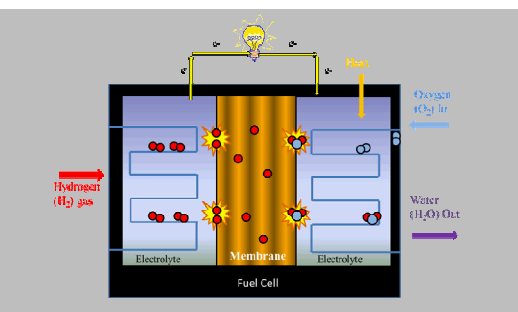
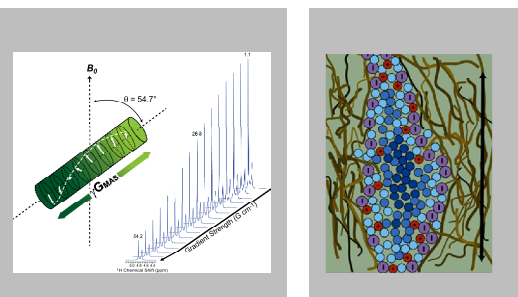


Opening the Door on Heterogeneous Diffusion in Polymer Membranes Using PFG HRMAS NMR



Todd M. Alam

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87185

245th ACS National Meeting, New Orleans, April 9th, 2013

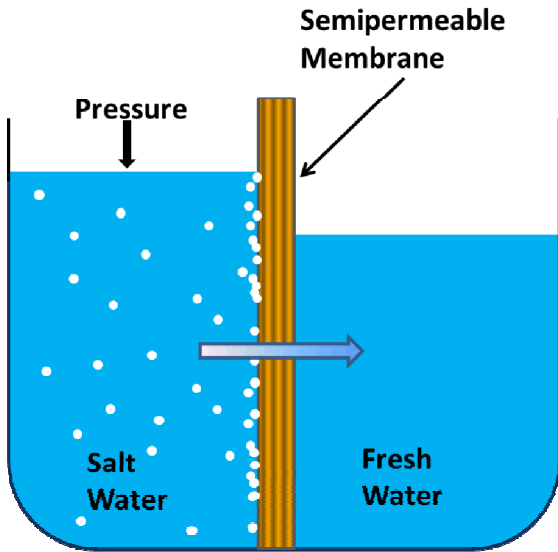


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interest*

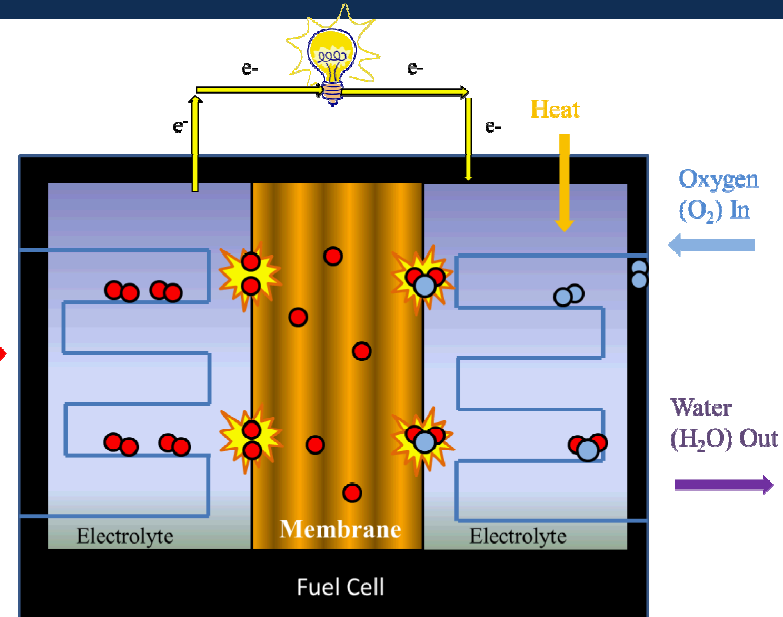


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Fuel Cells and Desalination Membranes



Hydrogen (H₂) gas



Oxidation
Half-reaction
 $H_2 = 2H + 2e^-$

Reduction
Half-reaction
 $O_2 + 4H^+ + 4e^- = 2H_2O$

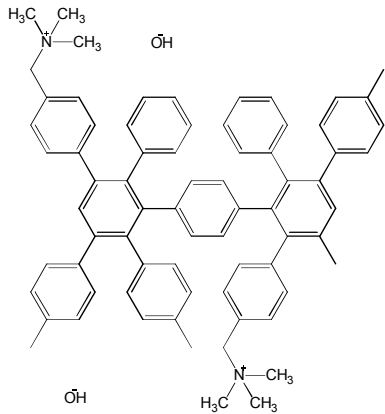
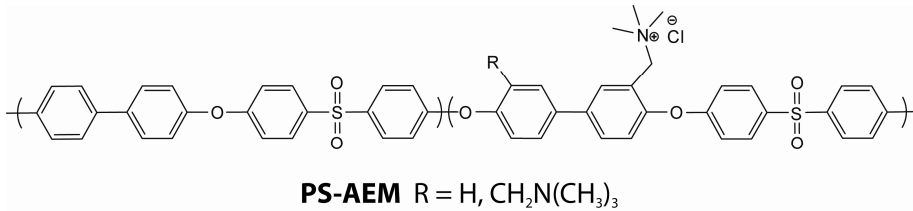
- Desalination
- Reverse Osmosis
- Electrolysis

- 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.

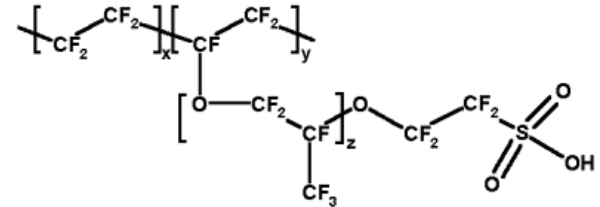
AEM and PEM Membranes

Anion Exchange Membranes (AEM)

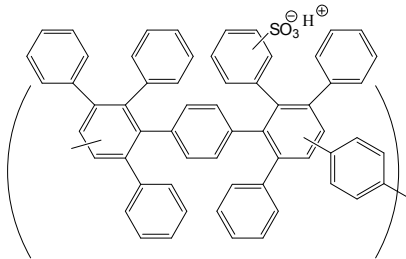


(ATMPP)
aminated trimethyl
polyphenylene

- 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.



Proton Exchange Membranes (PEM)

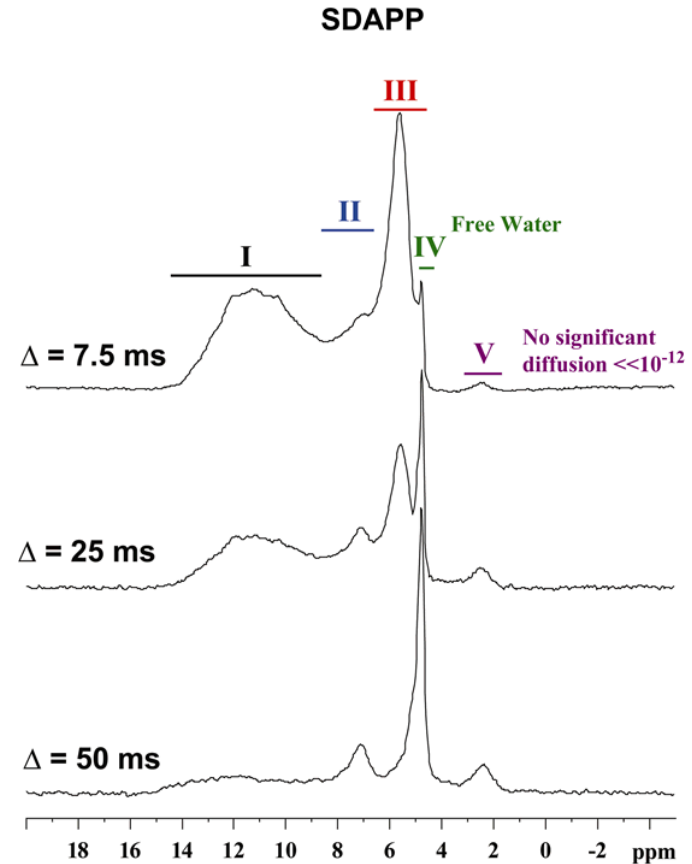
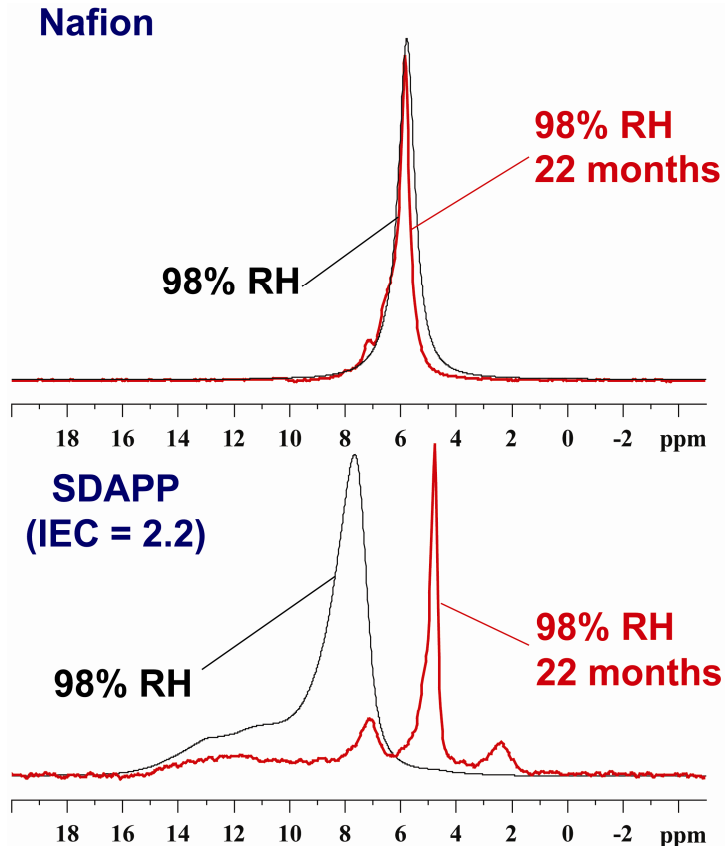


- High thermal chemical stability.
- Easily processed, lower cost.
- Wide range of functionalities.

Sulfonated Diels Alder Polyphenylene (SDAPP)

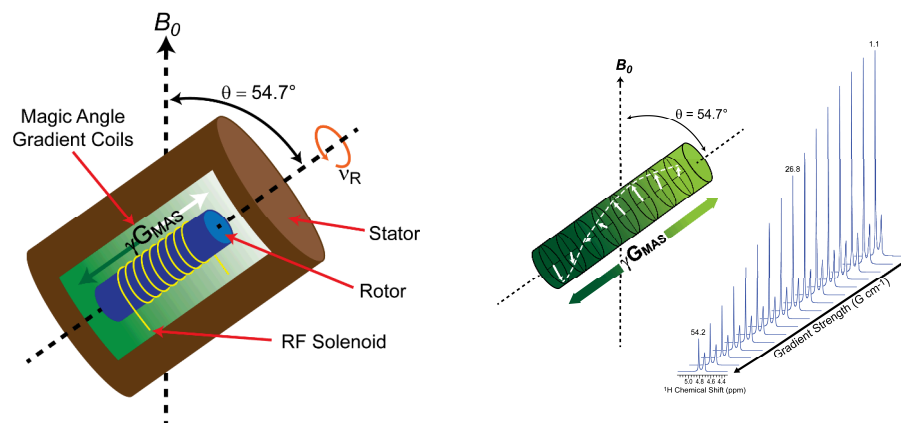
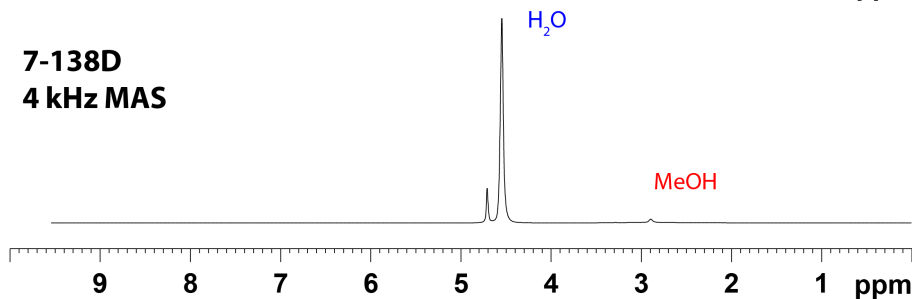
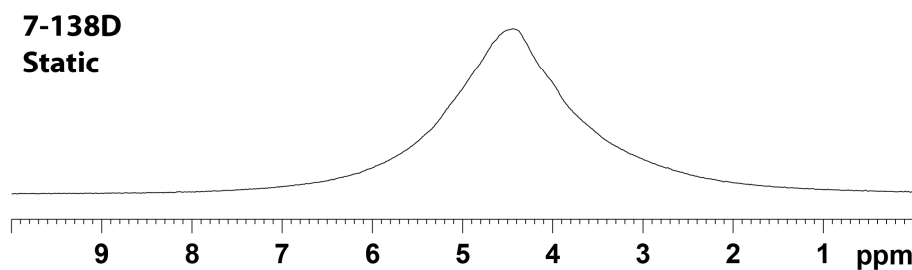
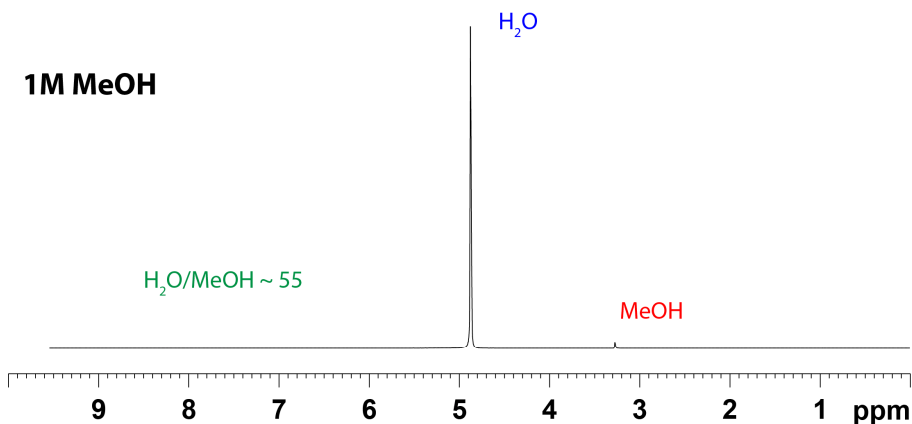
PFG NMR and Site Resolution

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!

Site Resolution in MeOH Fuel Cell Membranes

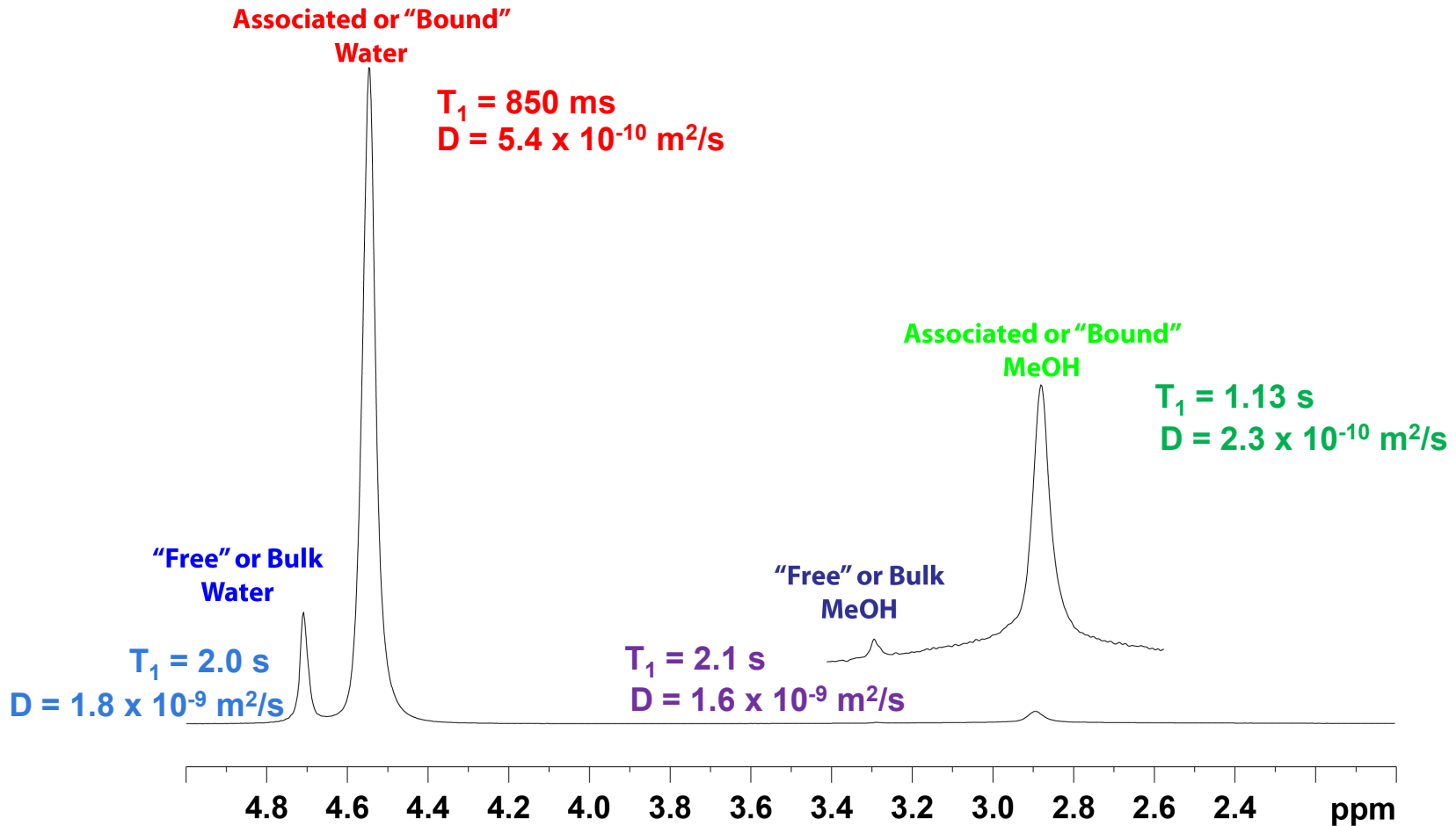


Different water environments in polymers

- 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.

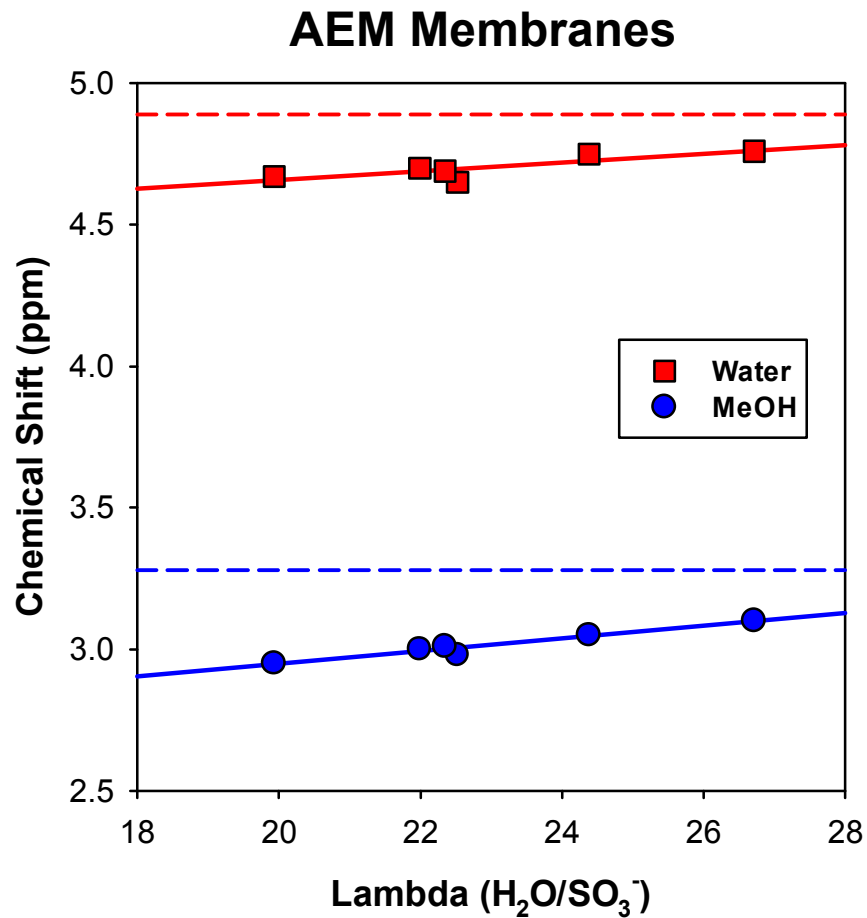
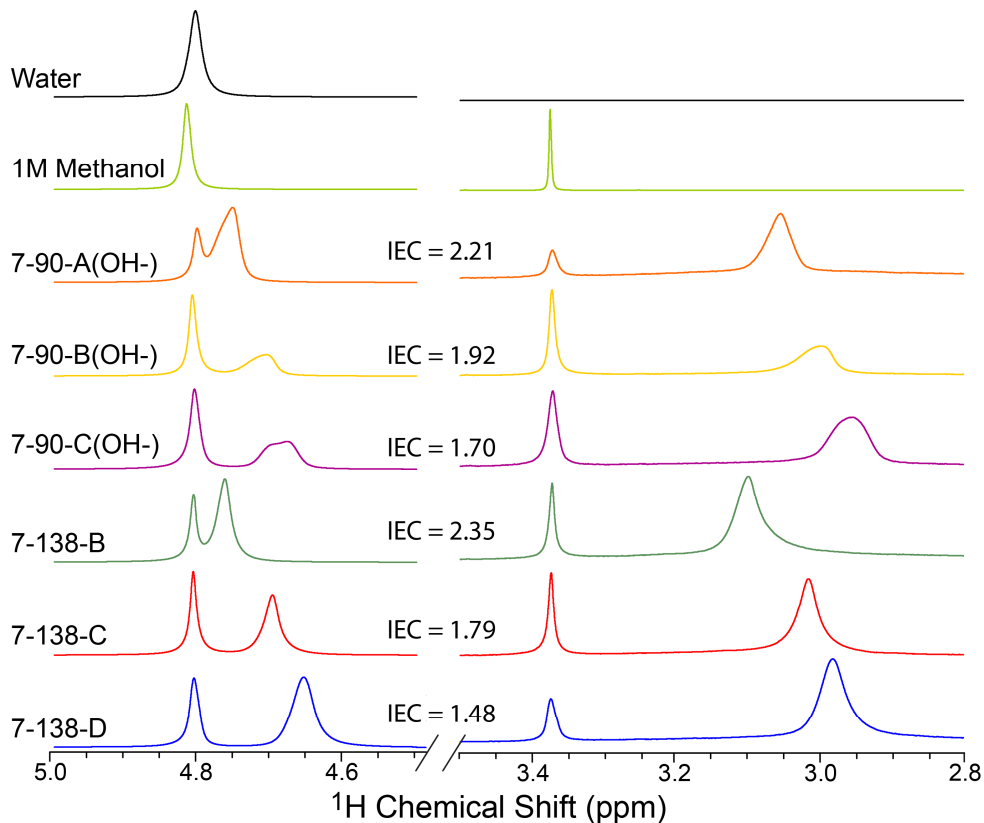
PFG NMR and Site Resolution

AEM 7-138D



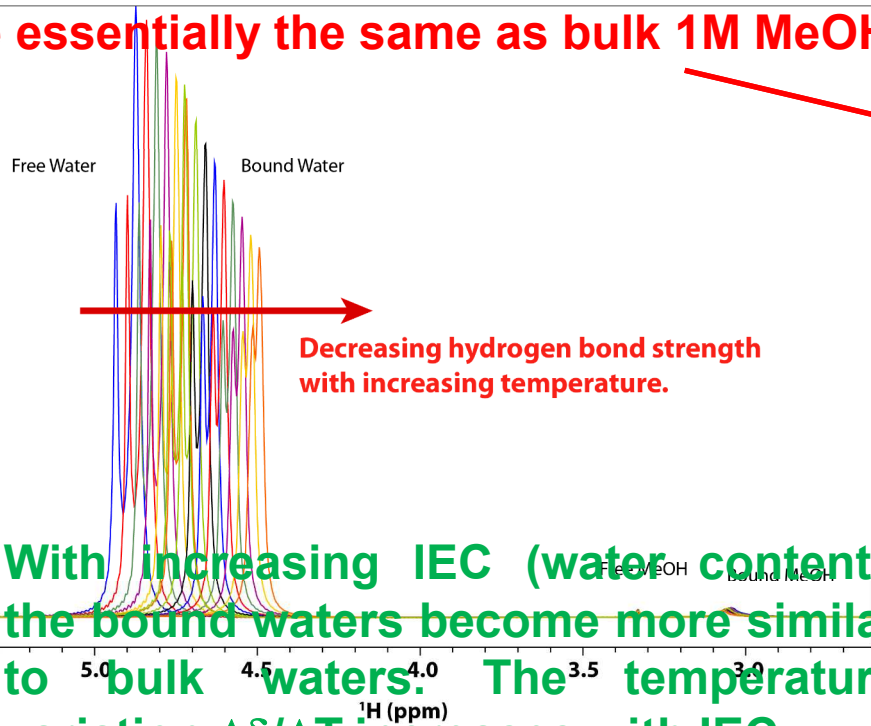
Resolution is always exciting! Can ask questions about differences between MeOH and water association with the membrane.

Chemical Shifts for Different Membranes



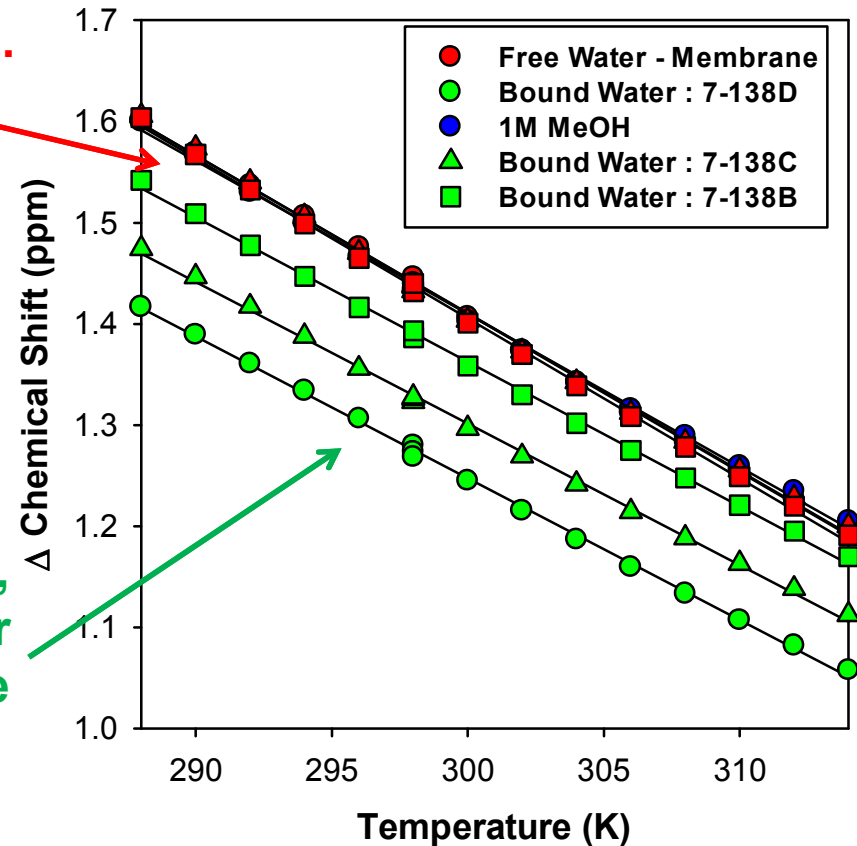
Temperature Effect on Hydrogen Bonding

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

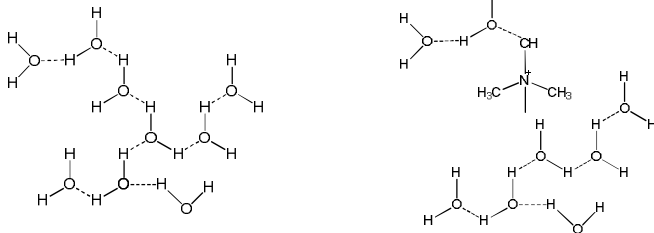


With increasing IEC (water content), the bound waters become more similar to bulk waters. The temperature variation $\Delta\delta/\Delta T$ increases with IEC.

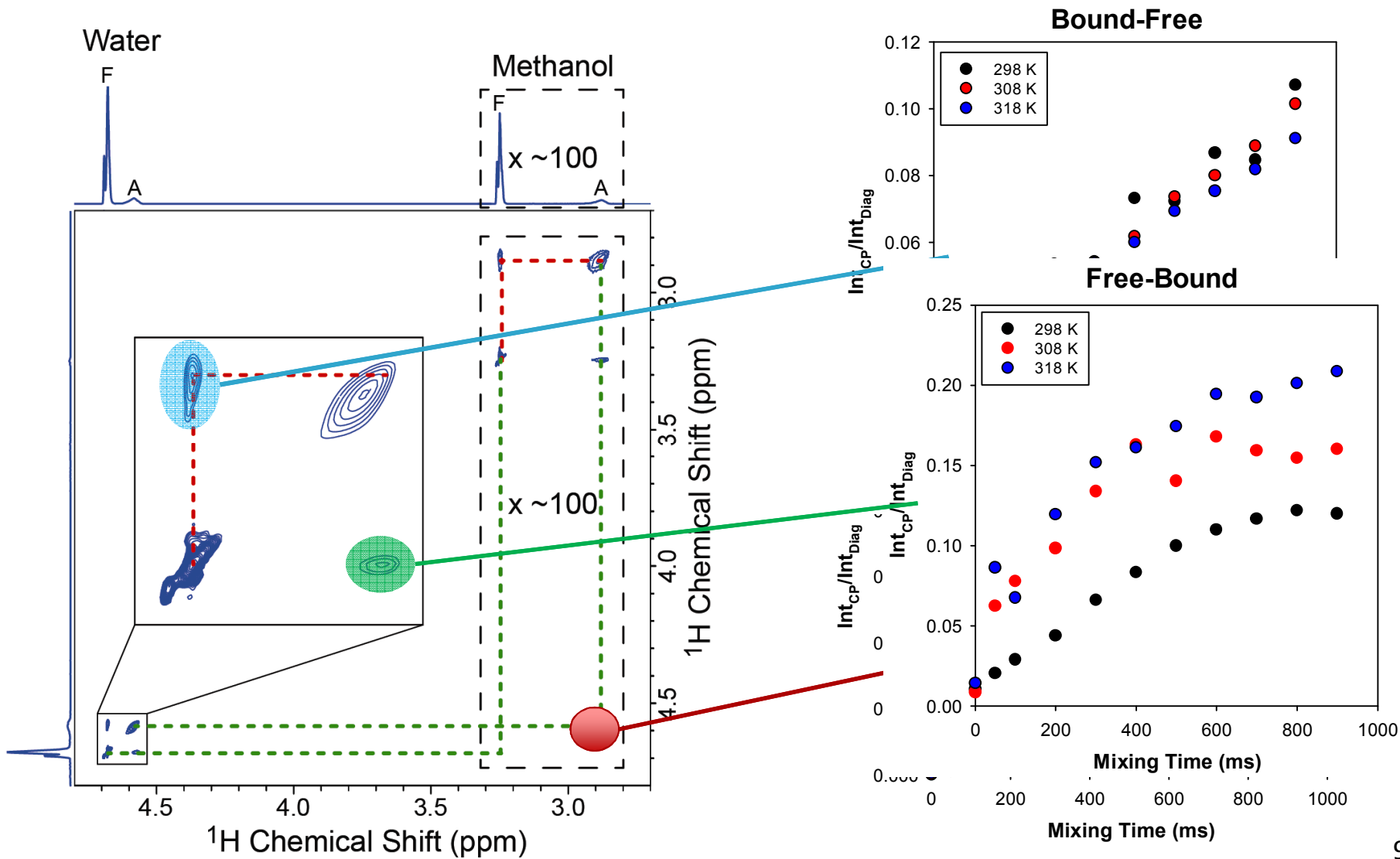
AEM Membranes Chemical Shift



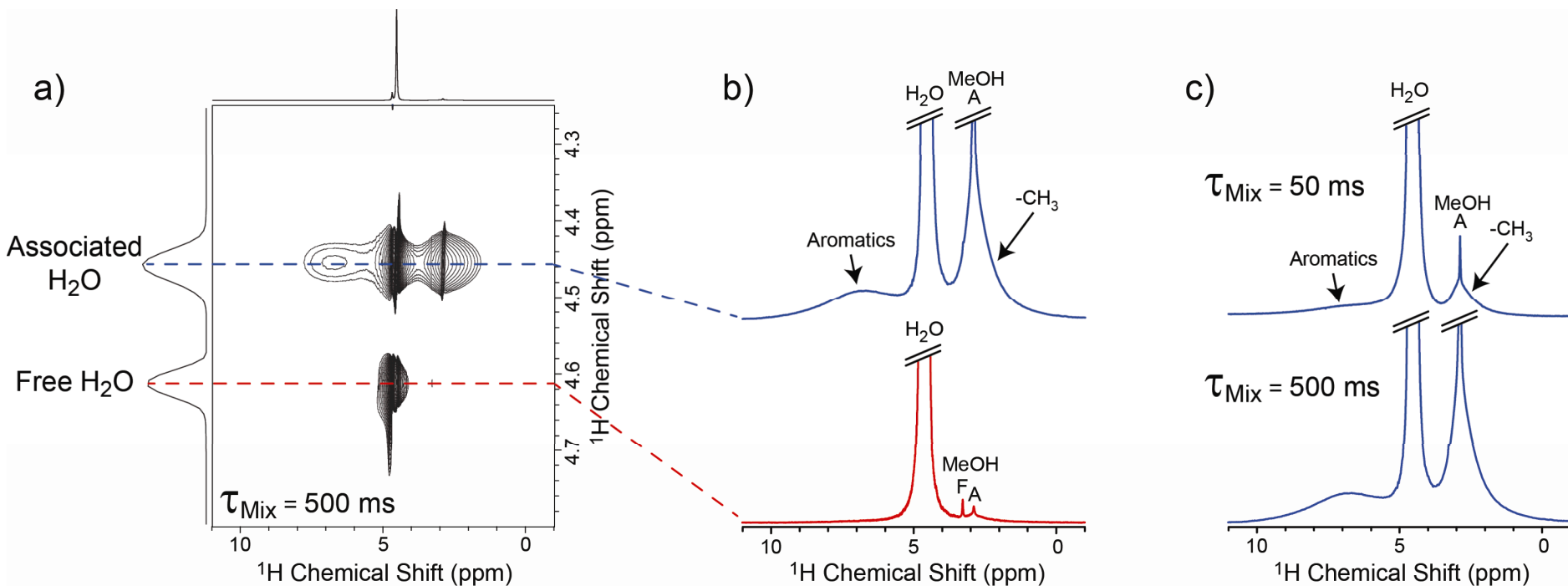
$$\Delta\delta = \delta(\text{H}_2\text{O}) - \delta(\text{MeOH})$$



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

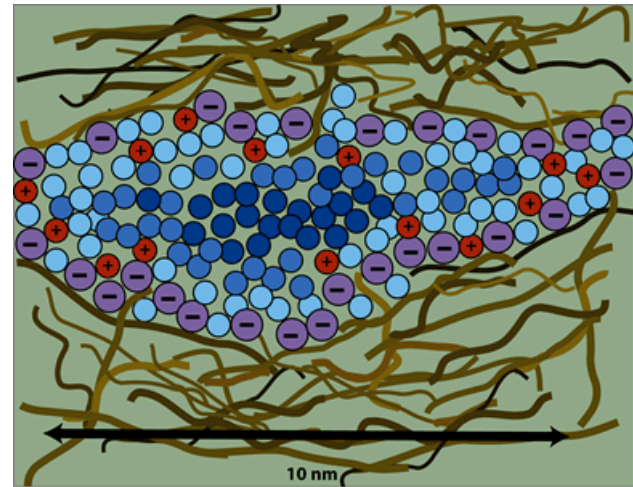
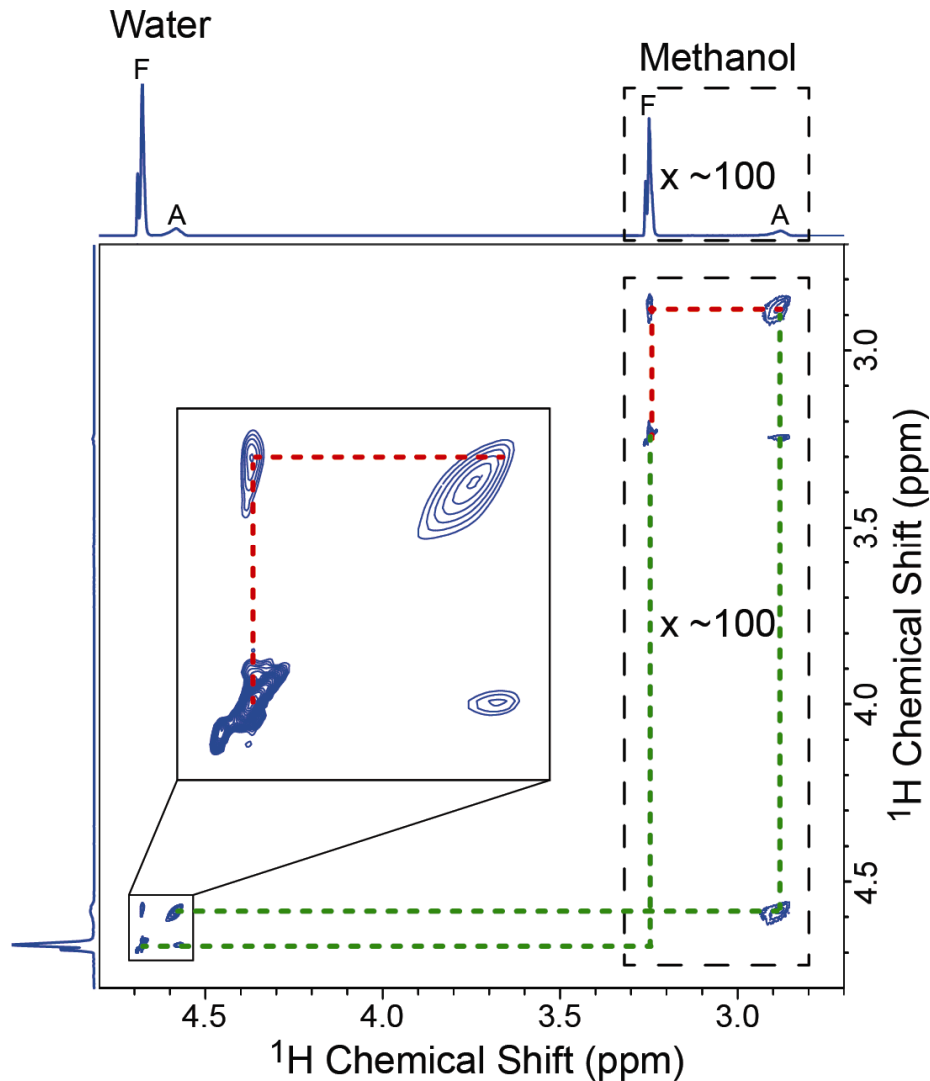


Where are these Associated Species?



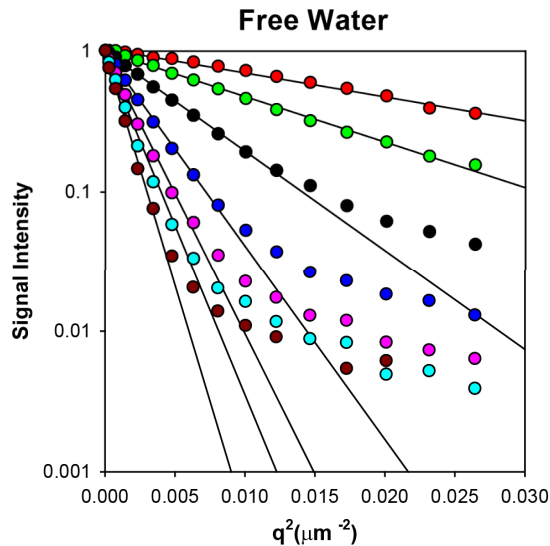
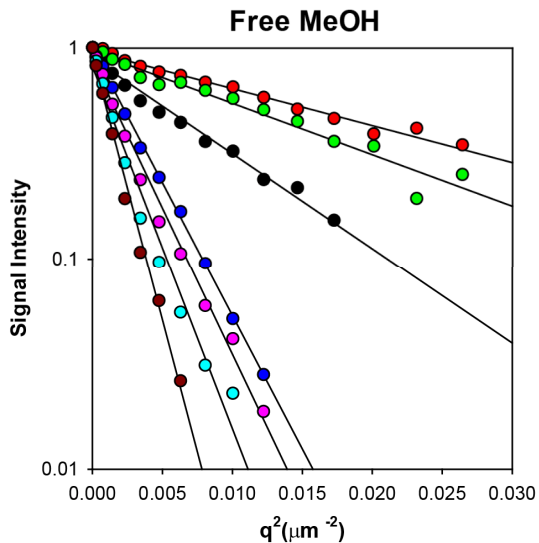
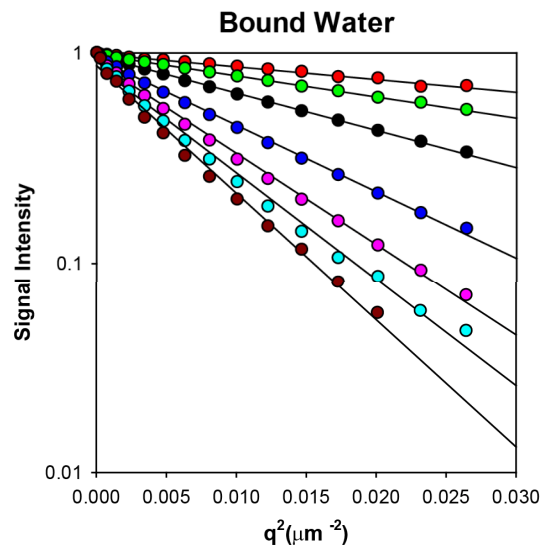
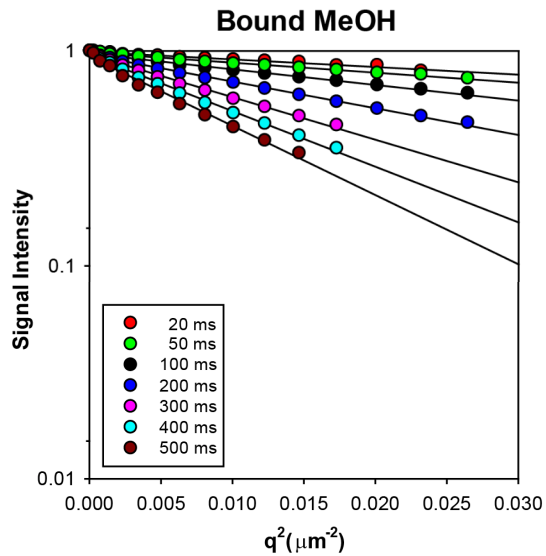
- The 2D NOESY data (faster spinning speeds) reveal correlation between the associated species (both H₂O and MeOH) and the membrane.
- Short mixing times suggest near the cation (N(CH₃)₃⁺).
- Free species do not reveal any strong NOE correlations.

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



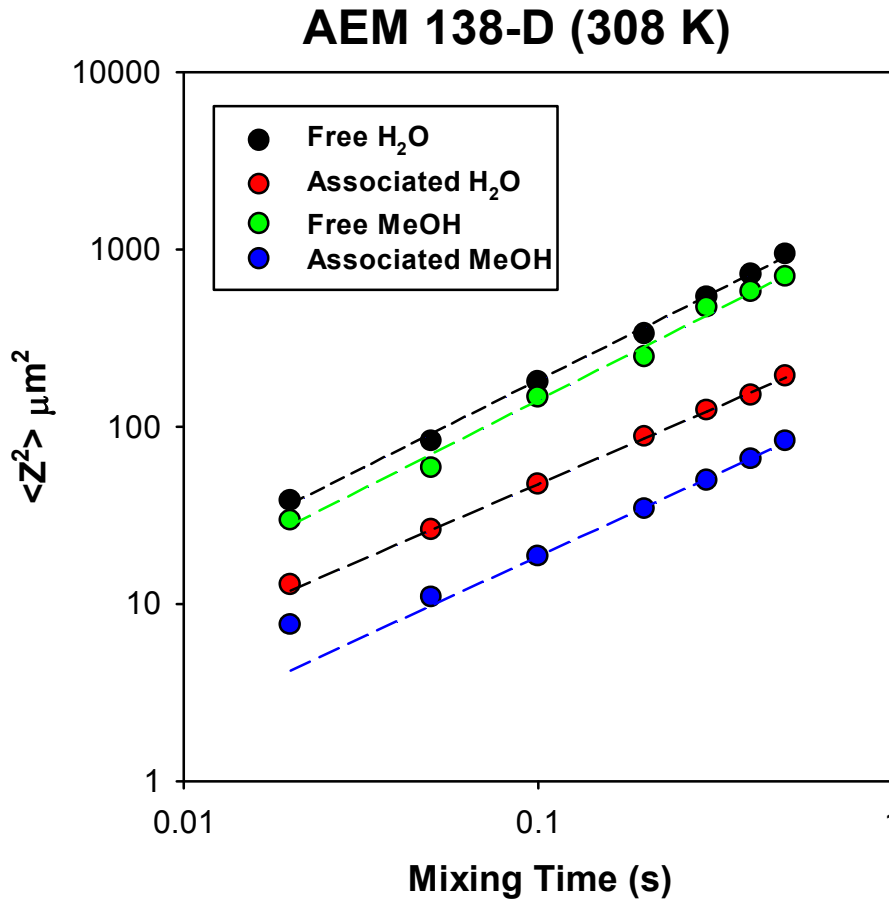
- Free and associated domains exist.
- These domains show some exchange.
- Associated water and MeOH in close contact with membrane.

Diffusion Analysis of Individual Species



- 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 $D_{\text{assoc}}/D_{\text{free}}$ is much smaller for MeOH, suggesting preferential association with membrane.
- For free water deviations due to confinement effects appear at $\langle z^2 \rangle = 130 \mu\text{m}^2$, $\langle z \rangle \sim 11 \mu\text{m}$.
- For associated water these confinement effects are also observed (at higher temperature, i.e. larger displacements) with $\langle z^2 \rangle = 125 \mu\text{m}^2$, or $\langle z \rangle \sim 11 \mu\text{m}$.

Anomalous Diffusion?

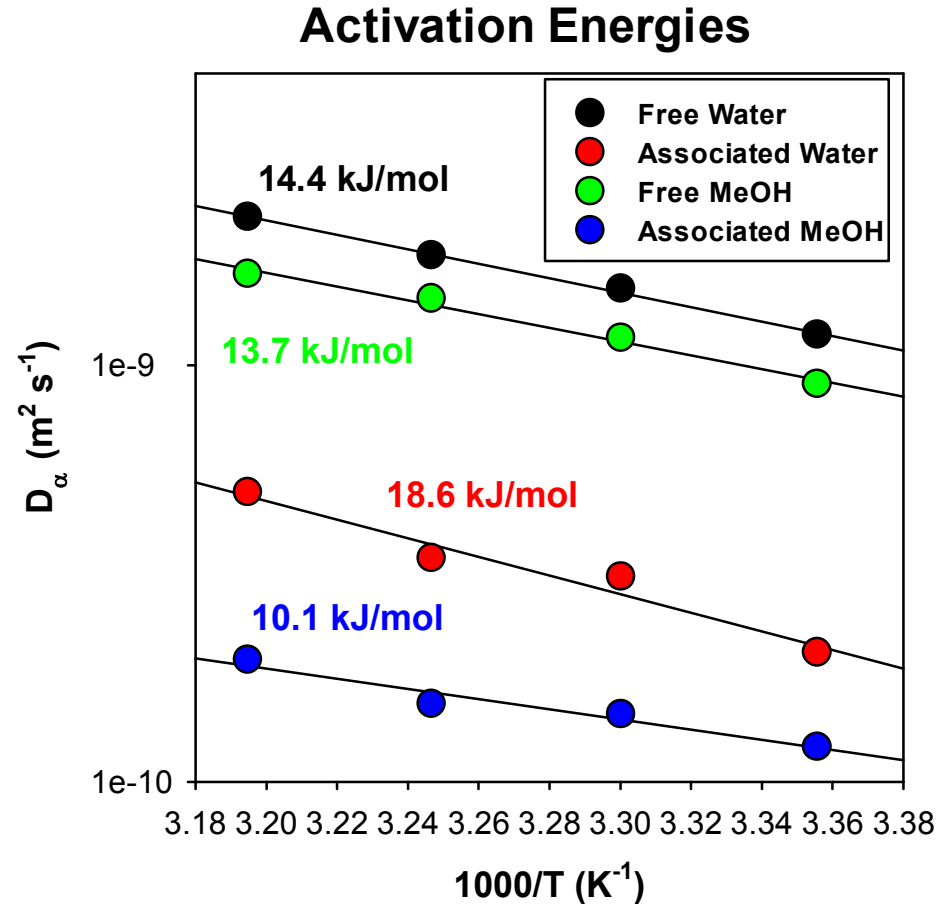
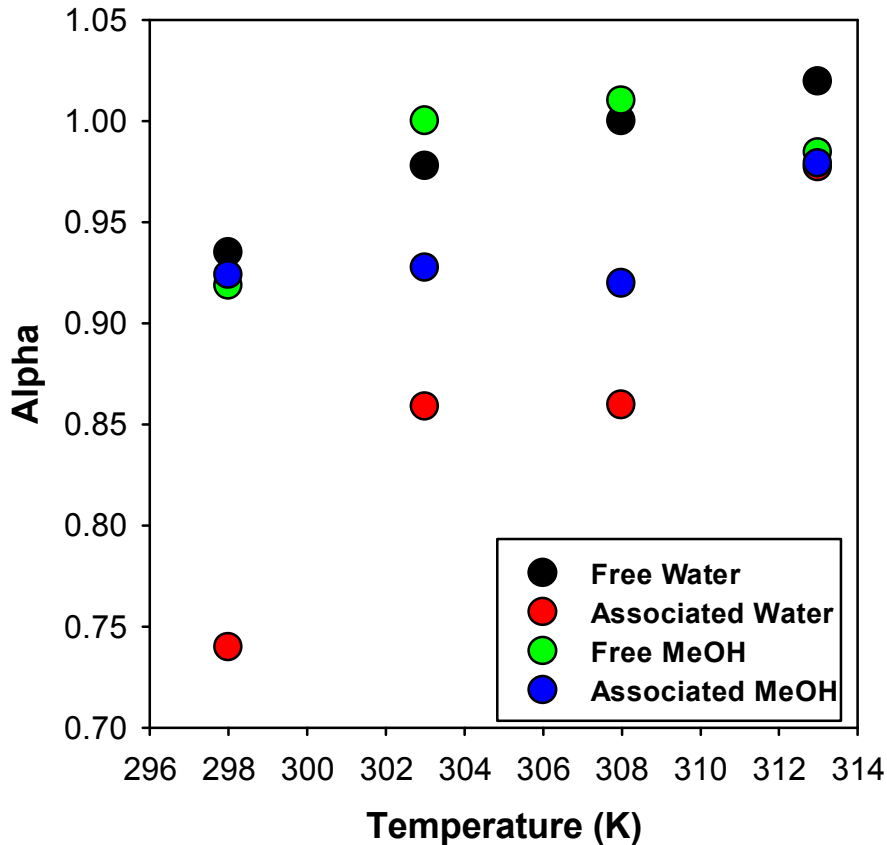


Anomalous diffusion can be expressed through the power law.

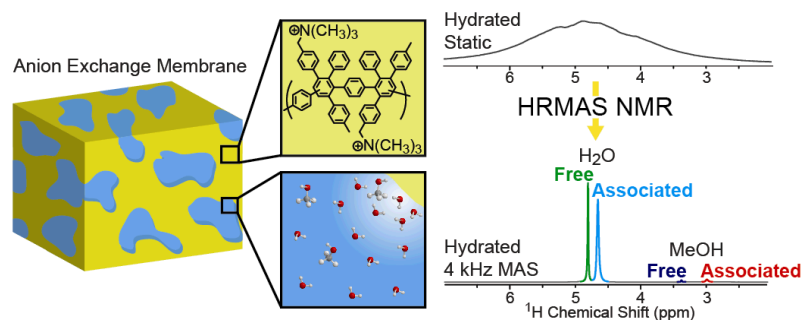
$$\langle z^2 \rangle = 2D_\alpha \Delta^\alpha$$

$\alpha = 1$, normal diffusion
 $\alpha < 1$, sub-diffusive
 $\alpha \sim 0.7$ 2D fractal

Anomalous Diffusion and Activation Energies

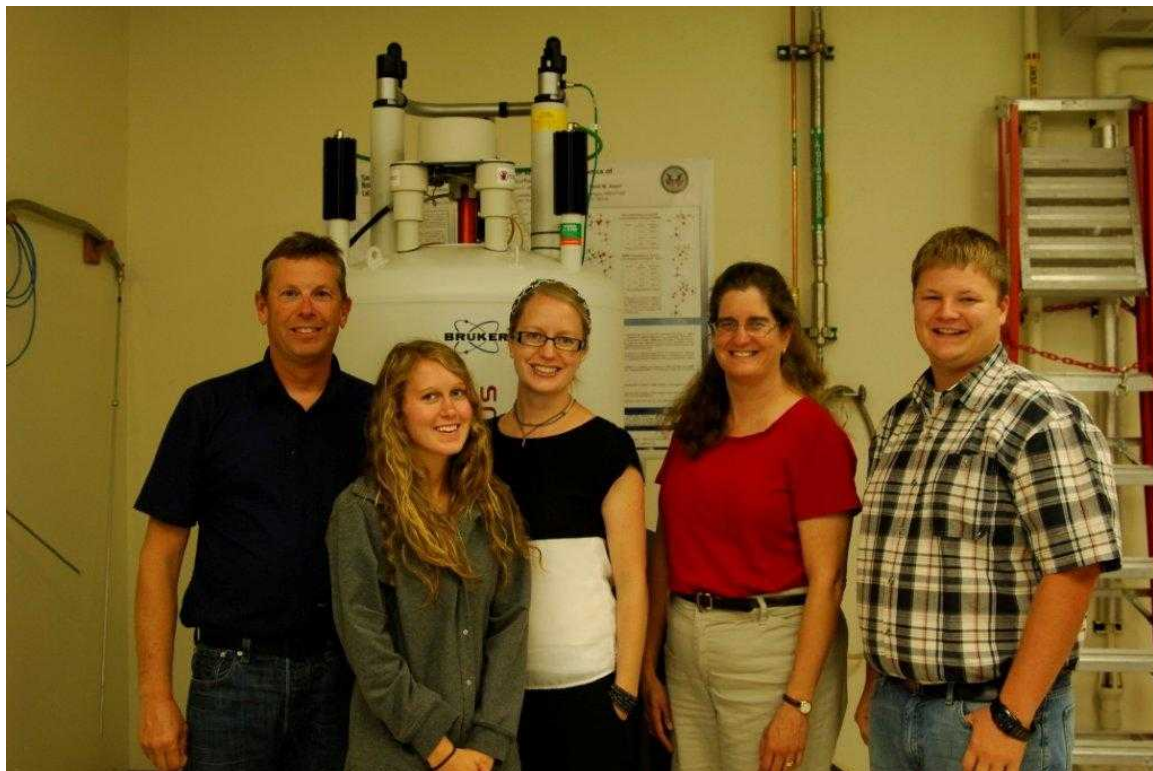


Conclusions



- HRMAS NMR provides increased resolution in MeOH fuel cell membranes.
- Combined with PFG gives diffusion of 4 unique sites within the membrane.
- This system may represent a special case, not a generalized solution for all membrane systems.
- The diffusion measurements of associated water and MeOH suggest sub-diffusion process (motion on membrane surface).
- Dimension of restricted diffusion in water $\langle z^2 \rangle \sim 125$ nm for both free and associated species.
- There is a large membrane influence on the MeOH versus water species.
- HRMAS PFG NMR does provide a novel tool to study these heterogeneous diffusion processes in polymer membranes.

Acknowledgements



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Prof. Cathy Clewett
C.J. Pearce (UG)
Kim Childress (UG)

Postdoc position available:
Seeking enthusiastic, motivated individual with NMR experience and interest in chemistry and materials supporting national security. Contact me at tmalam@sandia.gov.

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