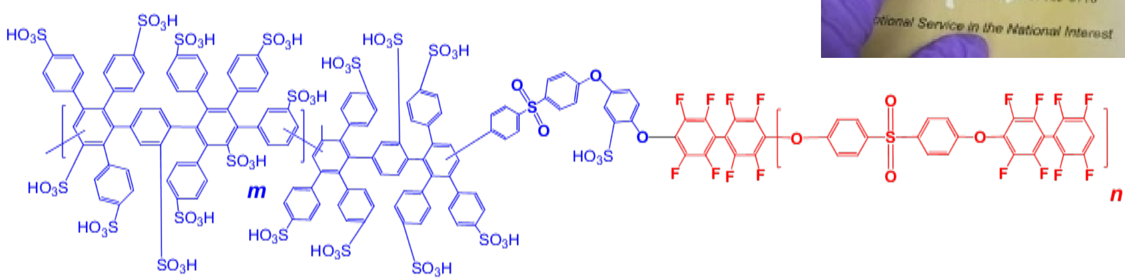


DAPP Analogues



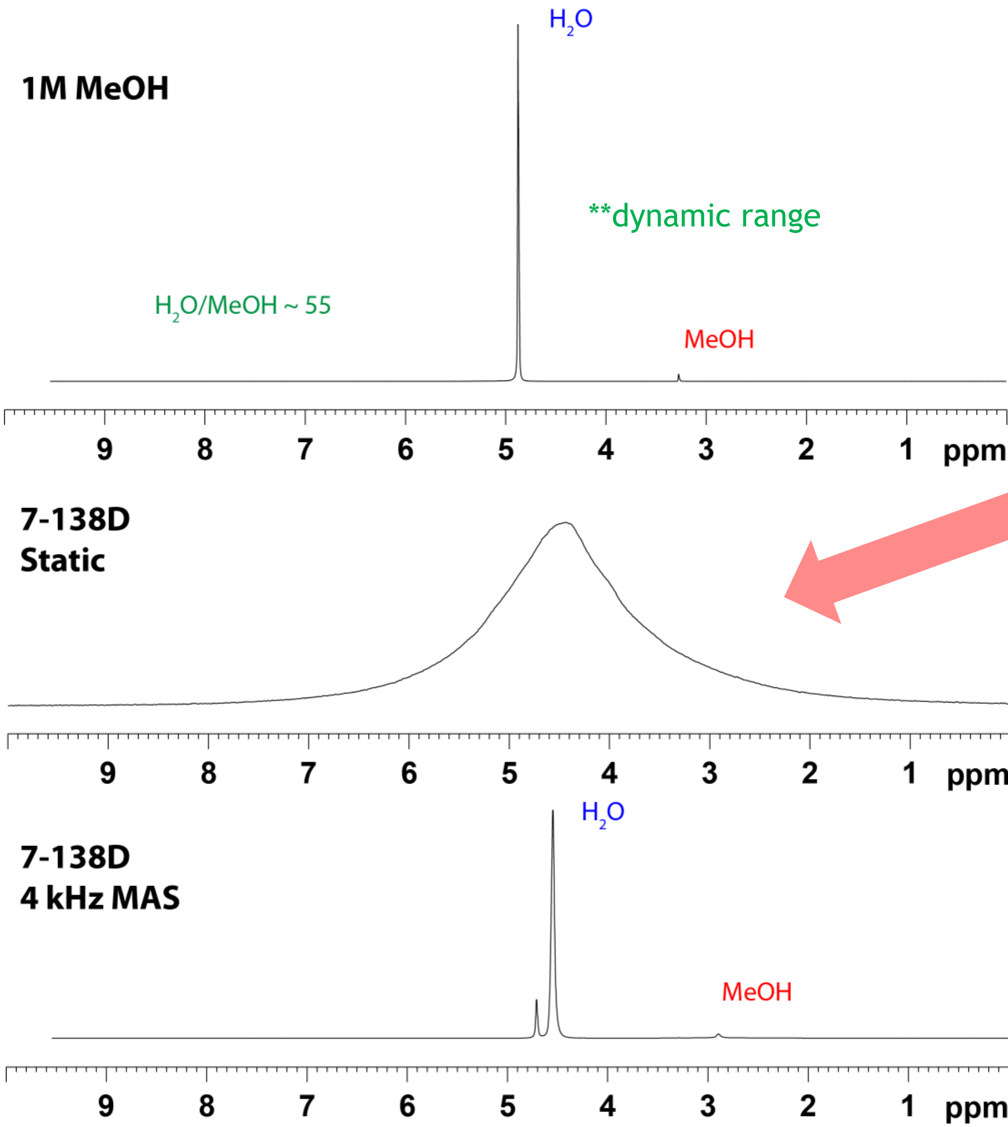
$TMAC_6PPC_6$

SDAPP-FDPS Copolymers



Fujimoto, C. H., Hickner, M. A., Cornelius, C. J., Loy, D. A., Macromolecules 2005, 38 (12), 5010-5016 .

Chemical Shift Resolution in MeOH Fuel Cells
"The Odyssey Begins"



<u>Very simple question</u>

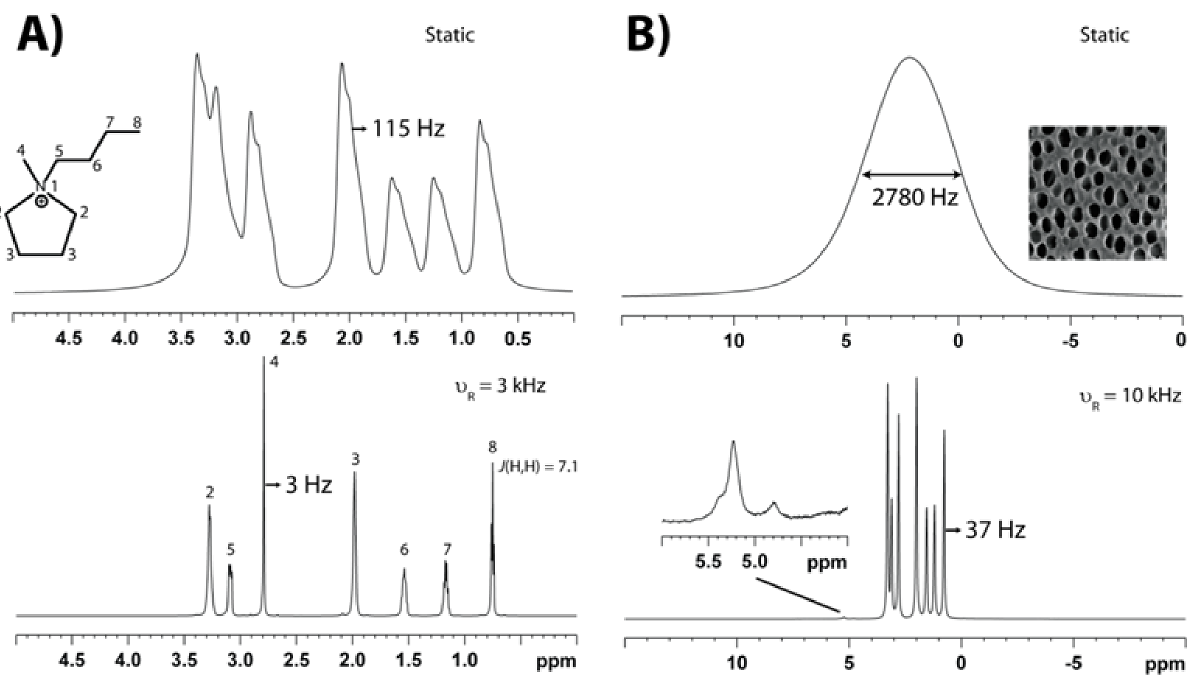
"Can you individually measure the MeOH and H_2O diffusion in fuel cell membranes?"

No resolution! Standard PFG NMR diffusometry techniques not going to work.

- Could use D_2O and CH_3OH
- ^{13}C detected for CH_3OH

- Elected to explore High Resolution NMR diffusometry .

High Resolution Magic Angle Spinning (HRMAS)

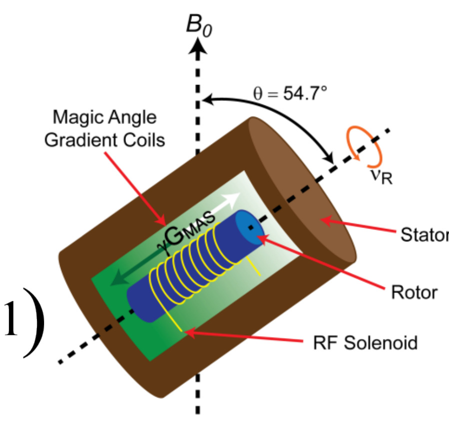


Magic angle spinning (MAS) helps reduce susceptibility effects in semi-solid materials:

- Combinatorial resins
- Tissues
- Cell dispersions
- Polymer gels

Local dipolar field due to heterogeneous magnetic susceptibilities.

$$\boldsymbol{B}(\boldsymbol{r}_i) = \sum_j \frac{\boldsymbol{M}_j}{r_{ij}^3} \frac{1}{4} \underbrace{\left(3\cos^2\theta - 1\right)}_{=\,0} \left(3\cos^2\beta_{ij} - 1\right)$$

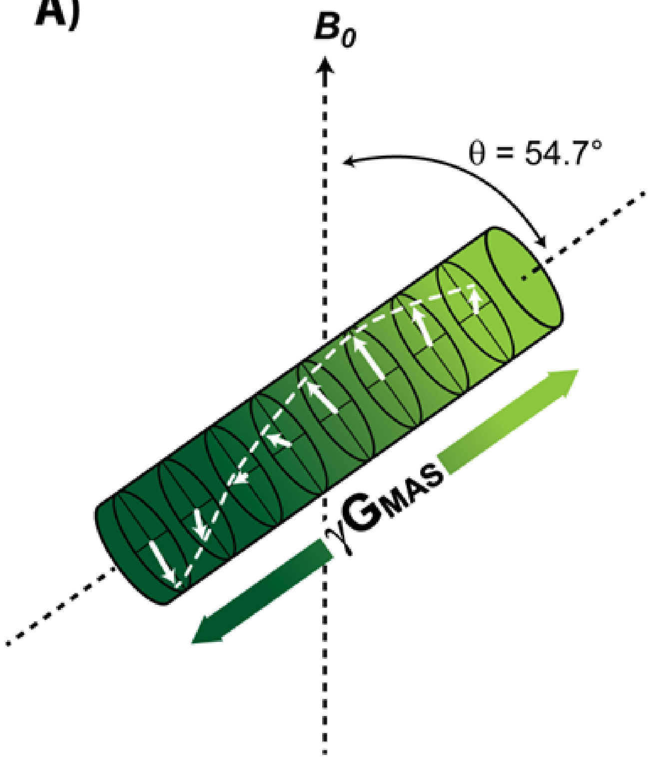


Todd M. Alam and Janelle E. Jenkins, " HR-MAS NMR Spectroscopy in Material Science", in Advanced Aspects of Spectroscopy, Muhammad Akhyar Farrukh (Ed.), ISBN: 978-953-51-0715-6, InTech, (2012).

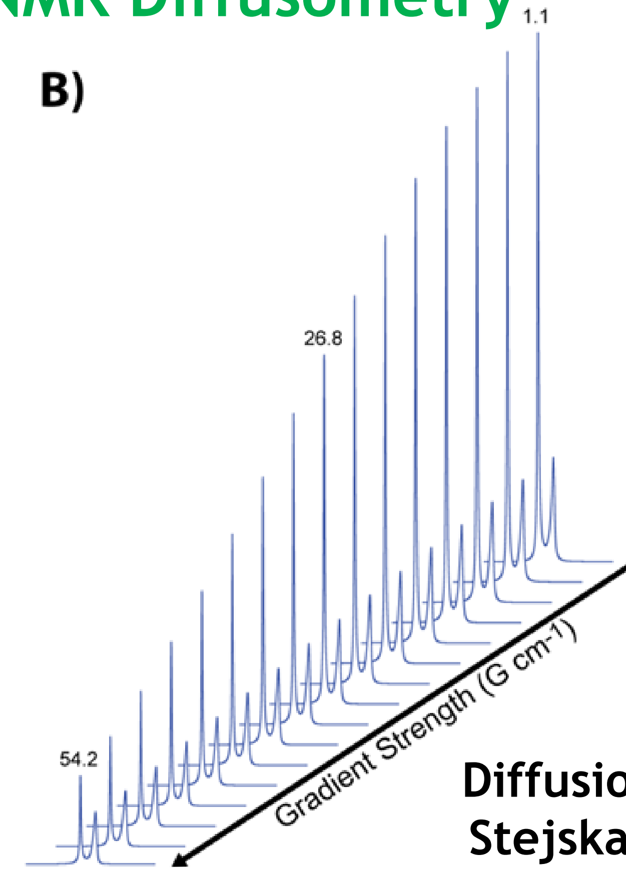
High Resolution Magic Angle Spinning (HRMAS) Pulse Field Gradient (PFG) Diffusion Experiments

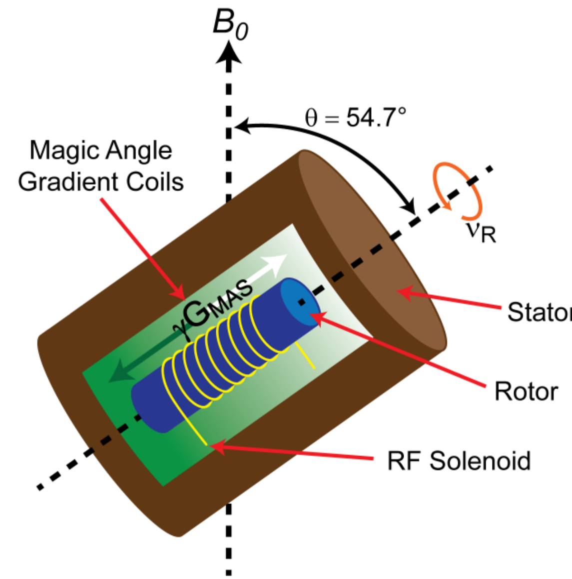
"NMR Diffusometry

A)



B)





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

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

Diffusion constant (D) via Stejskal-Tanner Formula

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

High Resolution Magic Angle Spinning (HRMAS)

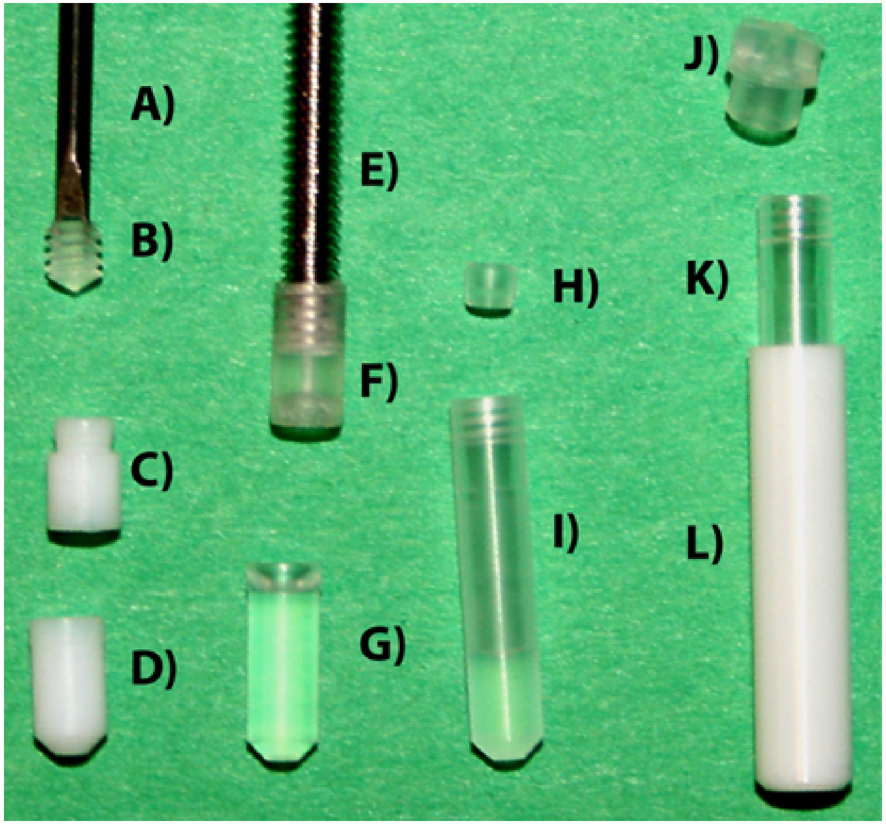
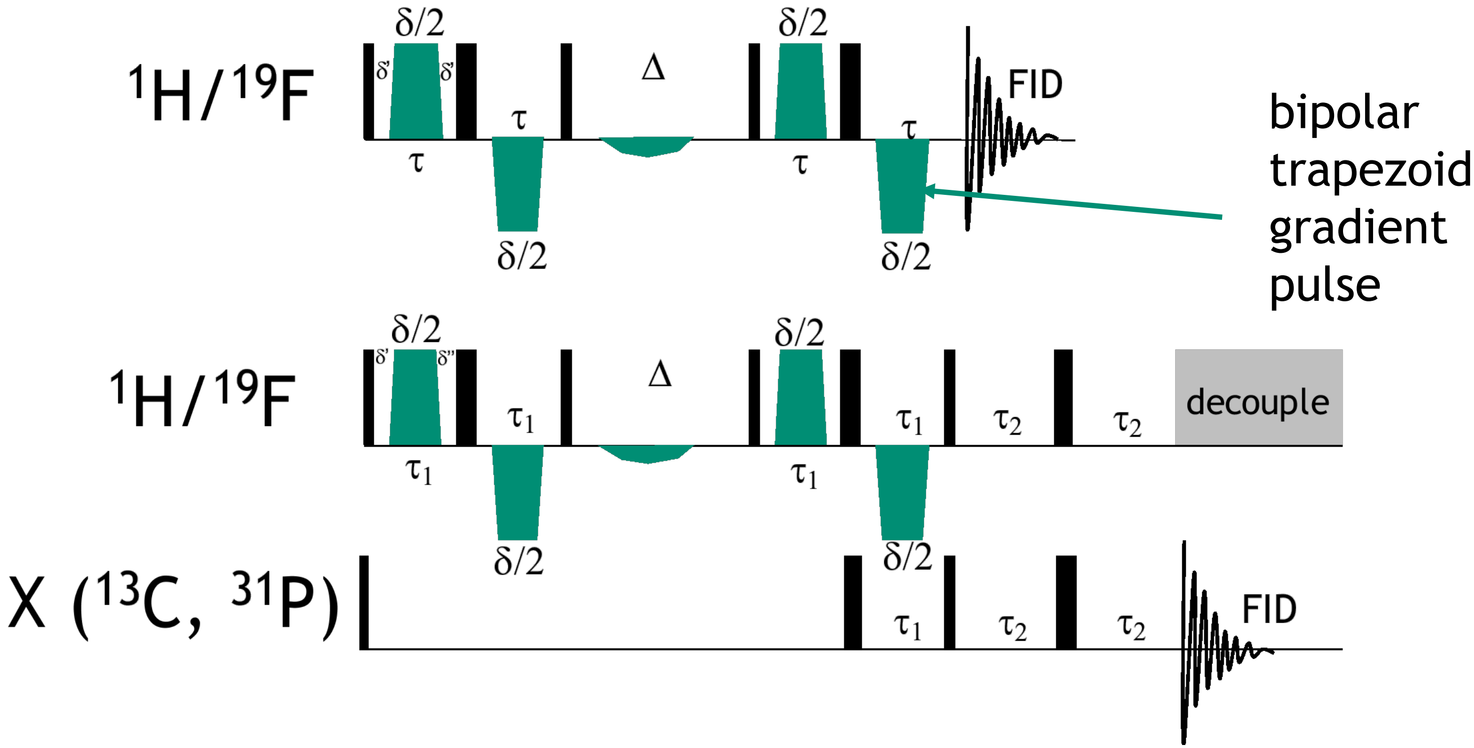


Figure 4: The tools and inserts used for HR-MAS NMR. These include A) the specialized tool for screw cap insertion, B) the sealing screw cap, C) the upper insert (Teflon®), D) lower Teflon® insert for 30 μL volume, E) screw for insertion/extraction of top insert, F) top Kel-F® insert, G) bottom Kel-F® 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.

PFG NMR Diffusometry Pulse Sequences

COTTS 13-interval PFG sequence



COTTS 13-interval PFG sequence with INEPT ^{13}C-detect

R. M. Cotts, M. J. R. Hoch, T. Sun and J. T. Marker, J. Magn. Reson., 1989, 83, 252-266.

HRMAS NMR Diffusometry in Polymer Membranes

ACS Macro Letters
Letter
pubs.acs.org/macroletters

Identification of Multiple Diffusion Rates in Mixed Solvent Anion Exchange Membranes Using High Resolution MAS NMR

Janelle E. Jenkins,*[,†] Michael R. Hibbs,[‡] and Todd M. Alam*[,†]

Macromolecules
Article
pubs.acs.org/Macromolecules

Characterization of Heterogeneous Solvent Diffusion Environments in Anion Exchange Membranes

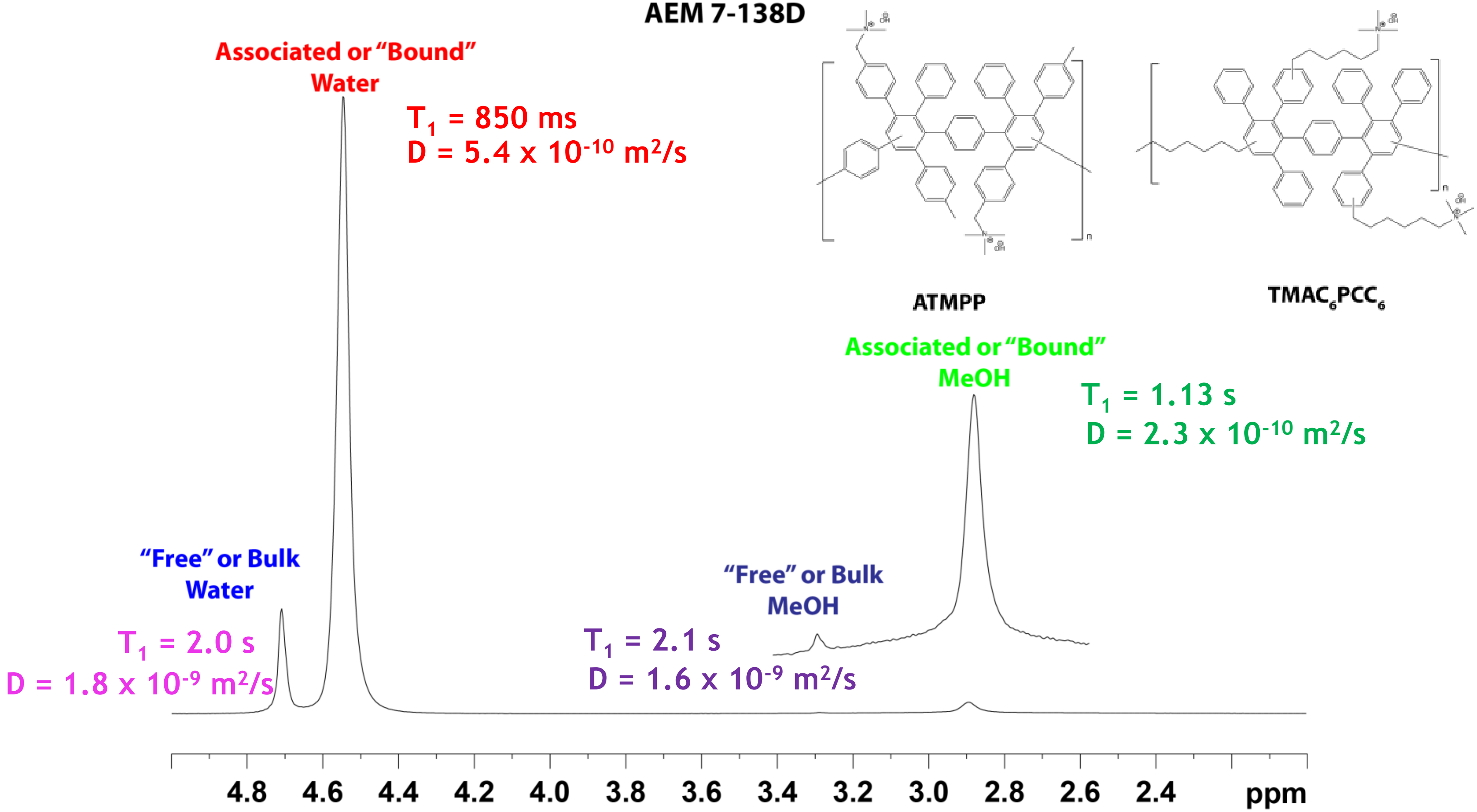
Todd M. Alam[†,*] and Michael R. Hibbs[‡]

Macromolecules
Article
Cite This: *Macromolecules* 2019, 52, 857–876
pubs.acs.org/Macromolecules

Impact of Hydration and Sulfonation on the Morphology and Ionic Conductivity of Sulfonated Poly(phenylene) Proton Exchange Membranes

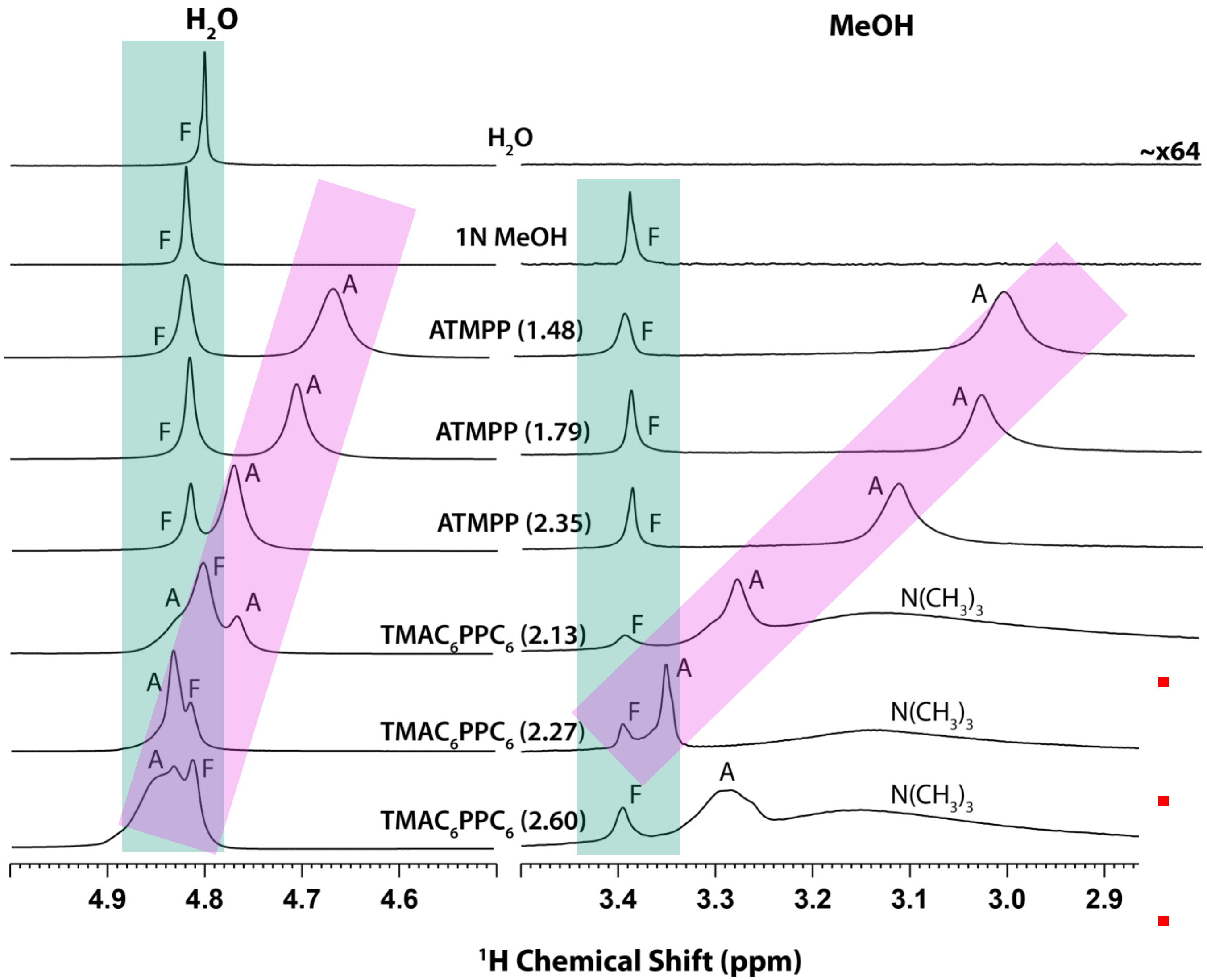
Eric G. Sorte,[†] Benjamin A. Paren,[‖] Christina G. Rodriguez,[⊥] Cy Fujimoto,[‡] Cassandria Poirier,[†] Lauren J. Abbott,[§] Nathaniel A. Lynd,[⊥] Karen I. Winey,[‖] Amalie L. Frischknecht,*[,§] and Todd M. Alam*[,†]

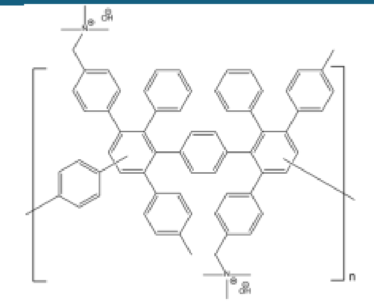
HRMAS PFG NMR and Site Resolution



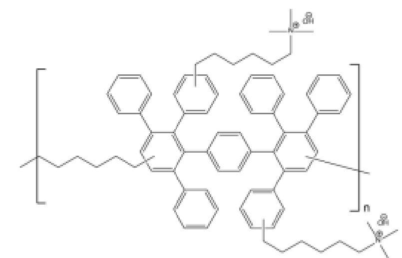
Resolution is always exciting! ***Can ask questions about differences between MeOH and water association with the membrane.***

^{1}H HRMAS NMR of Different AEM Membranes





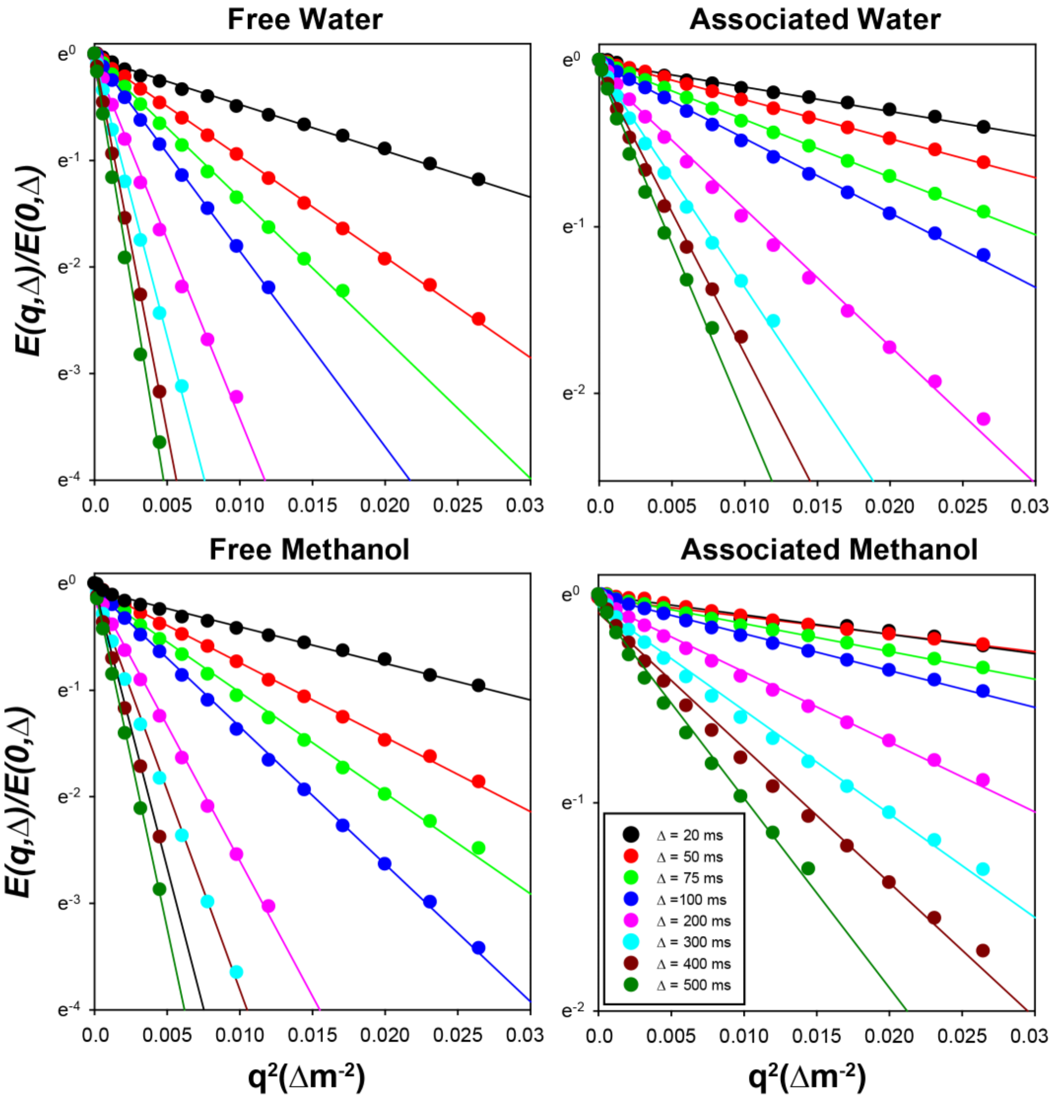
ATMPP



TMAC$_6$PCC$_6$

- 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



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

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

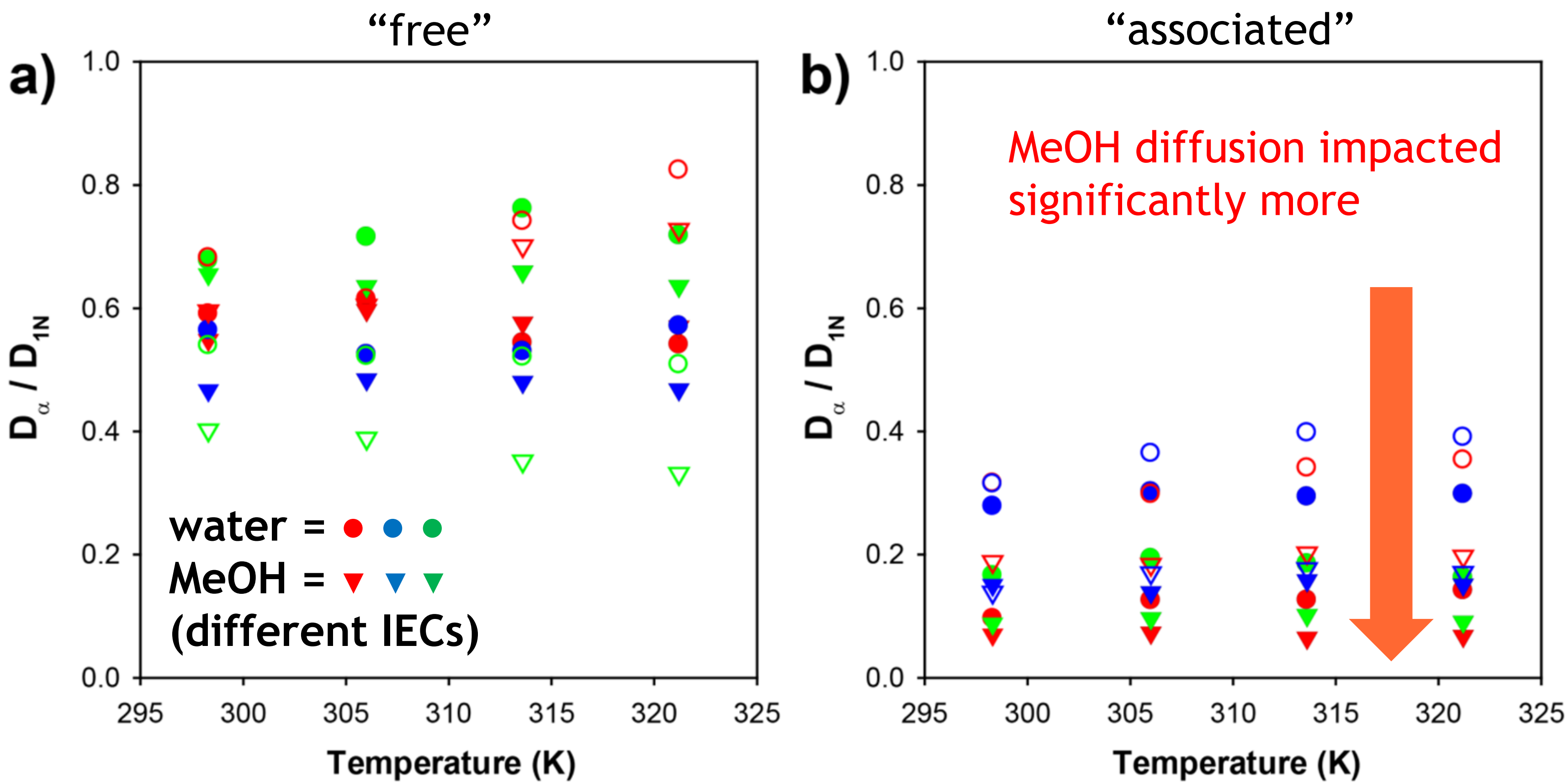
$$\left\langle z_M^2(\Delta)\right\rangle = -2\ln\left[E(q,\Delta)/E(0,\Delta)\right]/q^2$$

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

- Looking for anomalous diffusion
- Measured activation energies (E_a)
- 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 AEM 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

Diffusion Analysis of Individual Species



D_α/D_{1N} = ratio of diffusion in membrane/solution mixture

Outline

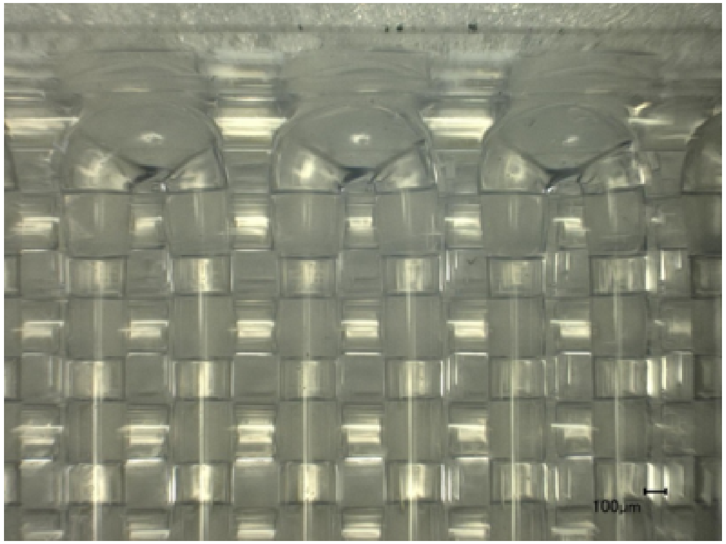
Diffusion in DAPP fuel cell membranes

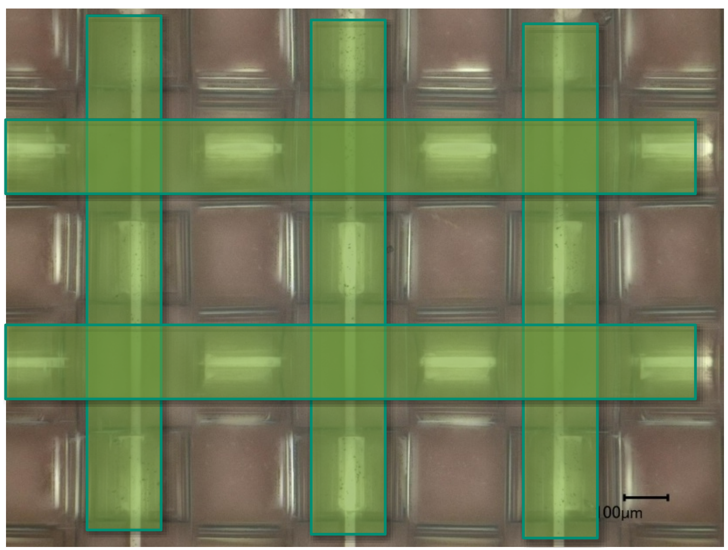
- MeOH fuel cells
- hydrogen fuel cells

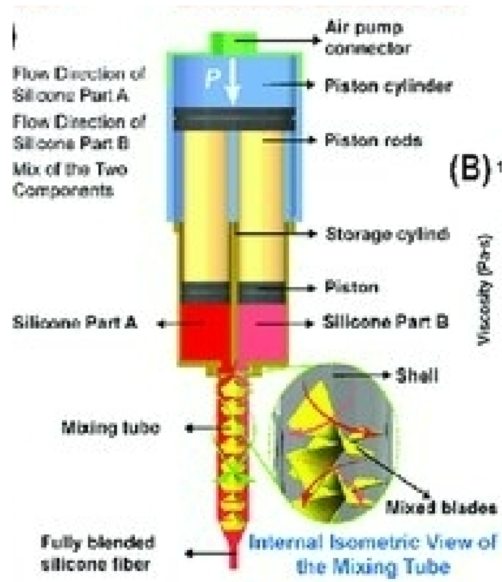
Solvent diffusion in swollen PDMS gels

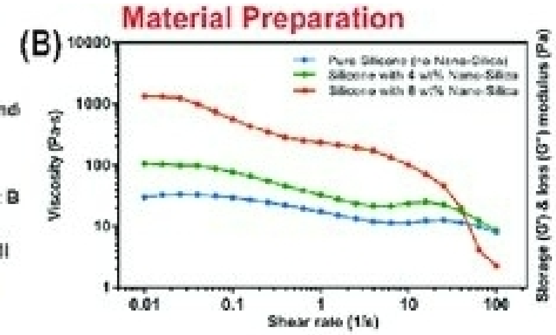
- Additive manufactured (AM) siloxane pads

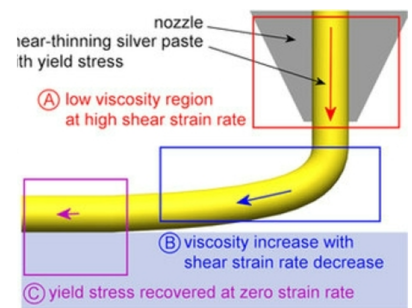
Solvent Diffusion in 3D Printed Advanced Manufactured (AM) Materials





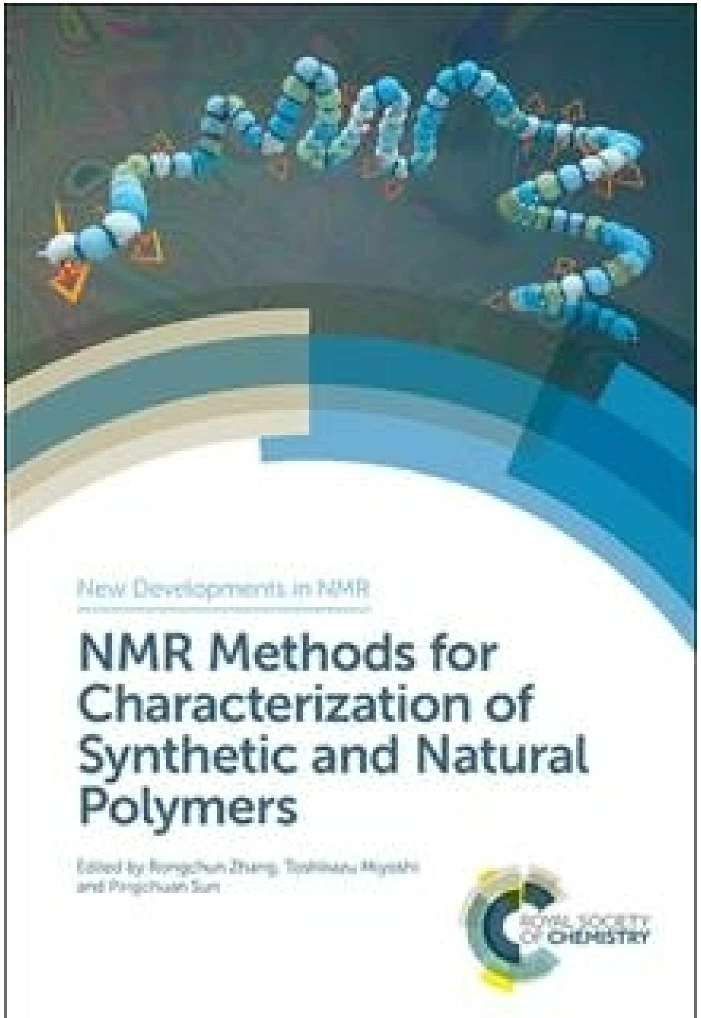






- Direct-write of Corning SE1700 siloxanes.
- Multi-layer (4 to 8 layers).
- Variable write and spacing (200 – 400 mm).
- Different cure protocol.
- *Diffusion of different penetrants?*

HRMAS NMR Diffusometry in Polymer Gels



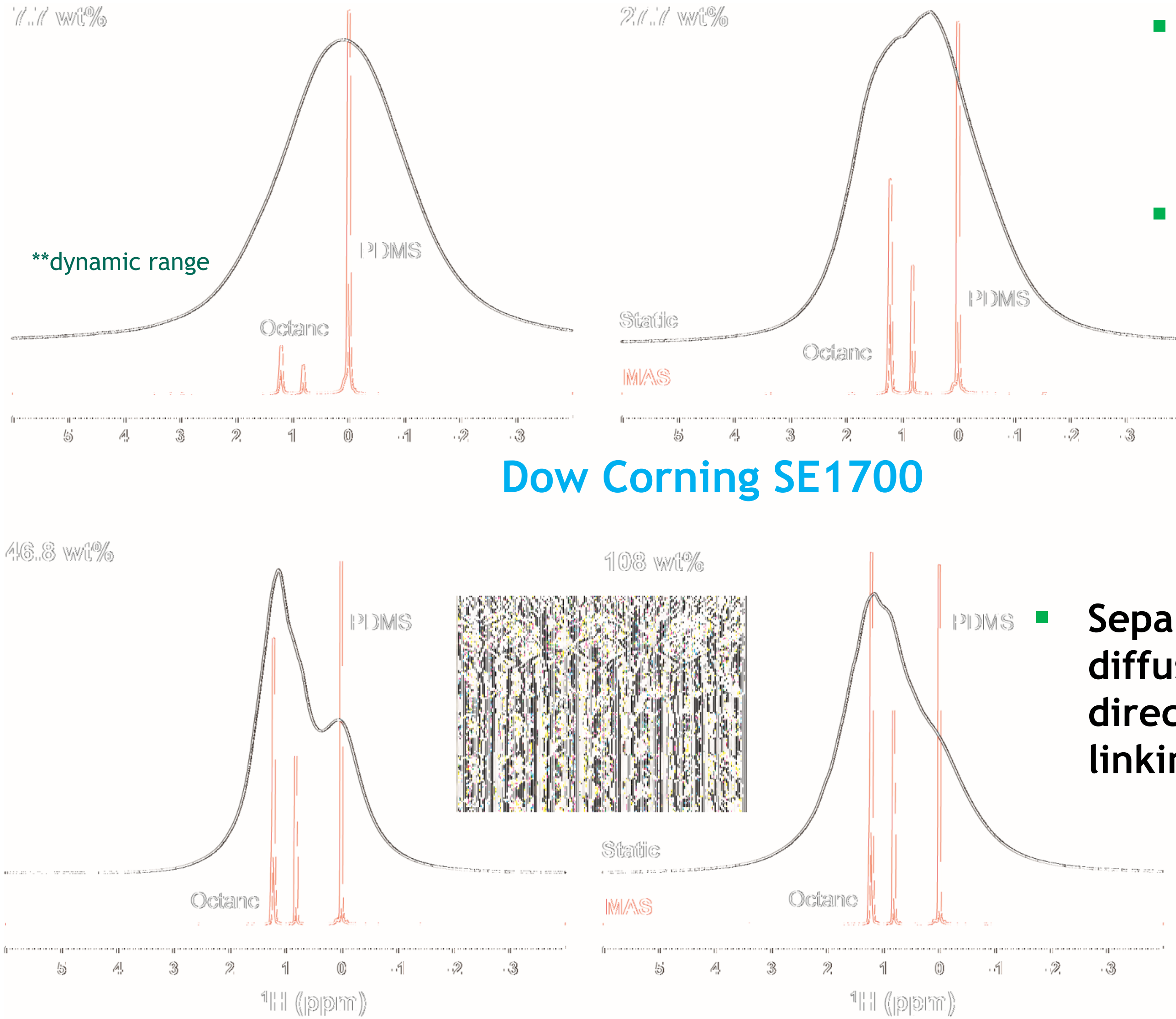
CHAPTER 4

High Resolution Magic Angle Spinning (HRMAS) Pulse Field Gradient (PFG) NMR Diffusometry Studies of Swollen Polymers

TODD M. ALAM

https://pubs.rsc.org/en/content/ebook/978-1-78801-400-7

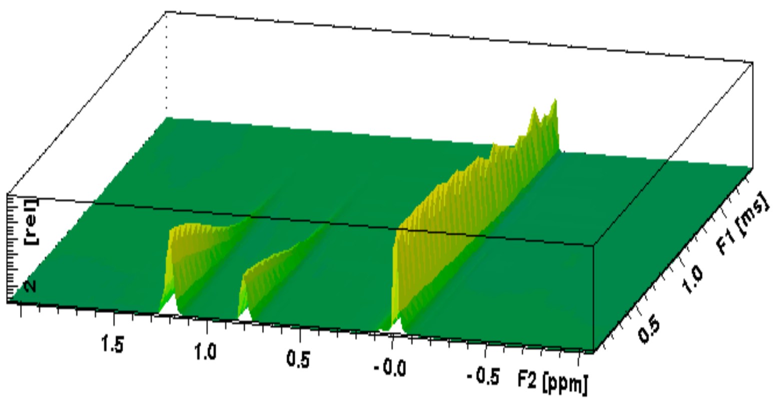
Penetrant Diffusion in 3D Printed Silicones



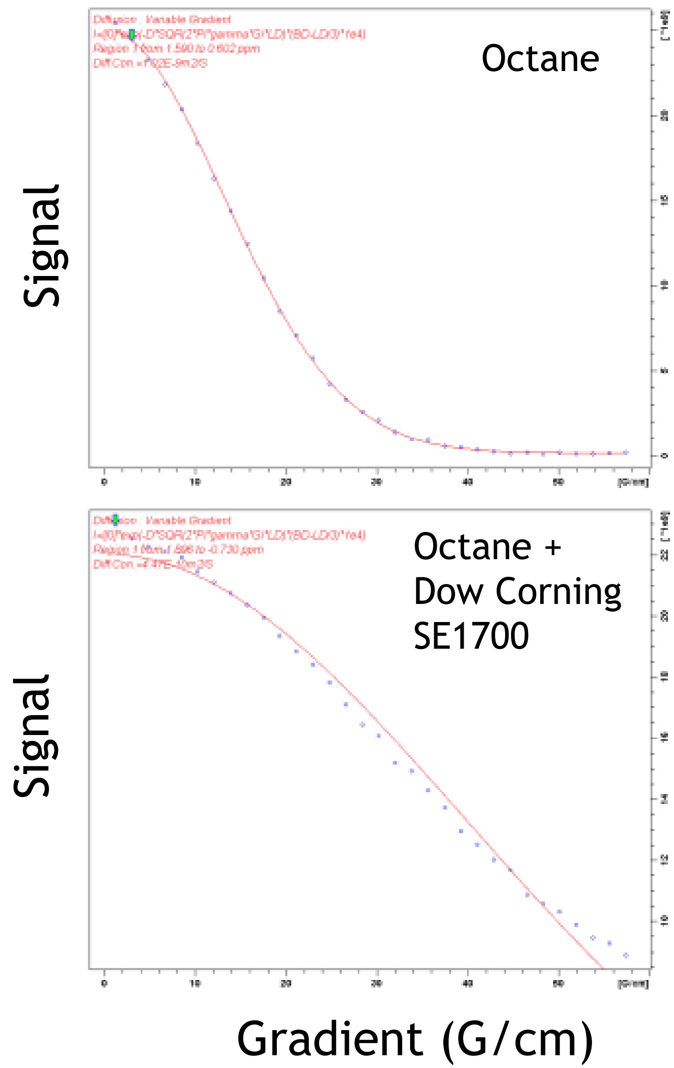
- **HRMAS NMR allows resolution of penetrant diffusion.**
- **Especially at low swelling concentrations (Q).**
- **Separation in static PFG NMR diffusion experiments impacted directly by degree of PDMS cross-linking.**

Overlap in ^{1}H NMR Diffusion Signal Decay

HRMAS NMR PFG Diffusion

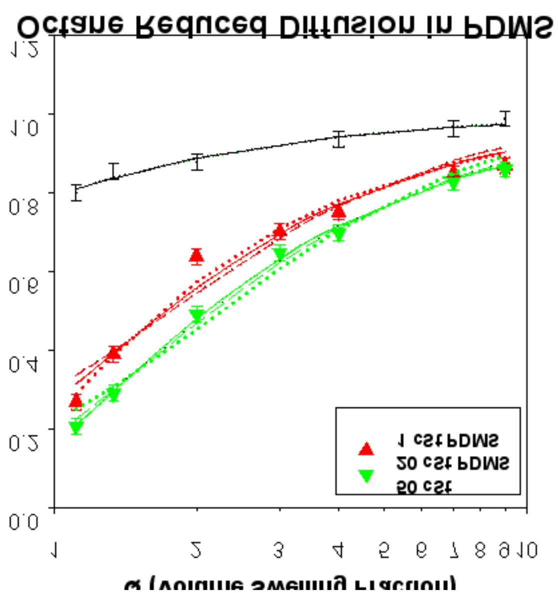


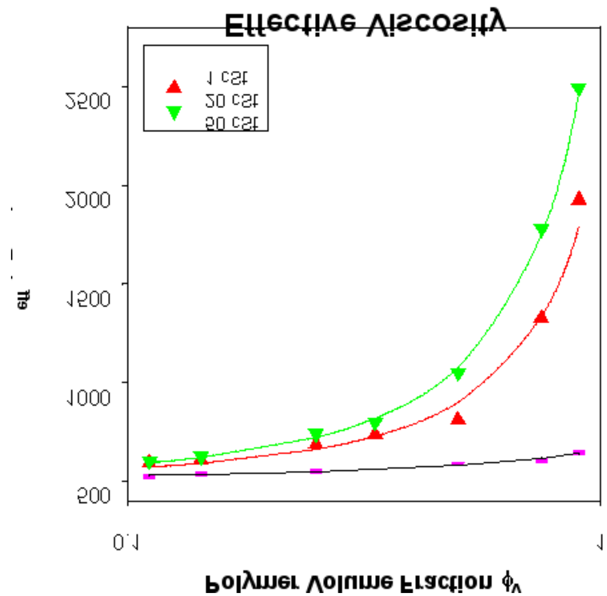
- **No need to separate/extract slowly decaying siloxane signal from mobile octane penetrant.**



Diffusion of Penetrants in Polymers

Linear PDMS





- **Diffusion is dependent on concentration of penetrant.**
- **Behavior varies with the polymer/penetrant system.**
- **Local effective viscosity can extracted from D/D$_0$.**

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)

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

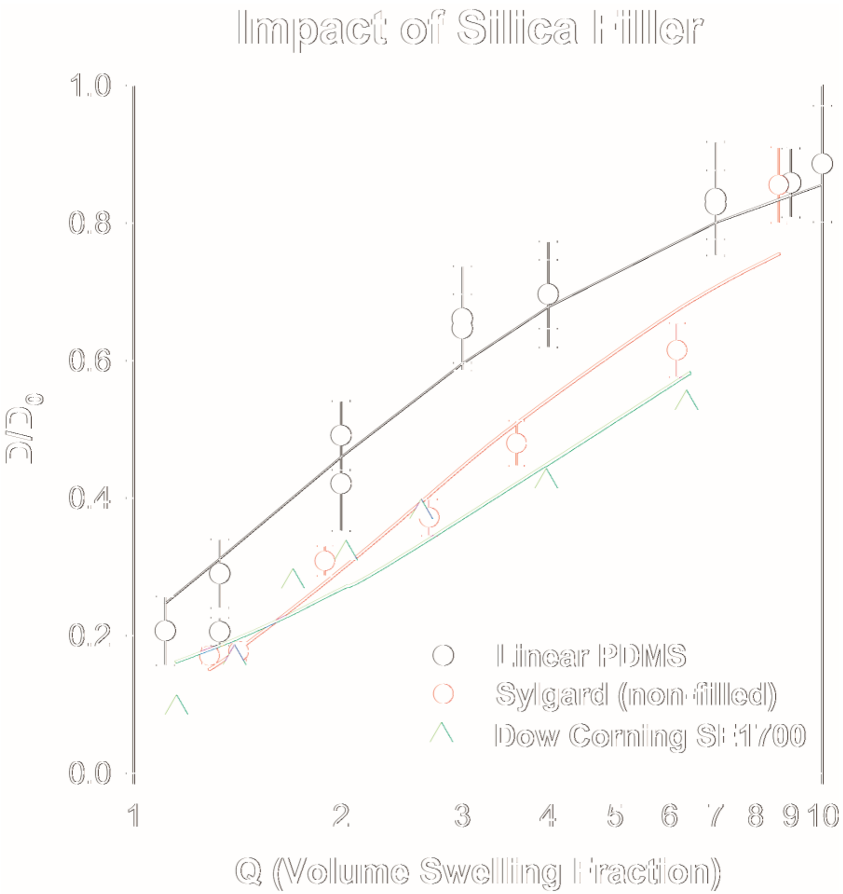
Petit (Hydrodynamic)

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

$$D = kT / \zeta$$

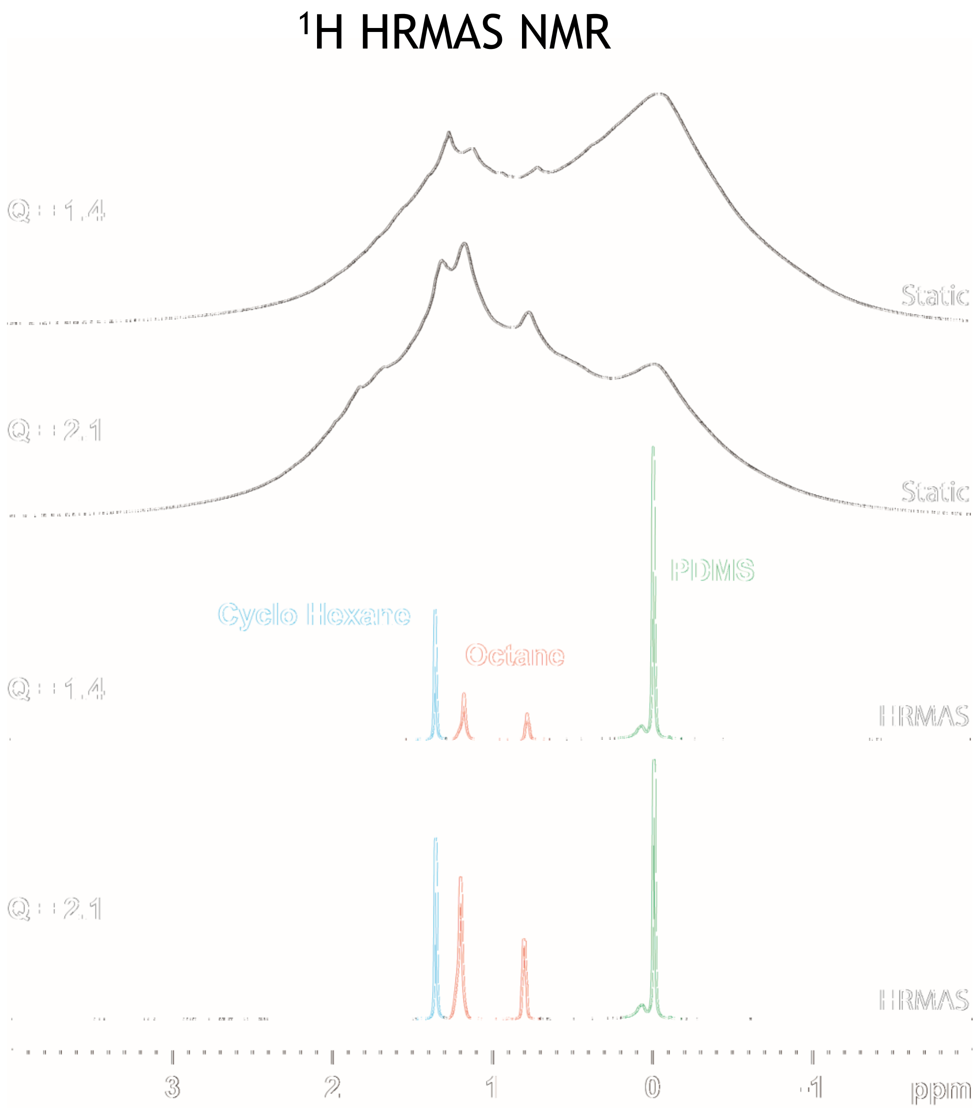
[1] Vrentas, Duba (1977) *J. Polym. Sci.*, **126**, 177-186. [2] Phillies, (1989) *J. Phys. Chem.*, **93**, 5029-5039.
[3] Petit, Roux, Zhu, MacDonald (1996), *Macromolecules*, **29**, 6031-6036.

Solvent Diffusion in 3D Printed Siloxanes



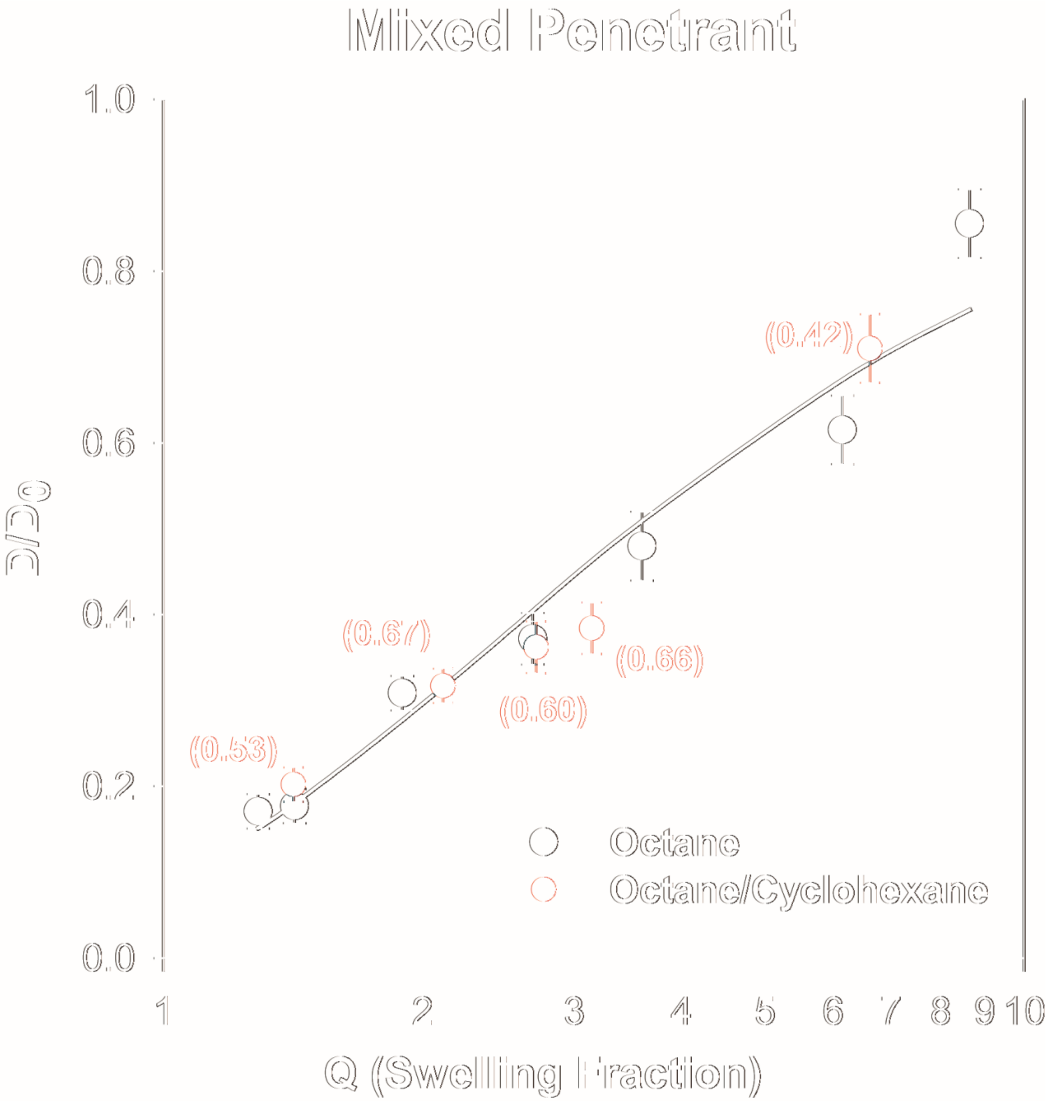
- Reduced diffusion in filled PDMS.
- Differences increase with swelling volume.
- In AM materials inconsistent material properties during production runs.
  - Variation on the % filler
  - Changes in the cross-link chemistry
  - Speed of AM impacted properties
- All of these reflected in the diffusion rate measured by HRMAS NMR diffusometry.

Penetrant Mixtures in Swollen Siloxanes

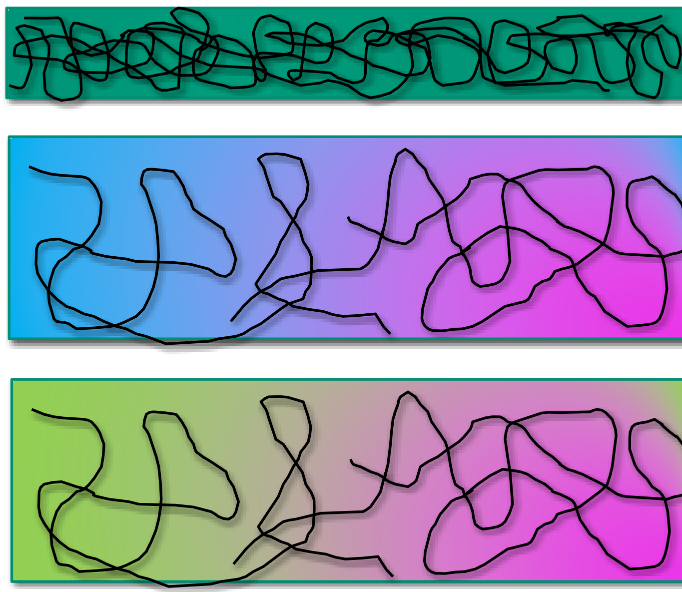


- **Different penetrant mixtures are unresolved under static conditions.**
- **Well resolved under HRMAS allowing individual diffusion constants to be measures.**
- **Also reveals differential PDMS species in swollen material.**

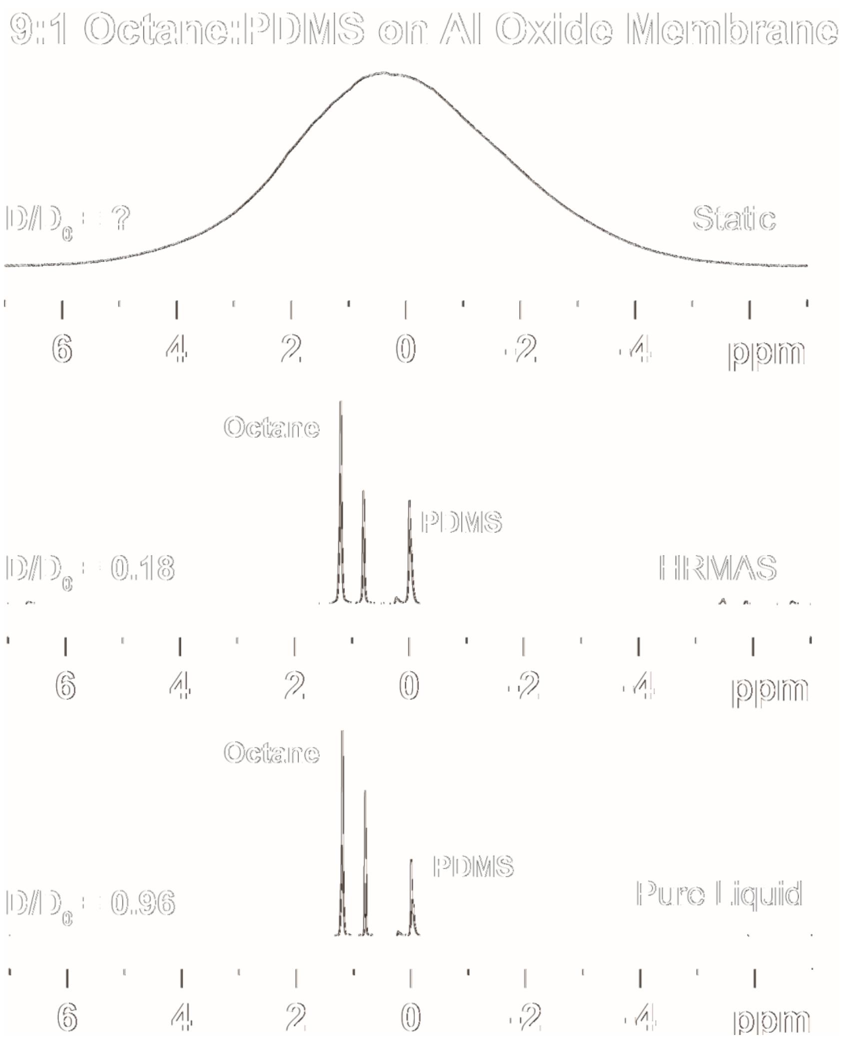
Diffusion for Penetrant Mixtures

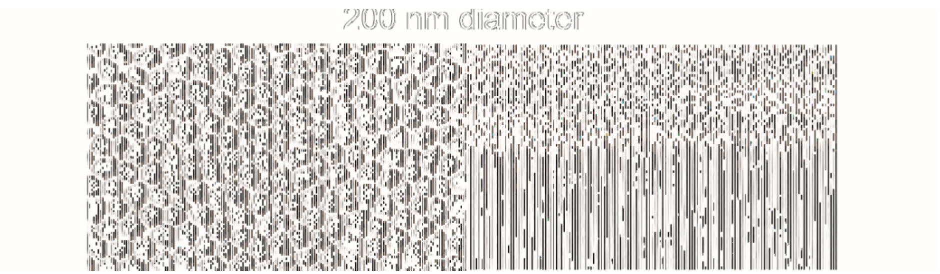


- **Diffusion of penetrants not strongly impact by solvent fraction [octane/(octane+cyclohexane).**
- **Diffusion well described by simple free volume description.**
- ***Need to investigate non-ideal solvent mixtures to identify preferential surface interactions.***



Resolution in Nanoporous Polymer Composites

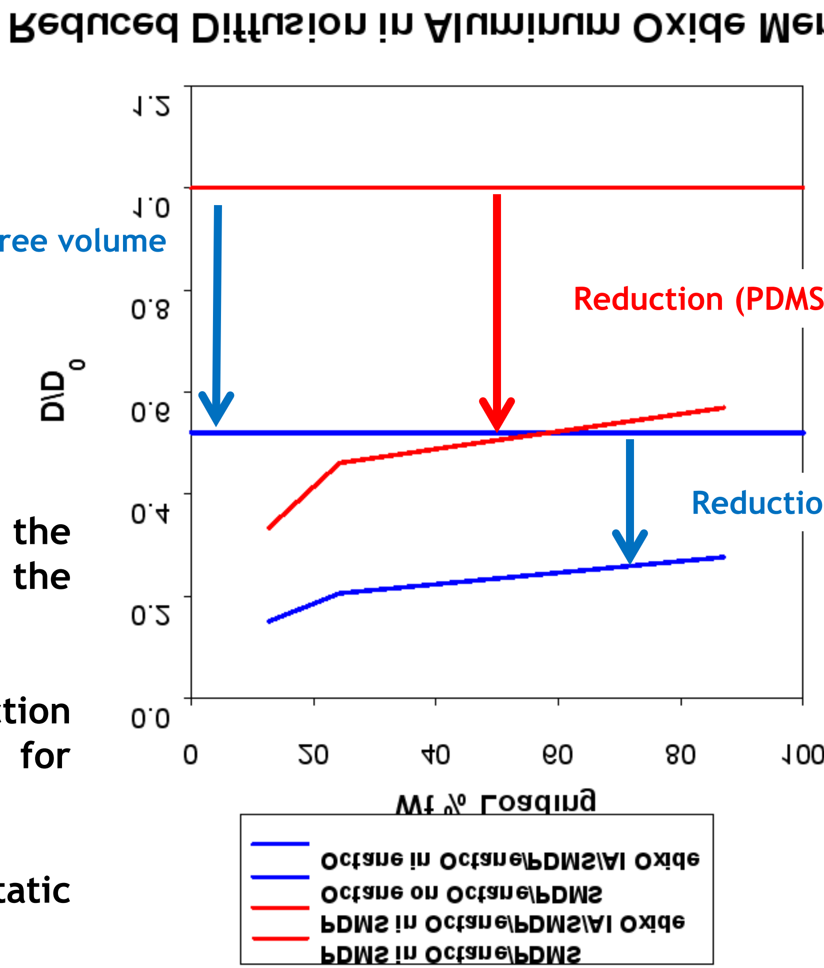




- **Example of surface interactions and confinement impacting diffusion.**
- **Adsorption into Al oxide membrane reduces diffusion of octane by a factor 5.**
- **Not a simple free volume effect!**

Diffusion in Nanoporous Membrane Polymer Composites (20 nm)

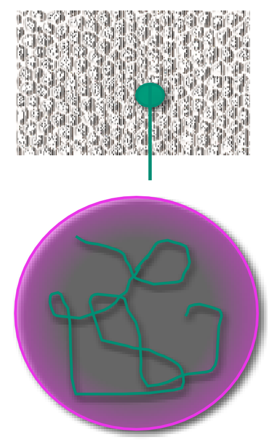
Reduction due to polymer free volume



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

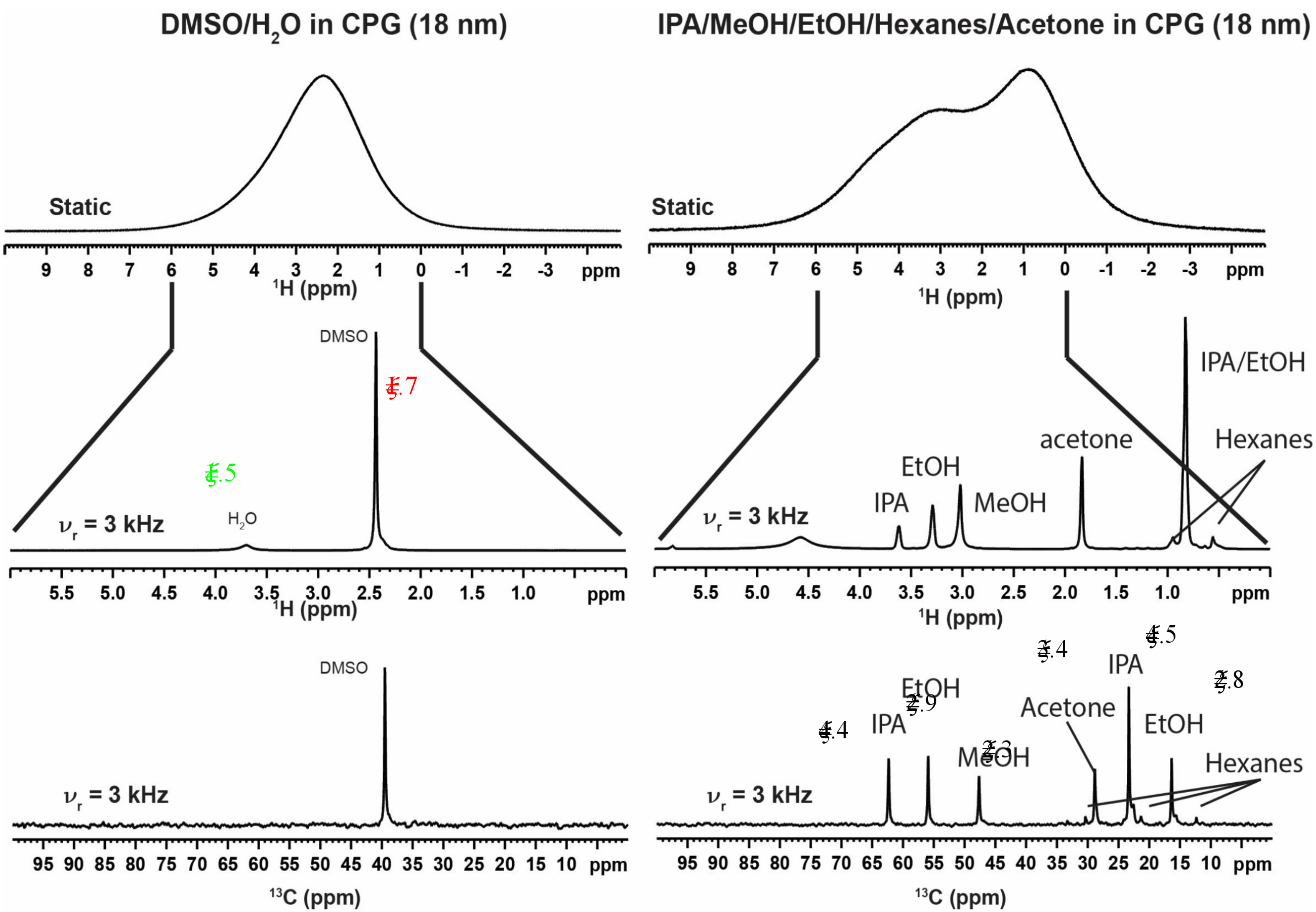
Reduction (PDMS) due to surface induced friction

Reduction due to surface induced friction

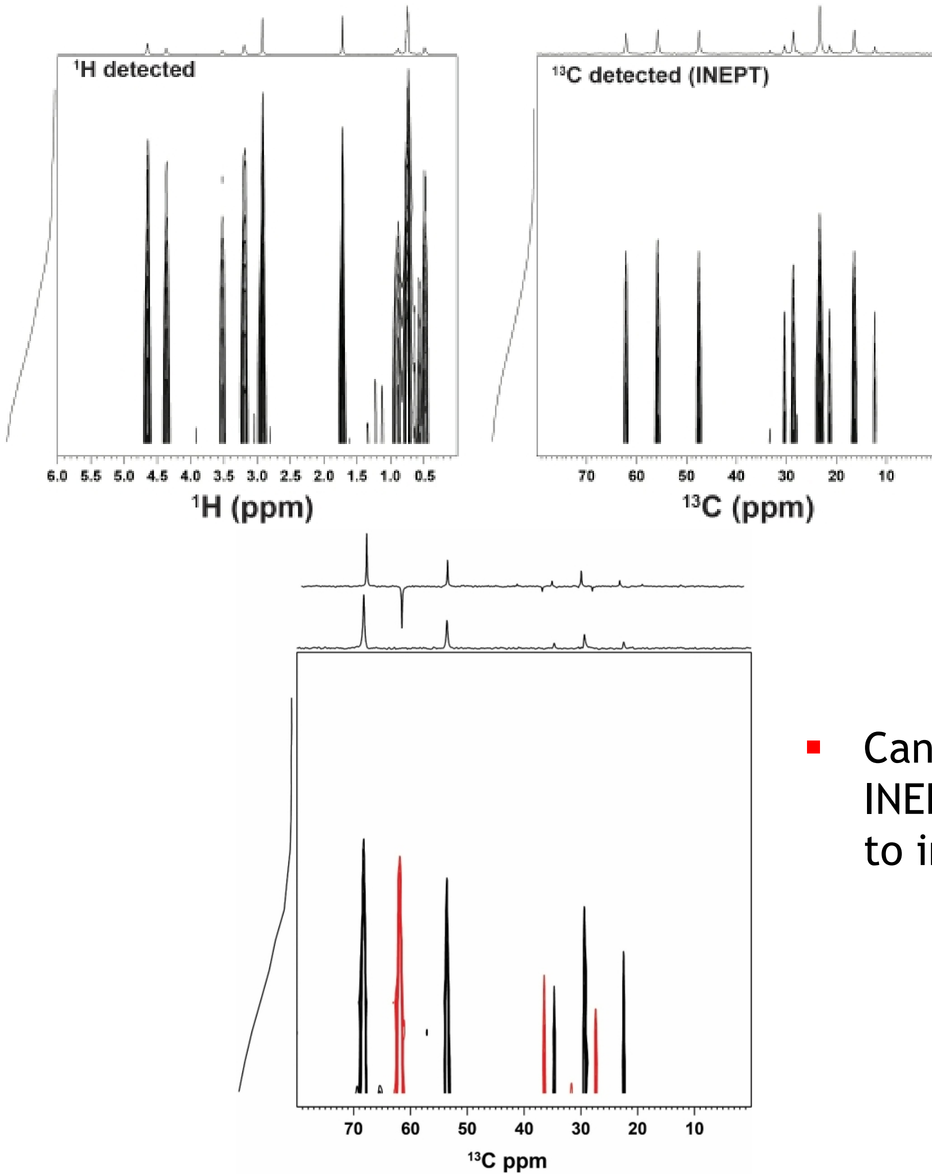


- **Cleary an impact of the confinement near the surface.**
- **Ratio of surface friction reduction similar for PDMS and Octane.**
- **Not resolvable in static PFG experiment.**

Examples: ^{1}H and ^{13}C Detected HRMAS Diffusometry



^{1}H-^{13}C INEPT Detected HRMAS NMR Diffusometry



- Can use J-filtering in INEPT (CH, CH_3 vs CH_2) to improve resolution)

Conclusions and Challenges

- HRMAS NMR diffusometry proves useful for resolving susceptibility broadened spectra in soft swollen materials (‘gels’).
- Gradient limited (50 g/cm) – defines this ***special niche***.
- Allows the ***direct measurement*** of PFG interaction parameters in multi-component mixtures!!!
- One of the few methods that can provide this type of diffusion characterization in multi-component mixtures.
- To maintain S/N required for ^{13}C detected experiments, need ***significant increase*** in the experimental time, and in many cases *would prove restrictive* for large number of samples! ^{1}H detection is still the best route to go.

Challenges

- Thermal convection at higher spinning speeds and low viscosity samples degrades diffusion measurements.
- **Major issues** with charged molecules (*i.e.* ionic liquids) - influence of varying magnetic field under MAS, magnetic convection? Magnetic mixing?

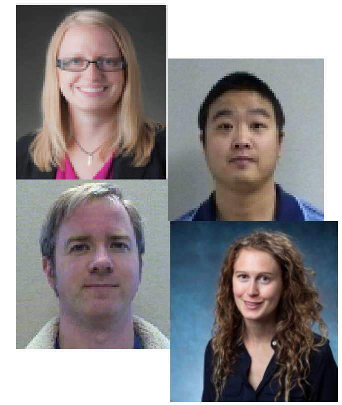
Acknowledgements

Prof. Janelle Jenkins (Prof. at E. Washington Univ.)

Dr. Cy Fujimoto (SNL) - SDAPP Synthesis

Dr. Michael Hibbs (SNL) - AEM Synthesis

Kim Childress (Graduate Student, UC-Boulder) - Lipid HRMAS



Thank you for your time….

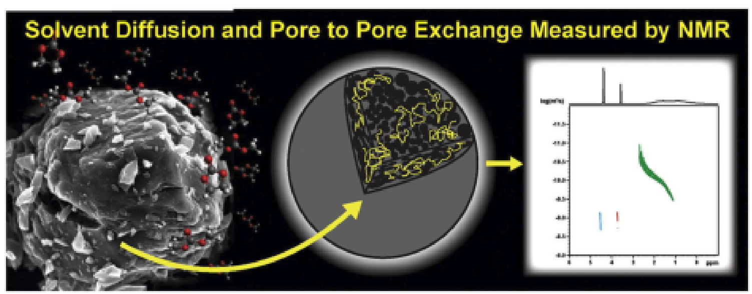
LDRD LABORATORY DIRECTED RESEARCH & DEVELOPMENT

Project funding through the Sandia LDRD program

Material Scientist NMR Spectroscopist

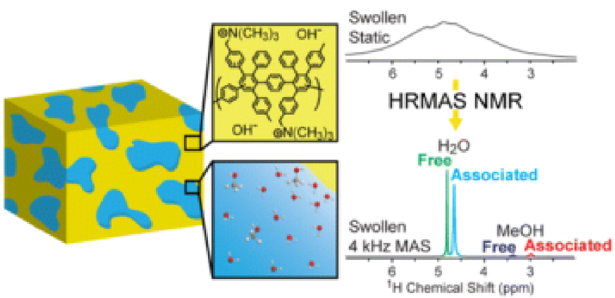
A Postdoc position will be available in the Organic Materials Science department and NMR facility at Sandia National Laboratories (SNL) in Albuquerque, NM. The staff position will be grounded in NMR spectroscopy and will be directed at developing methods to address material chemistry concerns for a wide range of national security applications including organic and polymeric materials, composites, ceramics, glasses and other energy and Nuclear Deterrence related materials. You will work directly with material scientists, engineers, and physicists to characterize these materials and to answer specific questions concerning structure, dynamics, kinetics, aging and lifetime in materials. Your responsibilities will include the operation, maintenance and future vision of the NMR facility at Sandia, the development and implementation of NMR methods for characterization, and to develop new and novel NMR methods as applied to materials chemistry.

The laboratory is well equipped for both solution and solid state NMR investigations. The position requires a Ph.D. in chemistry, physics, material science or closely related field. Excellent communication skills are required. Salary is industry-based, and is highly competitive for this position. The ability to obtain a clearance security will be required. Interested candidates should also apply directly to Job ID # XXXXXX LINK at www.sandia.gov

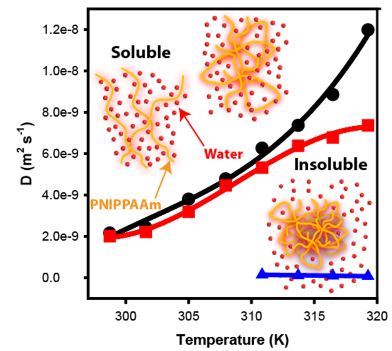


HRMAS NMR Diffusometry in Materials

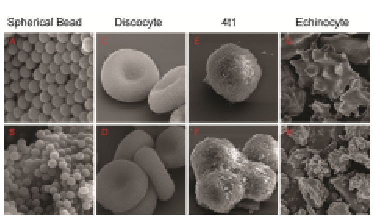
- "Identification of Multiple Diffusion Rates in Mixed Solvent Anion Exchange Membranes Using High Resolution MAS NMR", *ACS Macro Letters*, **1**, 910-914 (2012).
- "Characterization of Heterogeneous Solvent Diffusion Environments in Anion Exchange Membranes", *Macromolecules*, **47**, 1073-1084 (2014)

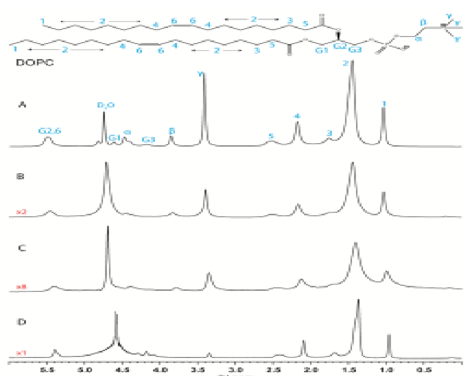


- "Characterization of Free, Restricted and Entrapped Water Environments in Poly(N-Isopropyl Acrylamide) Hydrogels via ^1H HRMAS PFG NMR Spectroscopy", *J. Polymer Science: Polymer Physics*, **52** 1521-1527 (2014).

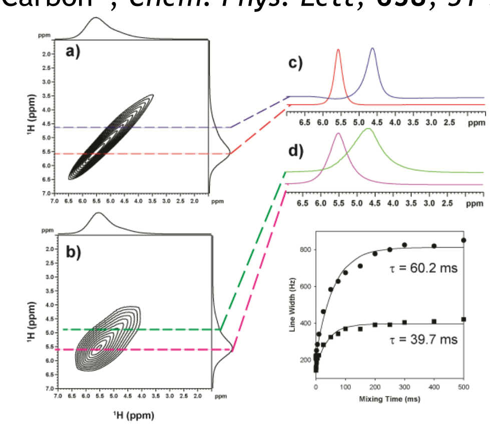


- "The Effect of Curvature on the Dynamic and Diffusional Properties of Phospholipids on Silica Materials using HRMAS NMR", *In Preparation*





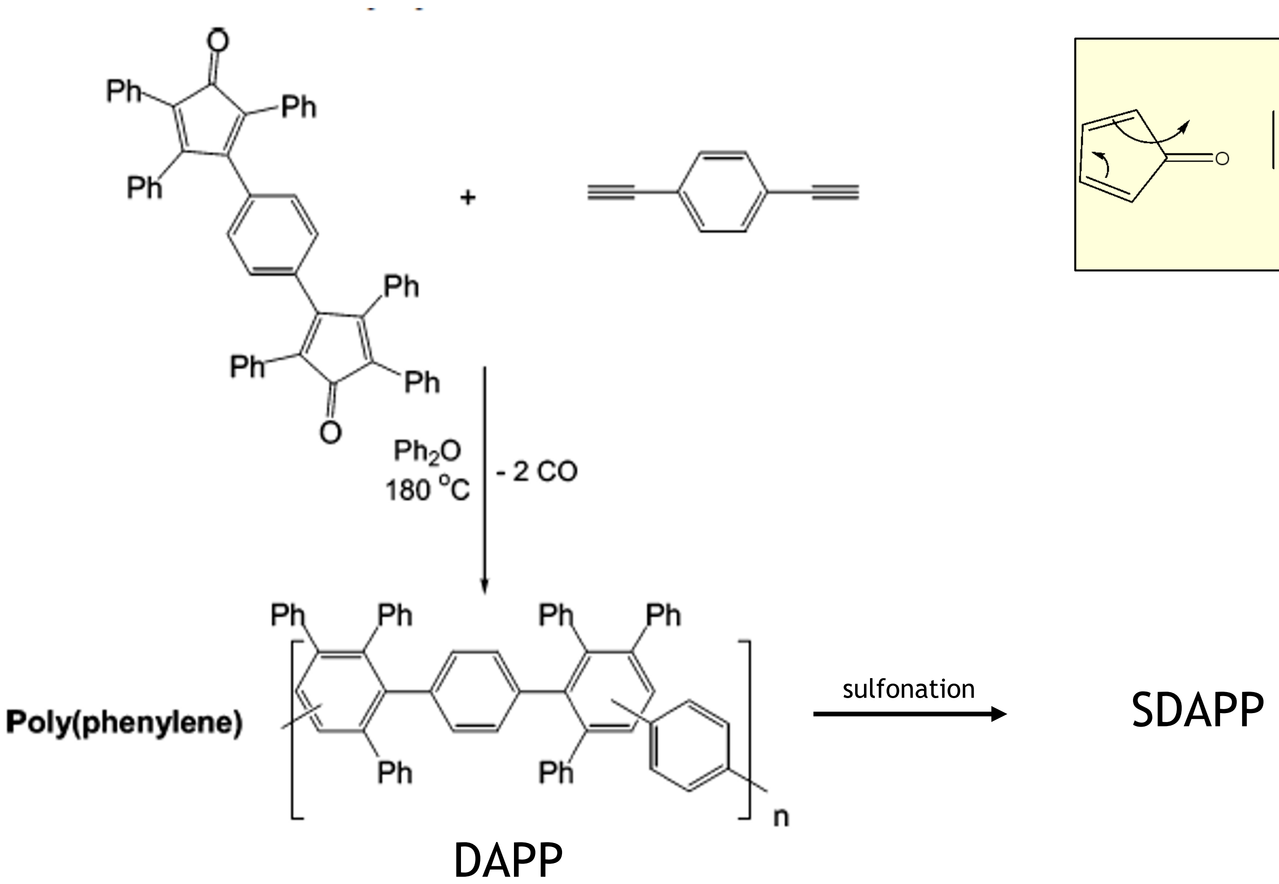
- "Measuring In-Pore Diffusion of Carbonate Solvent Mixtures in Nanoporous Carbon", *Chem. Phys. Lett*, **658**, *51-57*(2016).

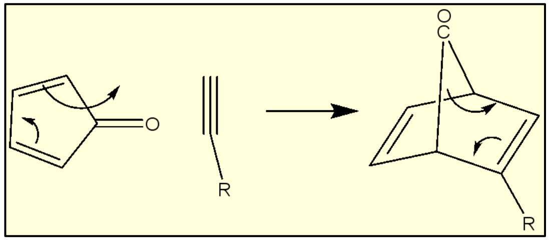


Current efforts: Machine Learning (ML) predictions of diffusion in multi-component mixtures

Backup Slides

Diels Alder Polymerization

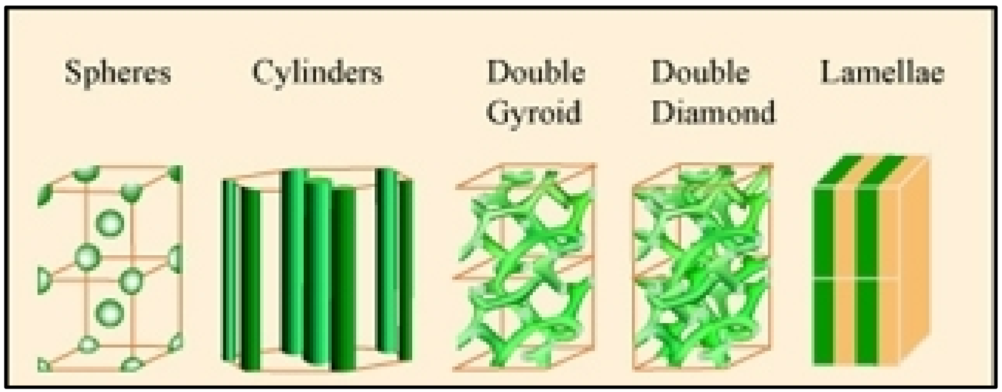




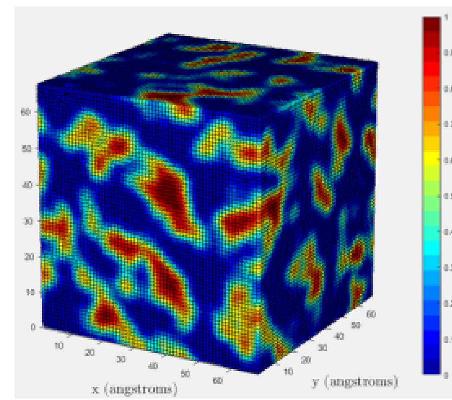
Nanoscale Morphology Impacts Design Principals for Improved Performance of Hydrocarbon Based PEMs

II. Morphology Control is Essential (Gross, 2009)

- Produce morphologies that provide percolation/transport pathways.
- Bicontinuous/random morphologies with numerous contacts between hydrophilic domains.
- Positional dependent diffusion constant (PDDC).
- Anisotropic directional alignment added benefit.

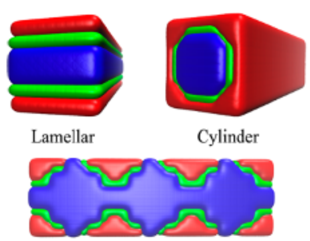


[1]

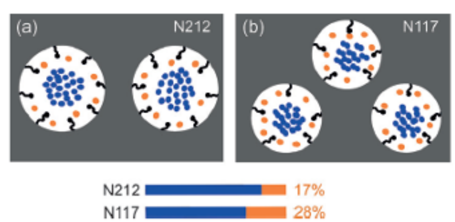


[3]

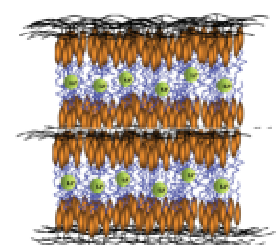
[2]



[4]

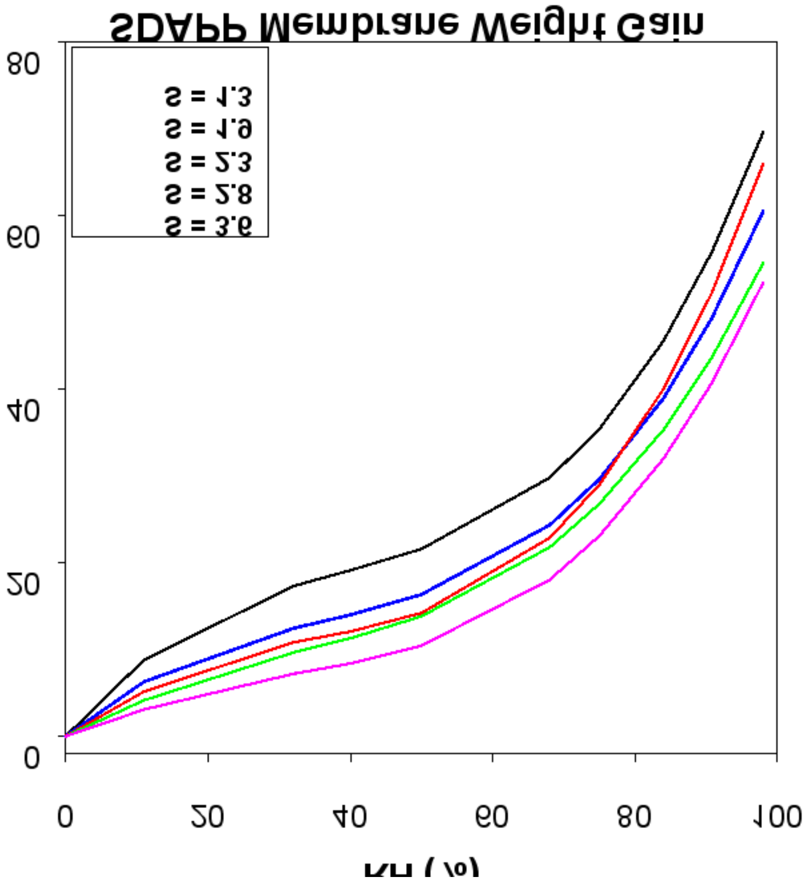


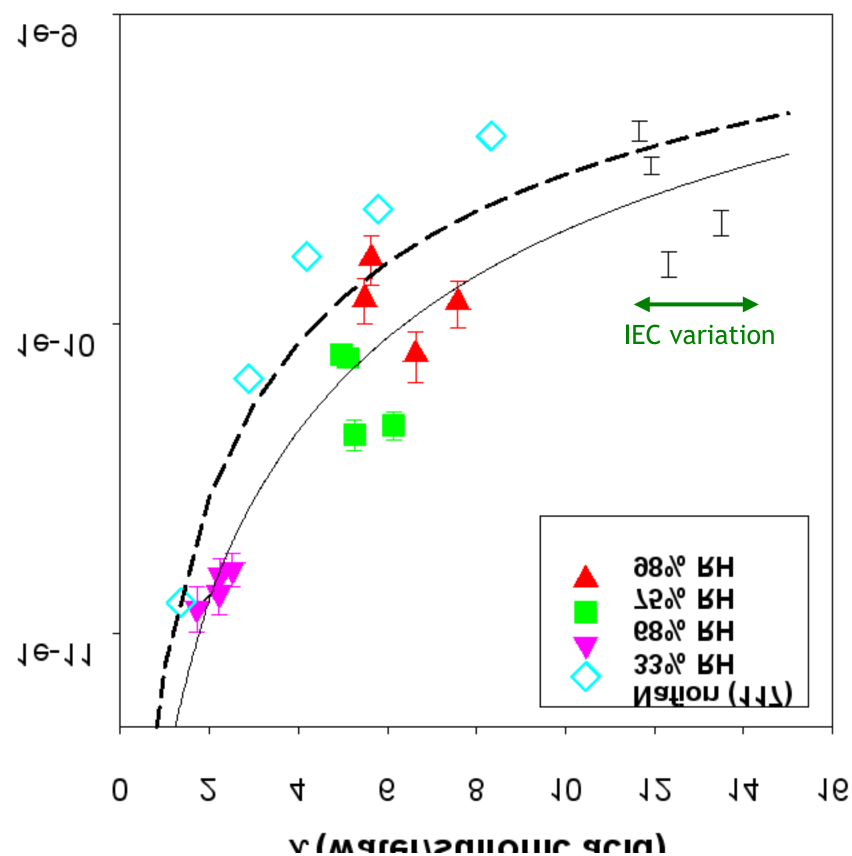
[5]



[1] Prof. Thomas, Figure by MIT OpenCourseWare. [2] Liu, S.; Savage, J.; Voth, G. A., Mesoscale Study of Proton Transport in Proton Exchange Membranes: Role of Morphology. The Journal of Physical Chemistry C 2015, 119 (4), 1753-1762. [3] Lauren J. Abbott and Amalie L. Frischknecht,"Nanoscale Structure and Morphology of Sulfonated Polyphenylenes via Atomistic Simulations" *Macromolecules 2017, 50(3), 1184-1192*. [4] Ling, X.; Bonn, M.; Parekh, S. H.; Domke, K. F., Nanoscale Distribution of Sulfonic Acid Groups Determines Structure and Binding of Water in Nafion Membranes. Angewandte Chemie International Edition 2016, 55 (12), 4011-4015. [5] P. W. Majewski *et al.*, "Anisotropic Ionic Conductivity in Block Copolymer Membranes by Magnetic Field Alignment" (2010), J. Am. Chem. Soc., 132, 17516-17522.

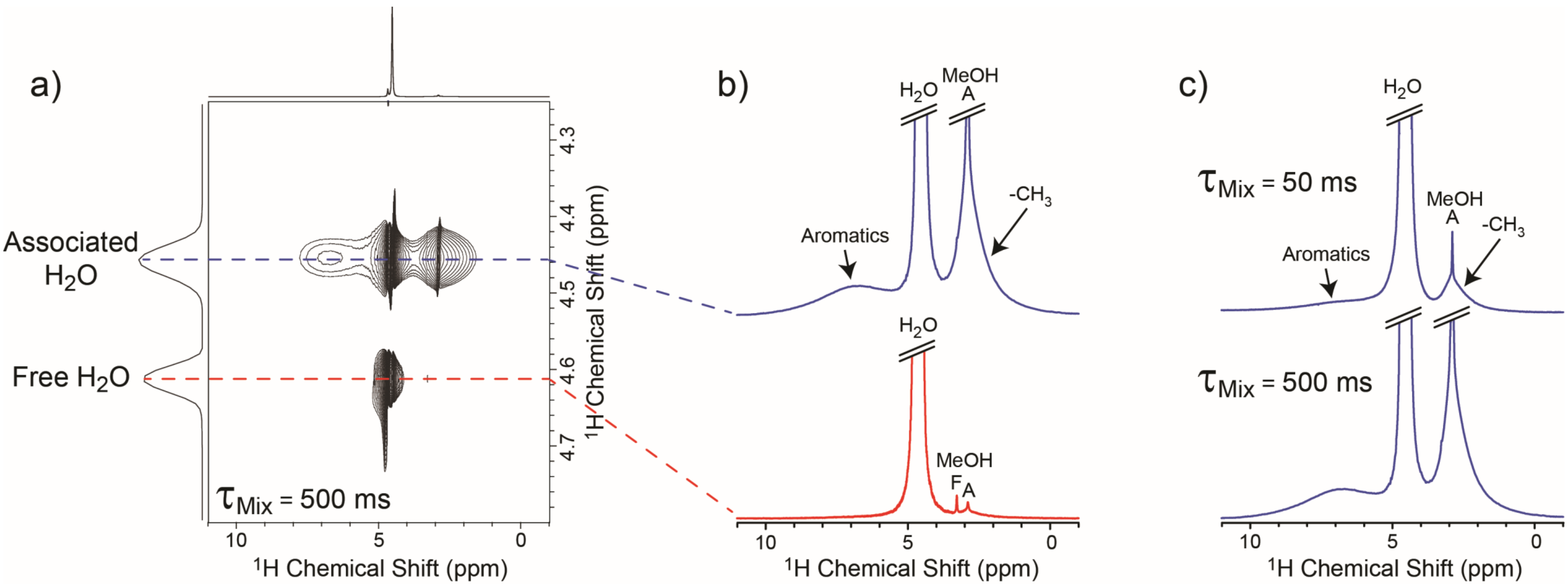
NMR Diffusometry - SDAPP Membranes



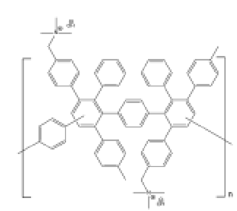


- Diffusion trends are same order of magnitude as Nafion.
- Small variations as a function of IEC.

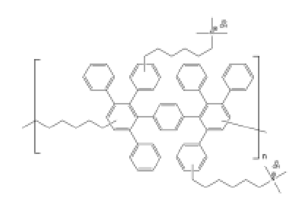
Where are these Associated Species?



- **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.**

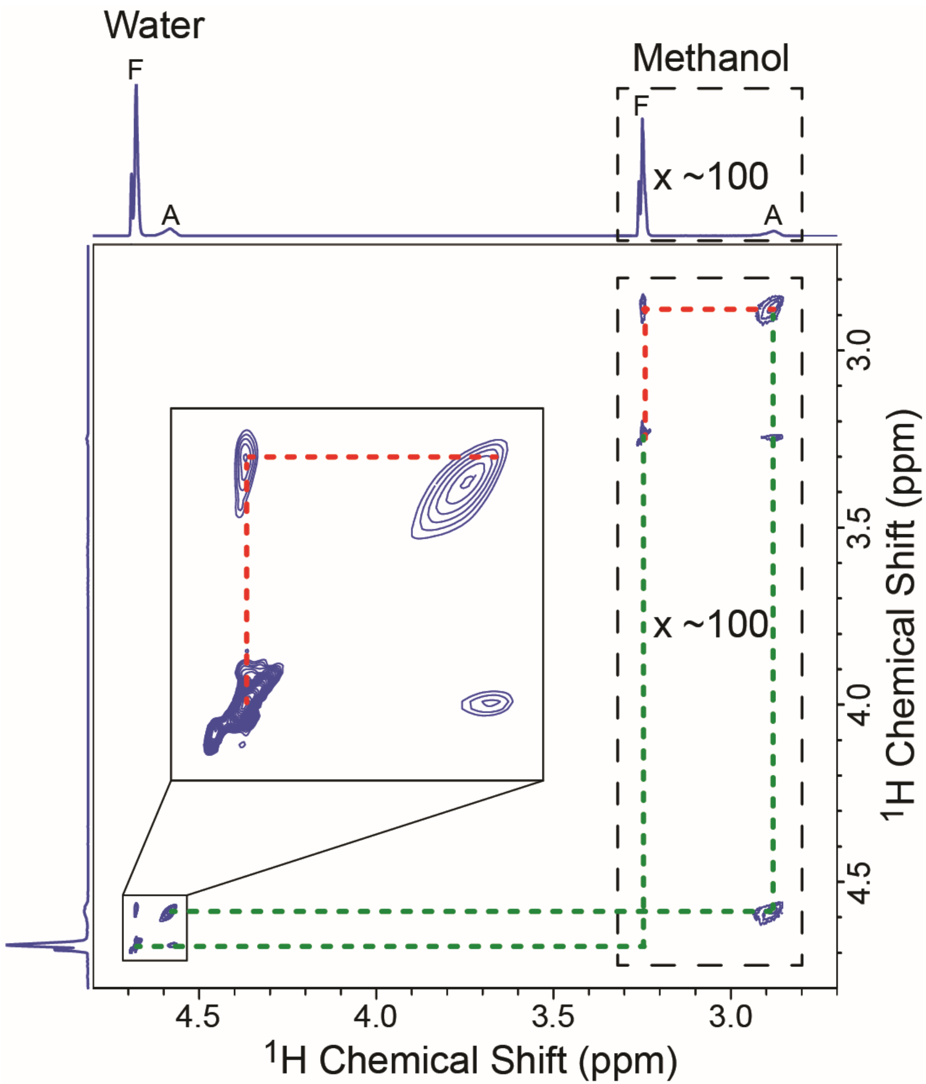


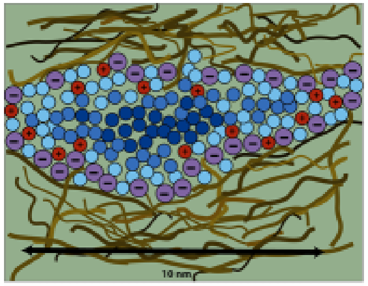
ATMPP



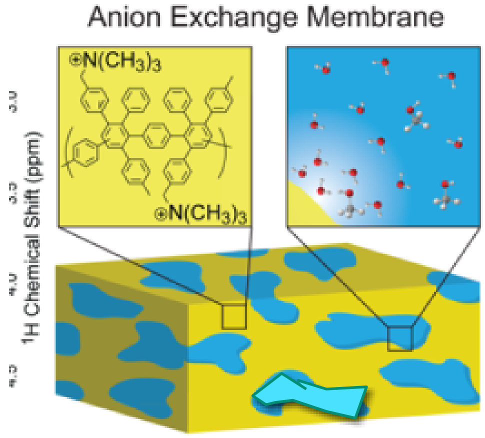
$TMAC_6PCC_6$

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

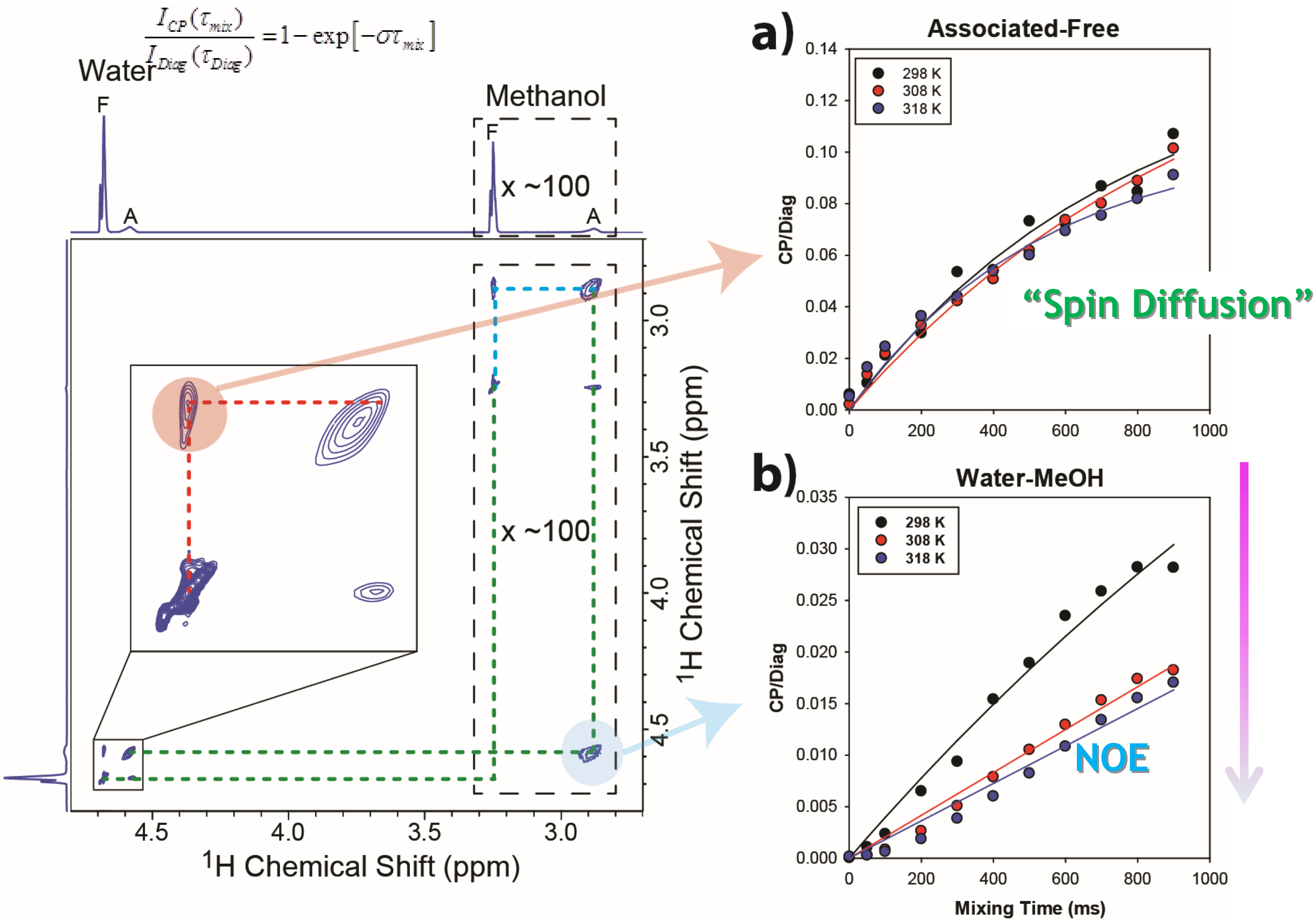




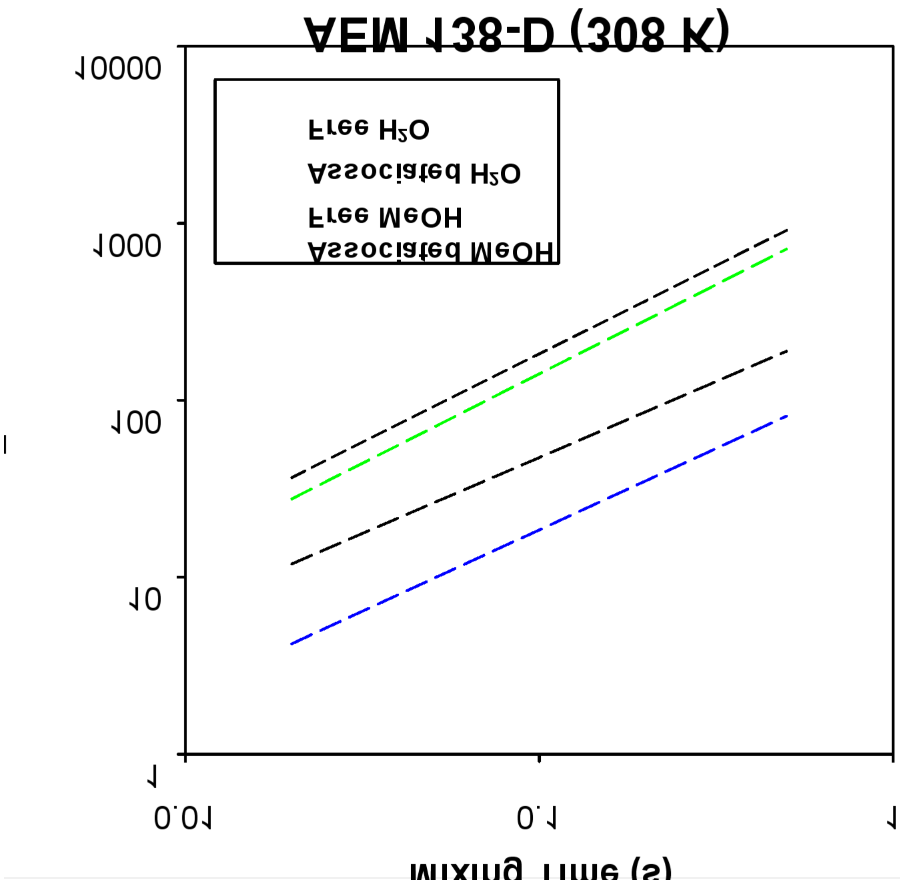
- Free and associated domains exist.
- These domains show some exchange.
- Associated water and MeOH in close contact with membrane.



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



Anomalous Diffusion?



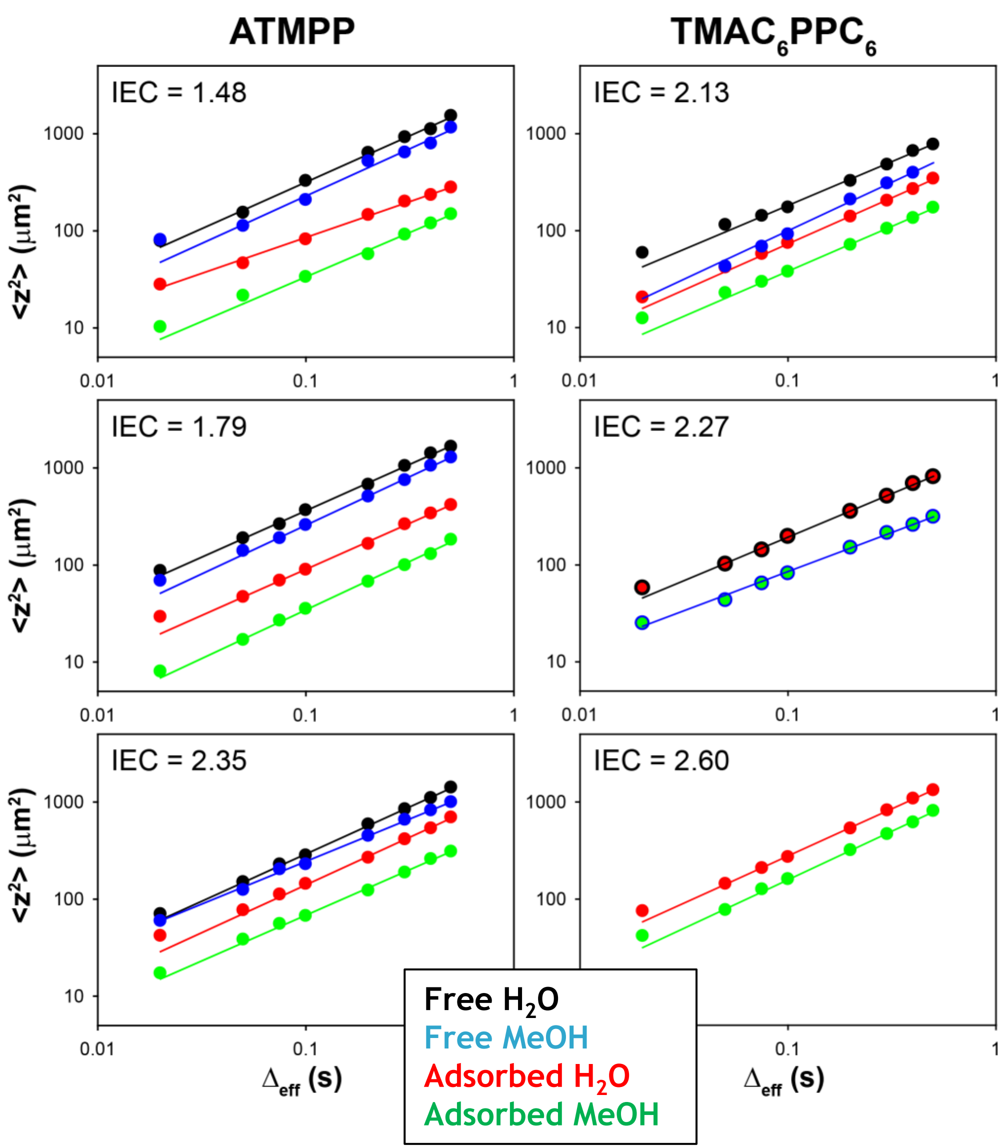
Anomalous diffusion can be expressed can be expressed through the power law.

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

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

Disappears with increasing temperature.

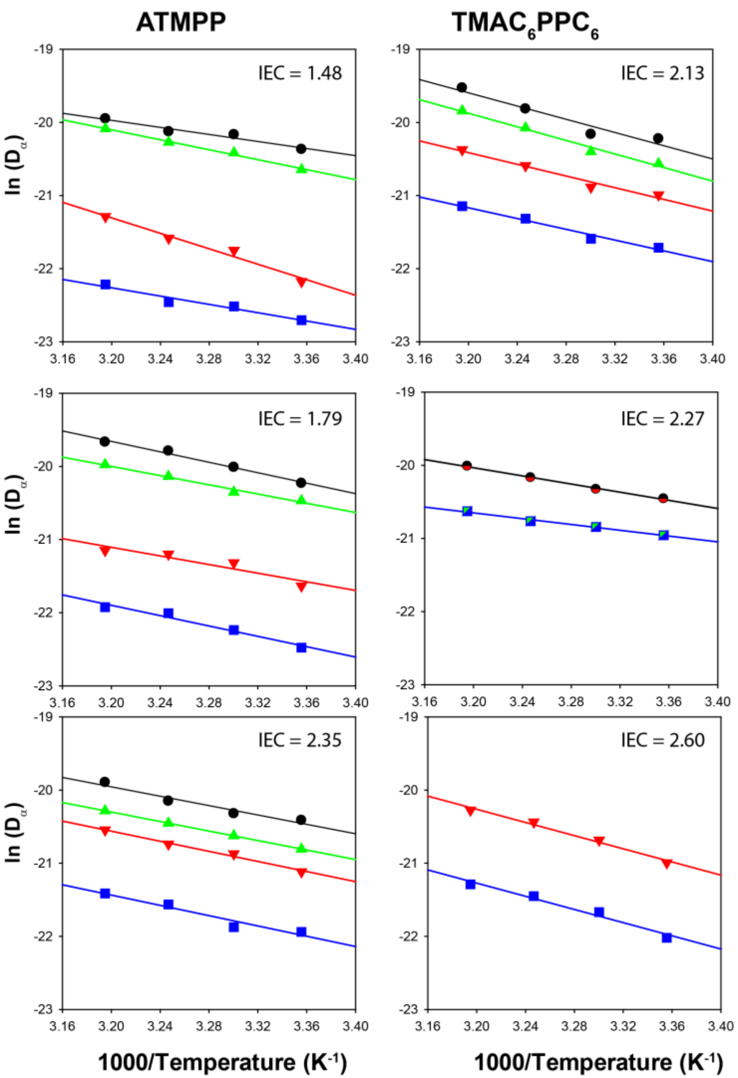
Diffusion Analysis of Individual Species



- Extract $\langle z^2 \rangle$ from multiple different Δ delays in PFG NMR
- Evaluate possibility of anomalous diffusion (α ≠ 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

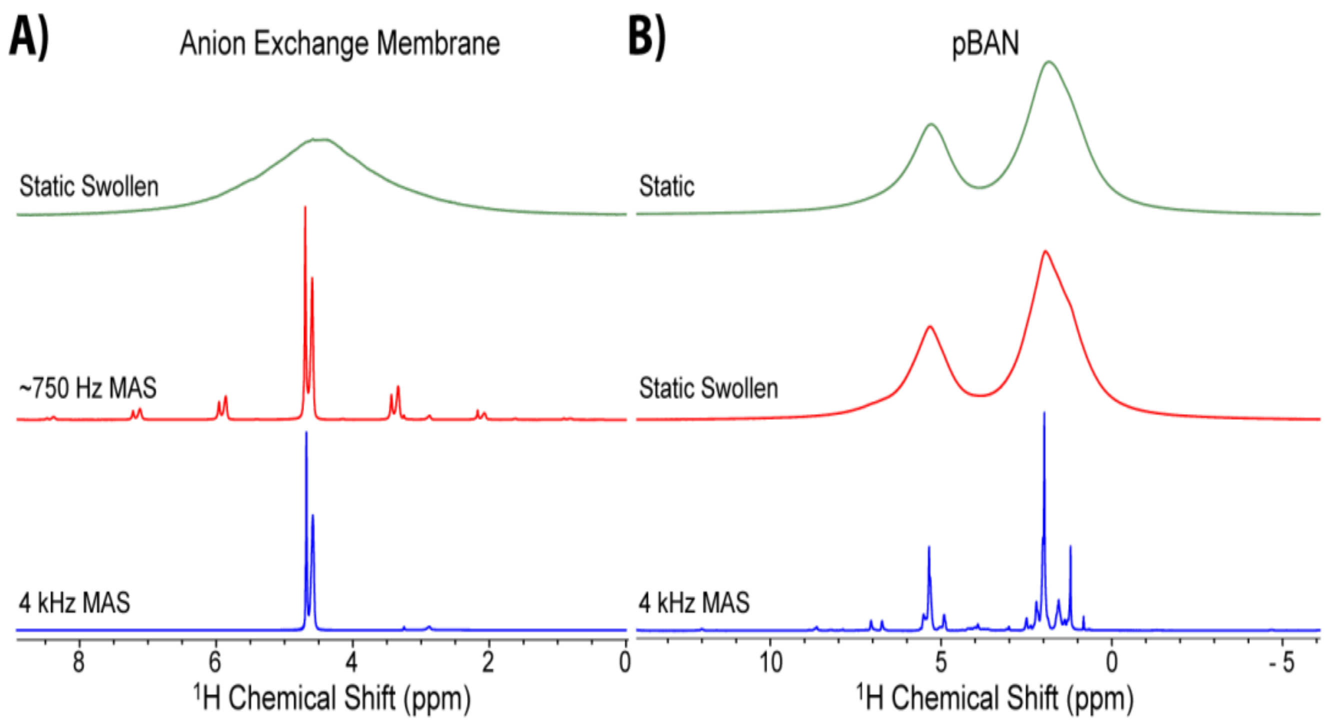
Activation Energies



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	44.0	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	33.3	38.6	30.6
$TMAC_6PCC_6$ (2.27)	--	23.2	--	16.5
$TMAC_6PCC_6$ (2.60)		37.4		37.5

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

Averaging Magnetic Susceptibility Differences



The improved resolution observed using ^{1}H HR-MAS NMR for the A) methanol swollen anion exchange membrane, and B) the $CDCl_3$ swollen pBAN (polyButadiene-AcryloNitrile) polymer.

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

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

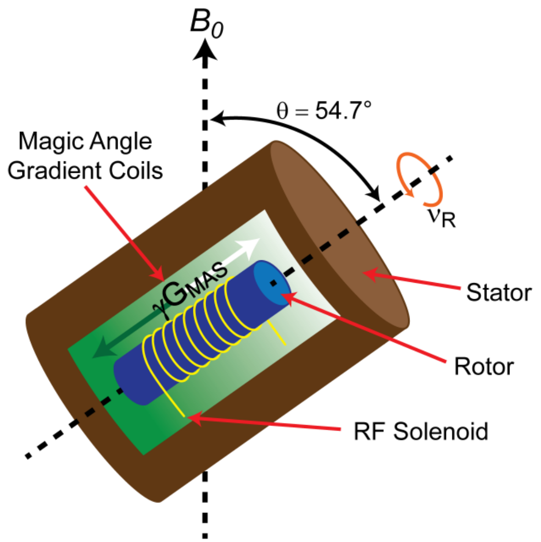
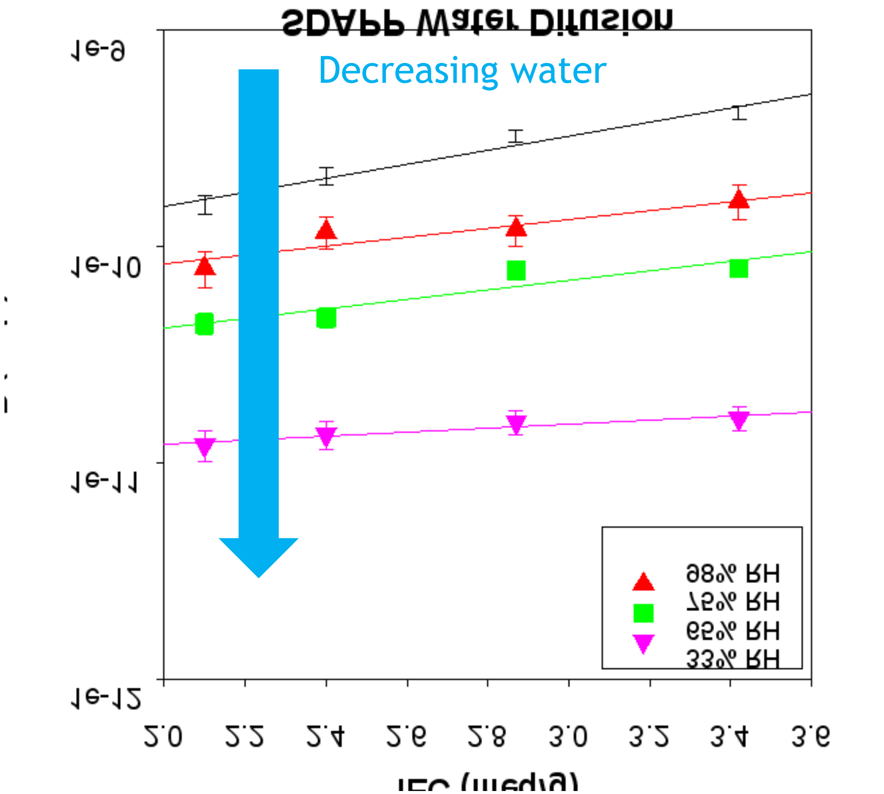
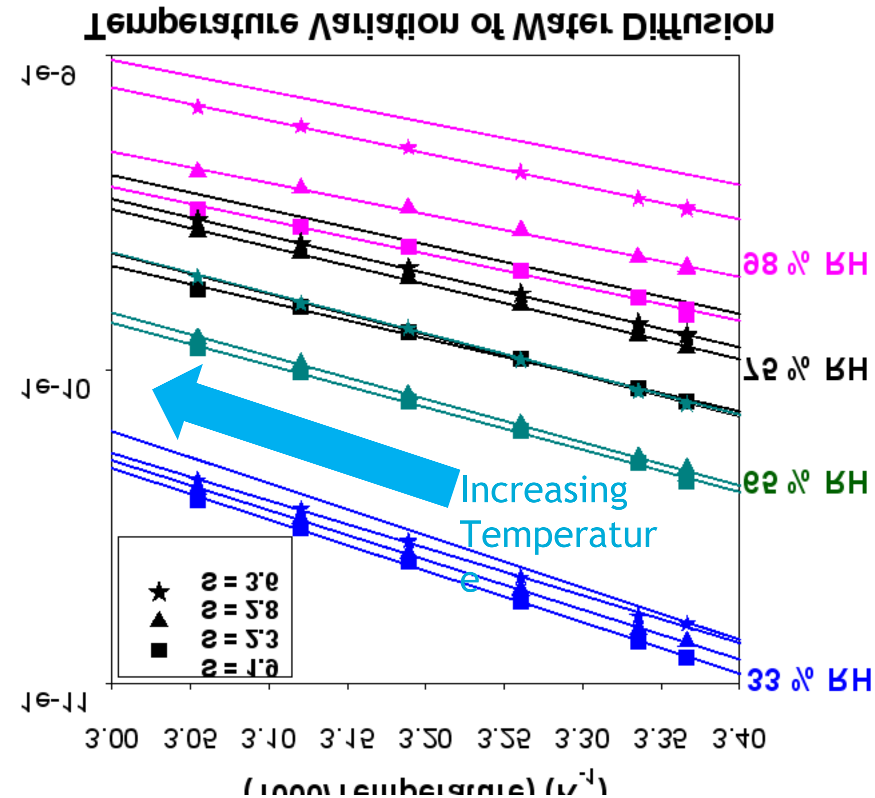


Table 1: MAS shims in terms of laboratory (Lab) frame.[25]

NMR Diffusometry - Water in SDAPP Membranes





Sample	E_a (kJ/mol)			
	33%	65%	75%	98%
S = 1.9	31.3	25.8	22.2	20.4
S = 2.3	30.4	26.4	22.9	19.1
S = 2.8	29.0	24.7	22.6	20.1
S = 3.6	31.8	24.7	21.1	19.0

- E_a similar to other PEMs at higher hydration levels.
- At < 33% RH increasing E_a.
- PFG NMR not obtainable at low RH%

Conductivity and Diffusion

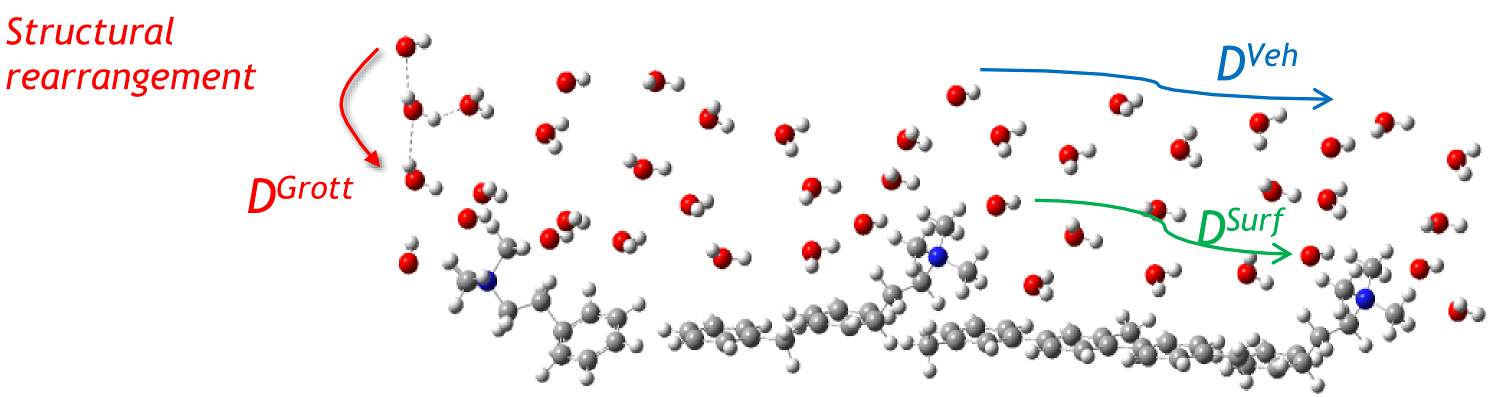
Nernst-Einstein Equation

$$\sigma = \frac{F^2 c\left(D_+ + D_-\right)}{RT} \xrightarrow{\text{Only involves } H^+ \text{ (or } OH^-\text{)}} \sigma = \frac{F^2 c\left(D_+\right)}{RT}$$

Surface **Grotthuss** **Vehicular**

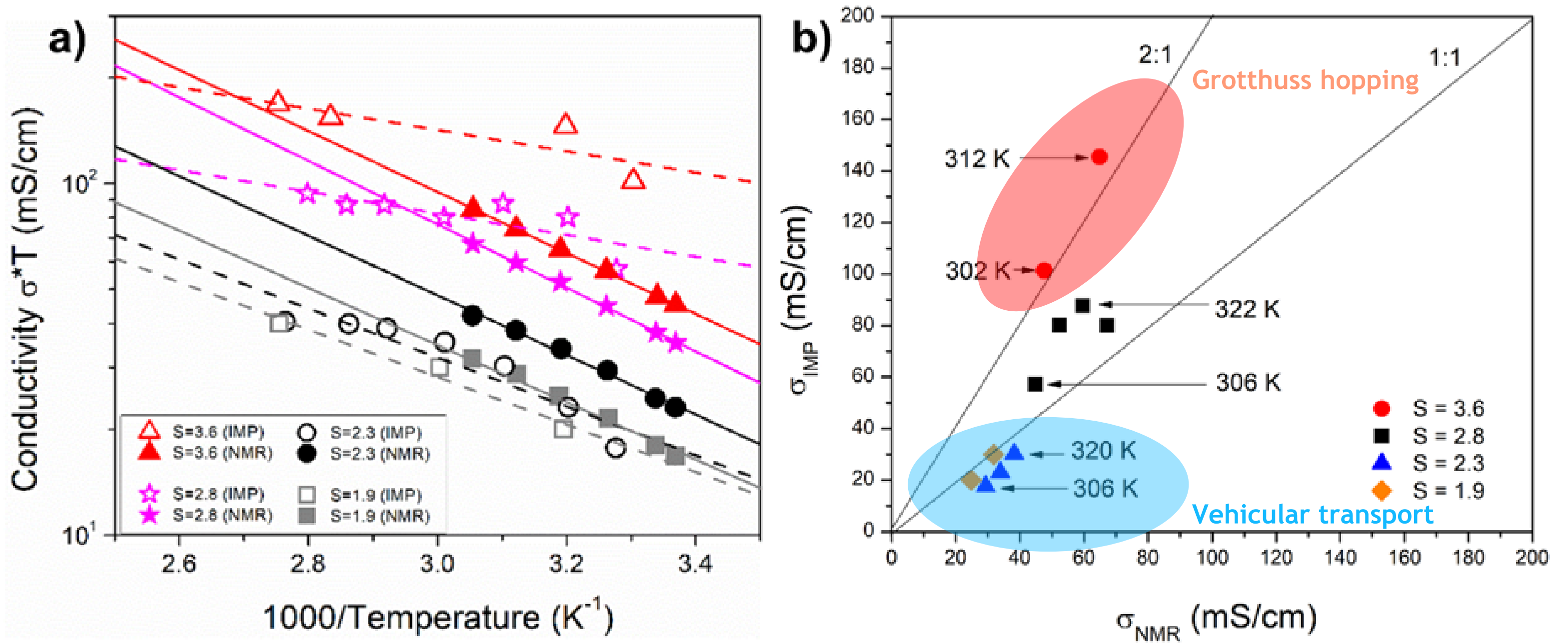
$$\sigma = \frac{F^2}{RT}\left(D_{H^+}^{Surf} C_{H^+}^{Surf} + D_{H^+}^{Grott} C_{H^+}^{Grott} + D_{H^+}^{Veh} C_{H^+}^{Veh}\right)$$

The transport of H^+ in PEMs can also be discussed in terms of different diffusion environments.



If we can measure diffusion individually, we can evaluate different contributions.

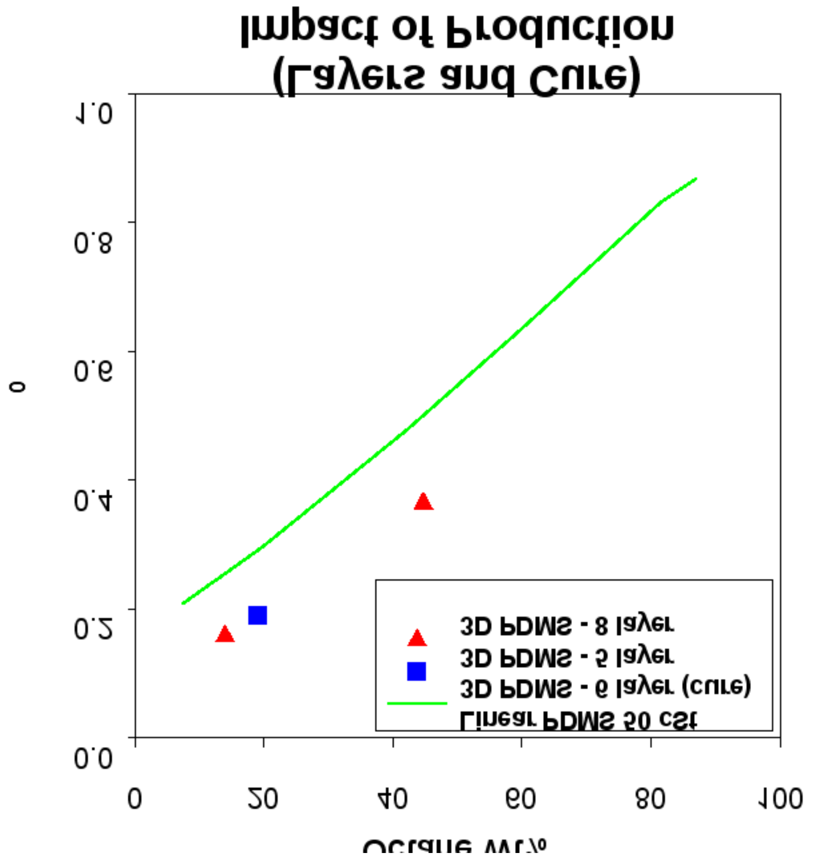
SDAPP Conductivity from Diffusivity

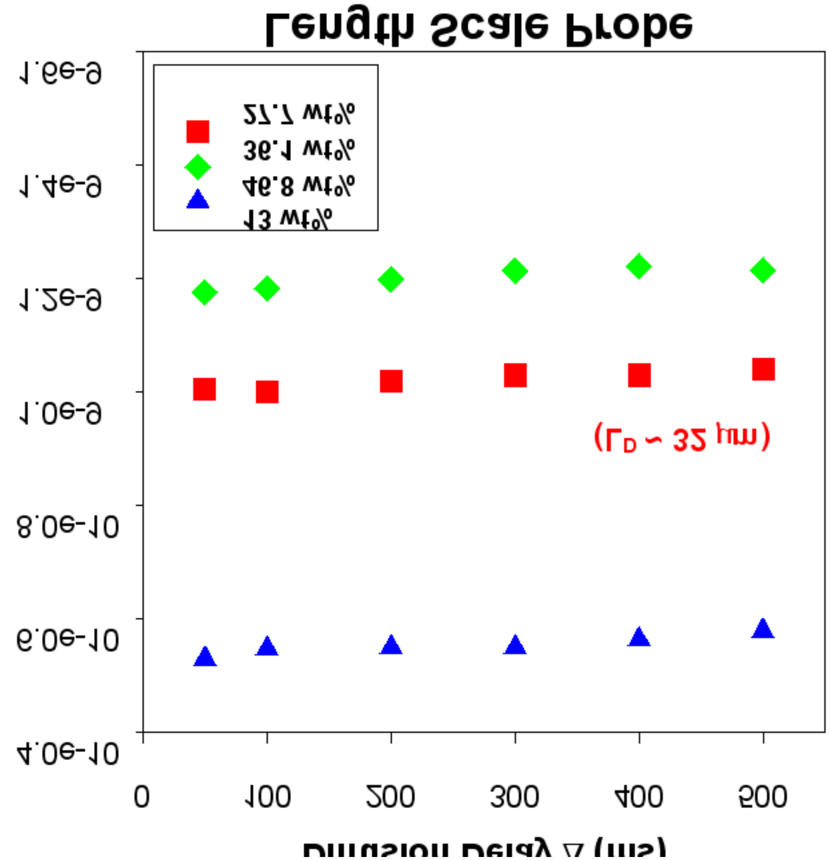


- At low-moderate S conductivity controlled by water vehicular transport at full hydration.
- With increasing S, Grotthuss mechanism becomes significant and leads to increased conductivity beyond simple diffusion.
- Membrane design rule strive for the highest D^{veh}, but H^+ requires an environment (hydrogen bond strength) allowing Grotthuss hopping.

Eric G. Sorte, Benjamin A. Paren, Christina G. Rodriguez, Cy Fujimoto, Cassandria Poirier, Lauren J. Abbott, Nathaniel A. Lynd, Karen I. Winey, Amalie L. Frischknecht, and Todd M. Alam, "Impact of Hydration and Sulfonation on the Morphology and Ionic Conductivity of Sulfonated Poly(phenylene) Proton Exchange Membranes", Macromolecules 52, 857-876 (2019).
DOI: 10.1021/acs.macromol.8b02013

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….)***
- ***T_2 variation (differences in crosslink density)***