SAND2014-0717C

NMR Spectroscopy Characterization of Silicone Polymers and Fluids Used in Electronic Components

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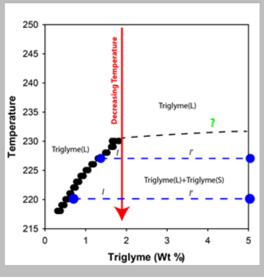
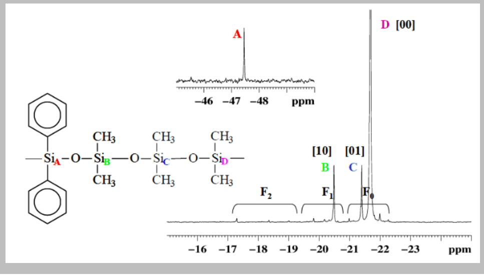
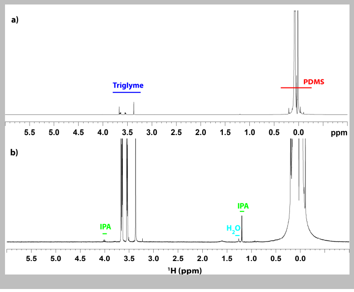
Charlotte, NC

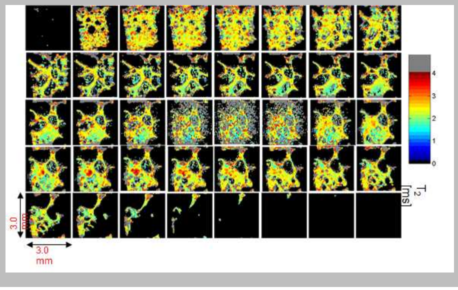
Exceptional service in the national interest

Sandia National Laboratories









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U.S. DEPARTMENT OF ENERGY

National Nuclear Security Administration

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History of Sandia National Laboratory

- Sandia National Laboratories is one of DOE's National Nuclear Security Administration's (NNSA) Labs.

- Originally the call "Z-Division" (1945): design, testing and assembly arm of Los Alamos National Lab.

- Moved to Sandia Base to be near air field and military.

- Livermore site developed in 1956.

- Take the physics package of LANL and LLNL and turn it into a deployable weapon.

Sandia's Sites

Sandia National Laboratories

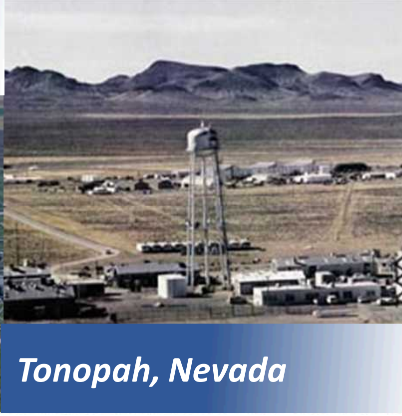
Albuquerque, New Mexico

Livermore, California

Kauai, Hawaii

Waste Isolation Pilot Plant, Carlsbad, New Mexico

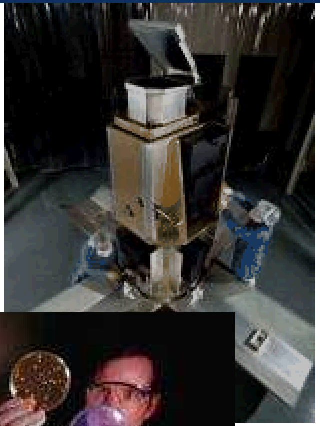
Pantex Plant, Amarillo, Texas

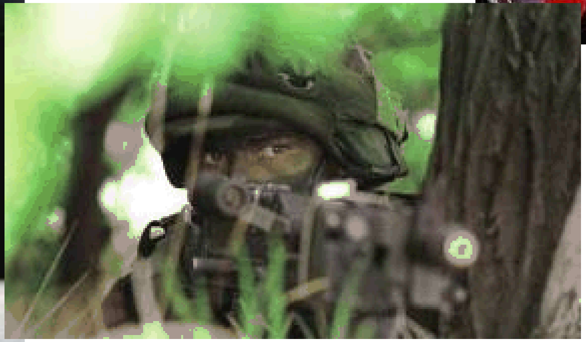


Tonopah, Nevada

What Do We Do? - Four Mission Areas

- **Nuclear Weapons**
- **Defense Systems and Assessments**
- **Energy, Climate and Infrastructure Security**
- **International, Homeland and Nuclear Security**





Nuclear Weapons

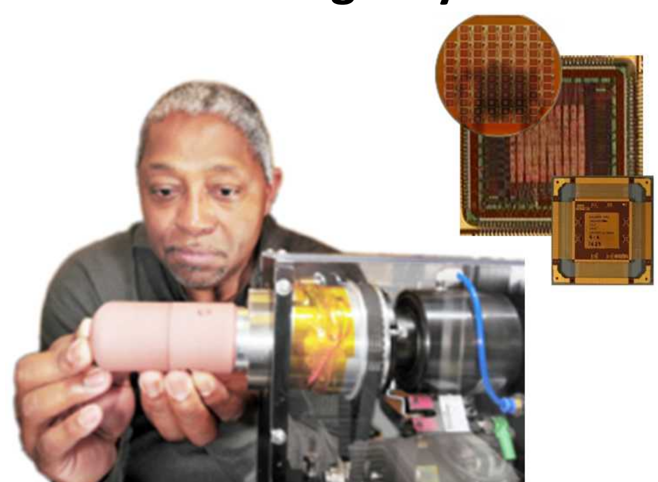
Pulsed power and radiation effects sciences

Design agency for nonnuclear components

- Neutron generators
- Arming, fuzing and firing systems
- Safety systems
- Gas transfer systems

Warhead systems engineering and integration

Production agency



NMR Analysis

Research and Development

- Development of NMR techniques for component analysis.
  - “^{17}O labeling and Imaging”

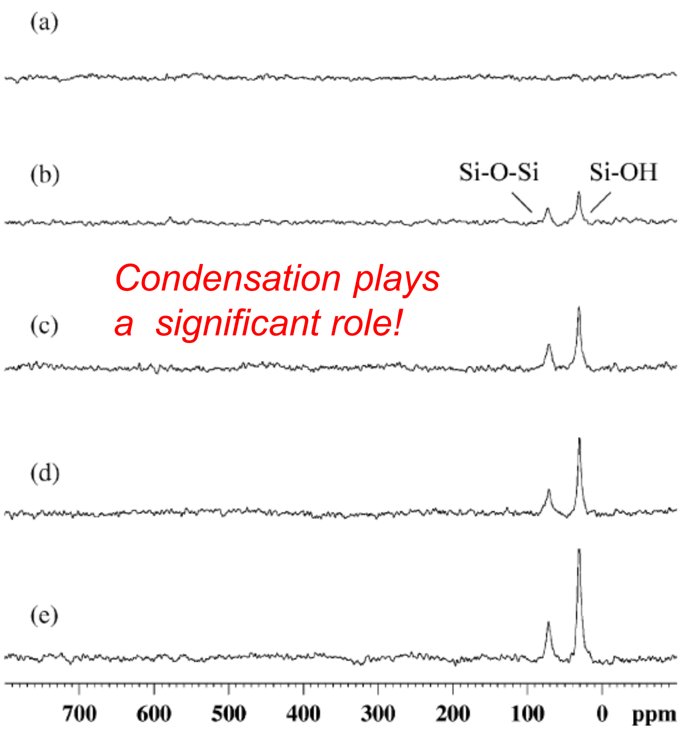
Production

- Contaminants, purity and mixtures.
- Matching quality from “qualification” from the 1980’s and 1990’s.
  - “Stereochemistry in PDMS/PDPS Copolymers”

Surveillance

- Aging and degradation properties (20 to 30+ years).
- Material Interactions.
- Prediction of aging/interactions for an additional 20 to 30 years.
- Reuse of components under different operating conditions.
  - “Low Temperature PDMS Fluid Behavior”

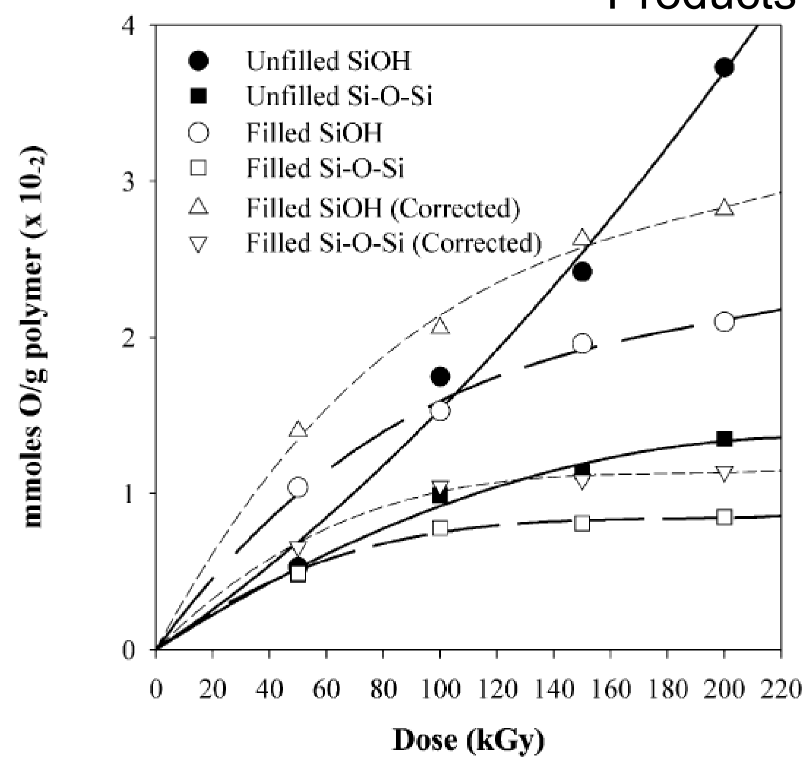
^{17}O NMR of γ-Irradiated PDMS



Condensation plays a significant role!

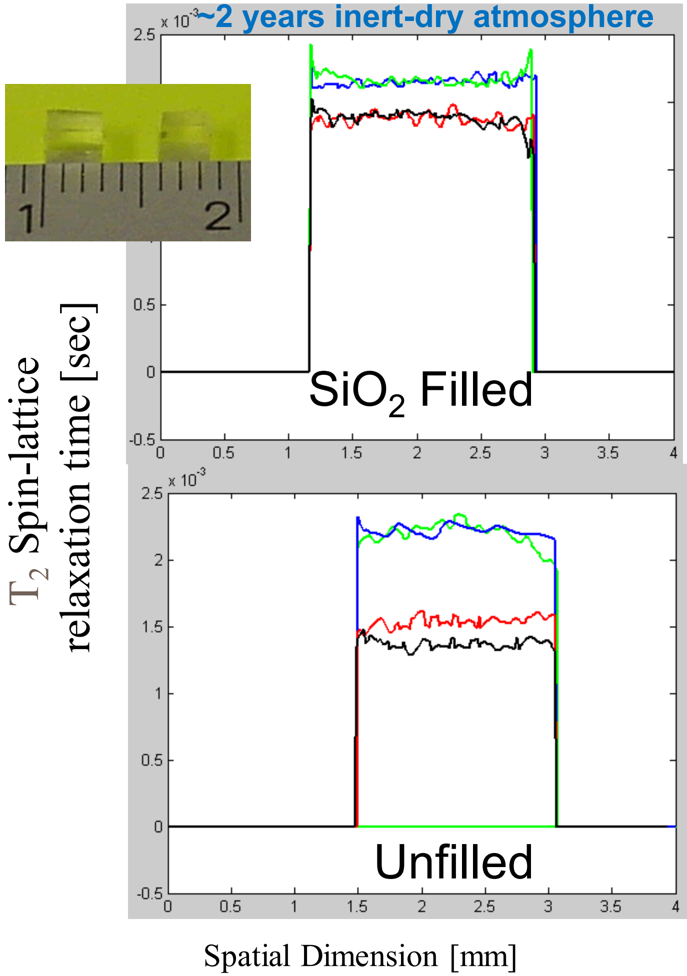
Fig. 1. High-resolution ^{17}O NMR spectra of γ-irradiated hydrolyzed silica-filled PDMS/PDPS copolymer as a function of total irradiation dose at 300 K. Spectra are shown for: (a) 0 kGy, (b) 50.2 kGy, (c) 100.3 kGy, (d) 150.8 kGy, (e) 200.4 kGy.

Polymer $\xrightarrow[\Delta \text{ or } \gamma]{H_2O \text{ or } O_2 \, (^{17}O)}$ ^{17}O-Labeled Degradation Products

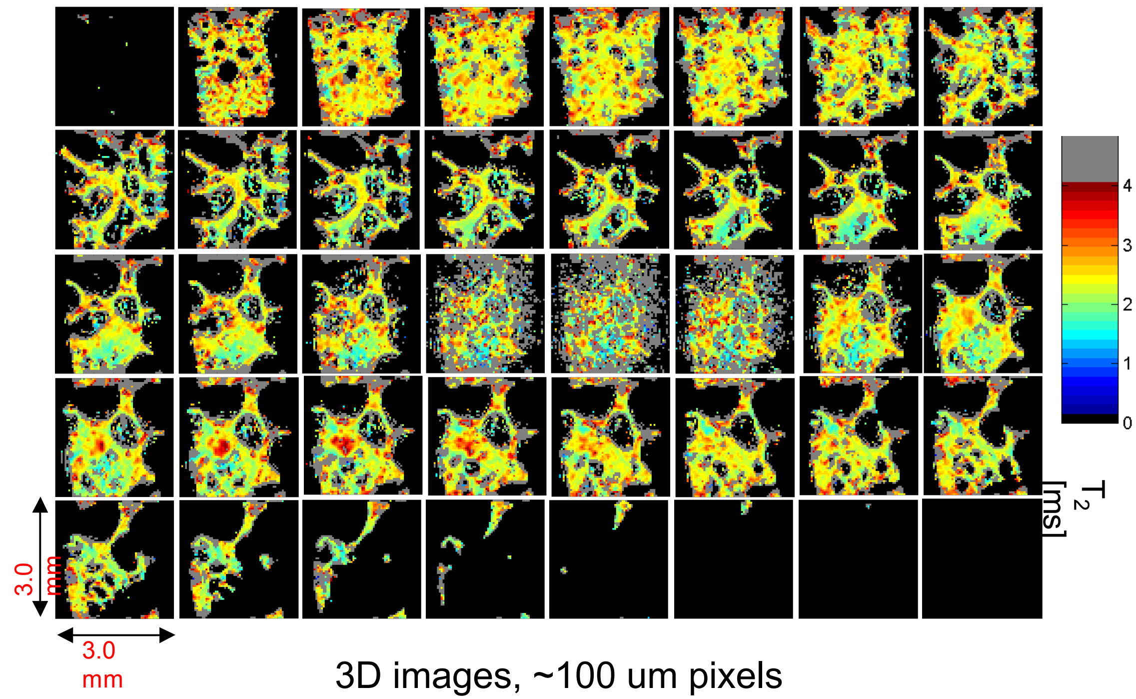


T. M. Alam "^{17}O NMR Investigation of Radiolytic Hydrolysis in Polysiloxane Composites", *Radiation Physics and Chemistry*, **62**, 145-152 (2001).
See also:
T. M. Alam, M. Celina, R. A. Assink, R. L. Clough, K. T. Gillen "^{17}O NMR Investigation of Oxidative Degradation in Polymers Under γ-Irradiation" *Radiation Physics and Chemistry*, 60 121-127 (2001). 50. ; T. M. Alam, M. Celina, R. A. Assink, R. L. Clough, K. T. Gillen, D. R. Wheeler "Investigation of Oxidative Degradation in Polymers Using ^{17}O NMR Spectroscopy", *Macromolecules*, 33, 1181-1190 (2000).

NMR T_2 Imaging of Silicones



Blown PDMS Foams



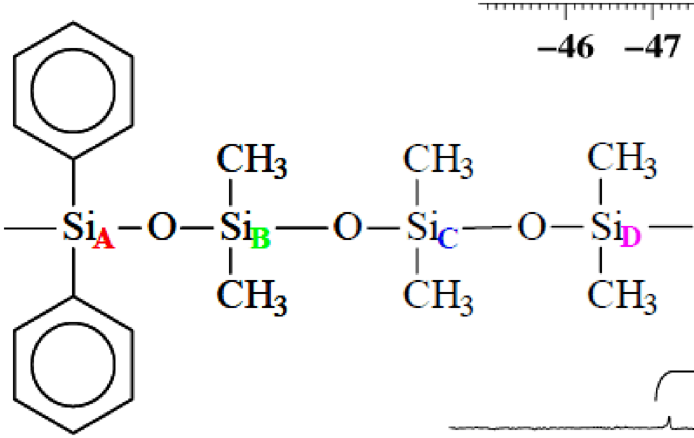
3D images, ~100 um pixels

B.R, Cherry and T. M. Alam, " *Relaxation NMR Imaging (R-NMRI) of PDMS/PDPS Siloxane Copolymer Desiccation*", Polymer (2004) 5611-5618.

- PDMS-pads: Change in T_2 during desiccation, homogeneous profile.
- PDMS-foams: T_2 (stiffness) very heterogeneous in curing profile.

Microstructure of Polysiloxanes Using^{29}Si NMR

Dimethyl – Diphenyl copolymers (vinyl precursors)



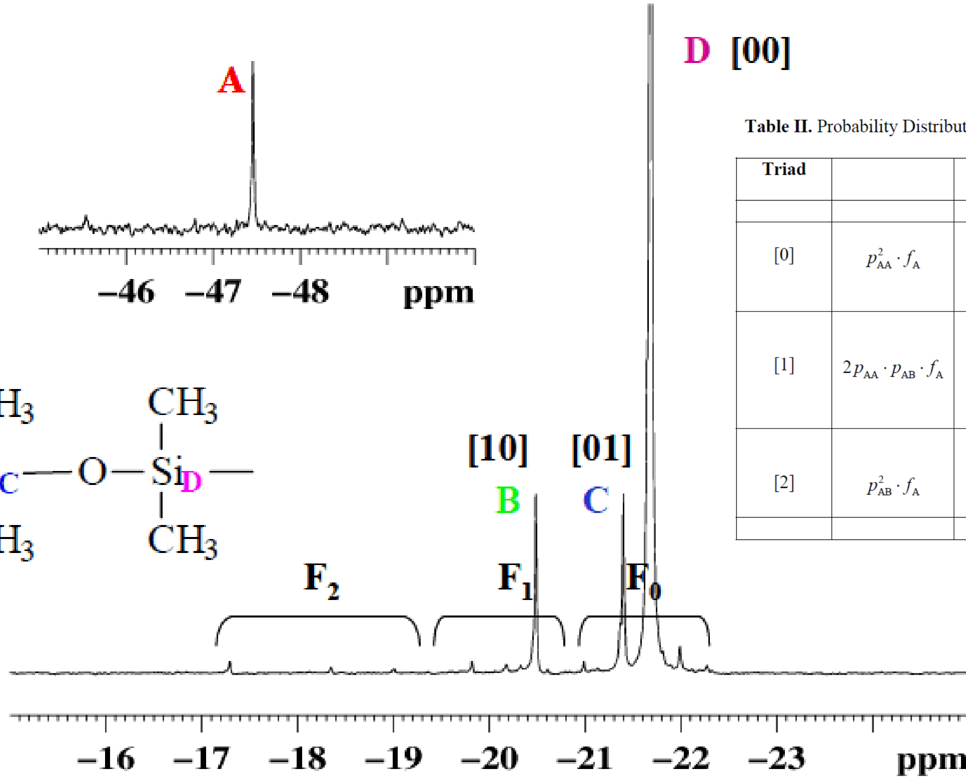


Table II. Probability Distributions and Signal Intensities for Triad and Pentad Sequences.

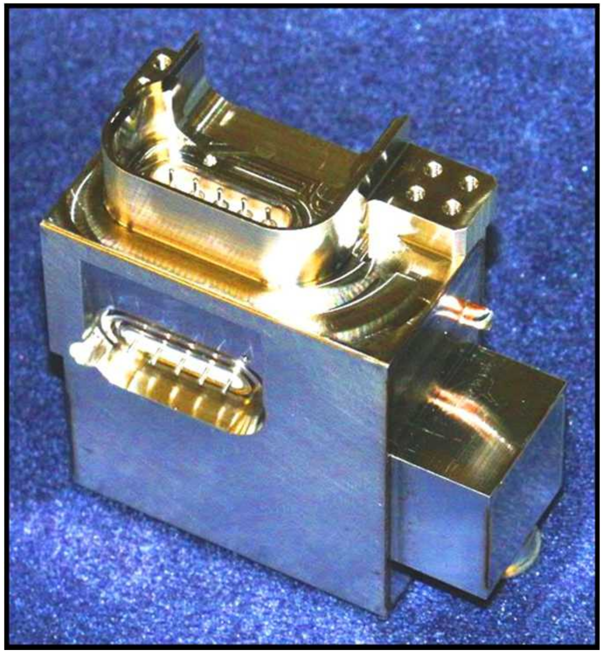
Triad		Triad Signal	Pentad		Pentad Signal
[0]	$p_{AA}^2 \cdot f_A$	F_0	[00]	$p_{AA}^4 \cdot f_A$	F_{00}
			[01]	$2p_{AA}^3 \cdot p_{AB} \cdot f_A$	F_{01}
			[02]	$p_{AA}^2 \cdot p_{AB}^2 \cdot f_A$	F_{02}
[1]	$2p_{AA} \cdot p_{AB} \cdot f_A$	F_1	[10]	$2p_{AA}^2 \cdot p_{AB} \cdot p_{BA} \cdot f_A$	F_{10}
			[11]	$2p_{AA}^2 \cdot p_{AB} \cdot p_{BB} \cdot f_A$	F_{11}
				$2p_{AA} \cdot p_{AB}^2 \cdot p_{BA} \cdot f_A$	
			[12]	$2p_{AA} \cdot p_{AB}^2 \cdot p_{BB} \cdot f_A$	F_{12}
[2]	$p_{AB}^2 \cdot f_A$	F_2	[20]	$p_{AB}^2 \cdot p_{BA}^2 \cdot f_A$	F_{20}
			[21]	$2p_{AB}^2 \cdot p_{BA} \cdot p_{BB} \cdot f_A$	F_{21}
			[22]	$p_{AB}^2 \cdot p_{BB}^2 \cdot f_A$	F_{22}

Microstructure impacting T_g and T_m – Sudden appearance of Lot-Lot variability.

T. M. Alam "Quantitative Analysis of Microstructure in Polysiloxanes Using High Resolution ^{29Si}NMR Spectroscopy: Investigation of Lot Variability in the LVM97 and HVM97 PDMS/PDPS Copolymers", SAND2002-3785.

ESD Electrical Devices

- Environmental sensing devices (ESD).
- Contain PDMS fluids for viscosity/density.
  - Vibration/shock damping.
  - Insulative properties.



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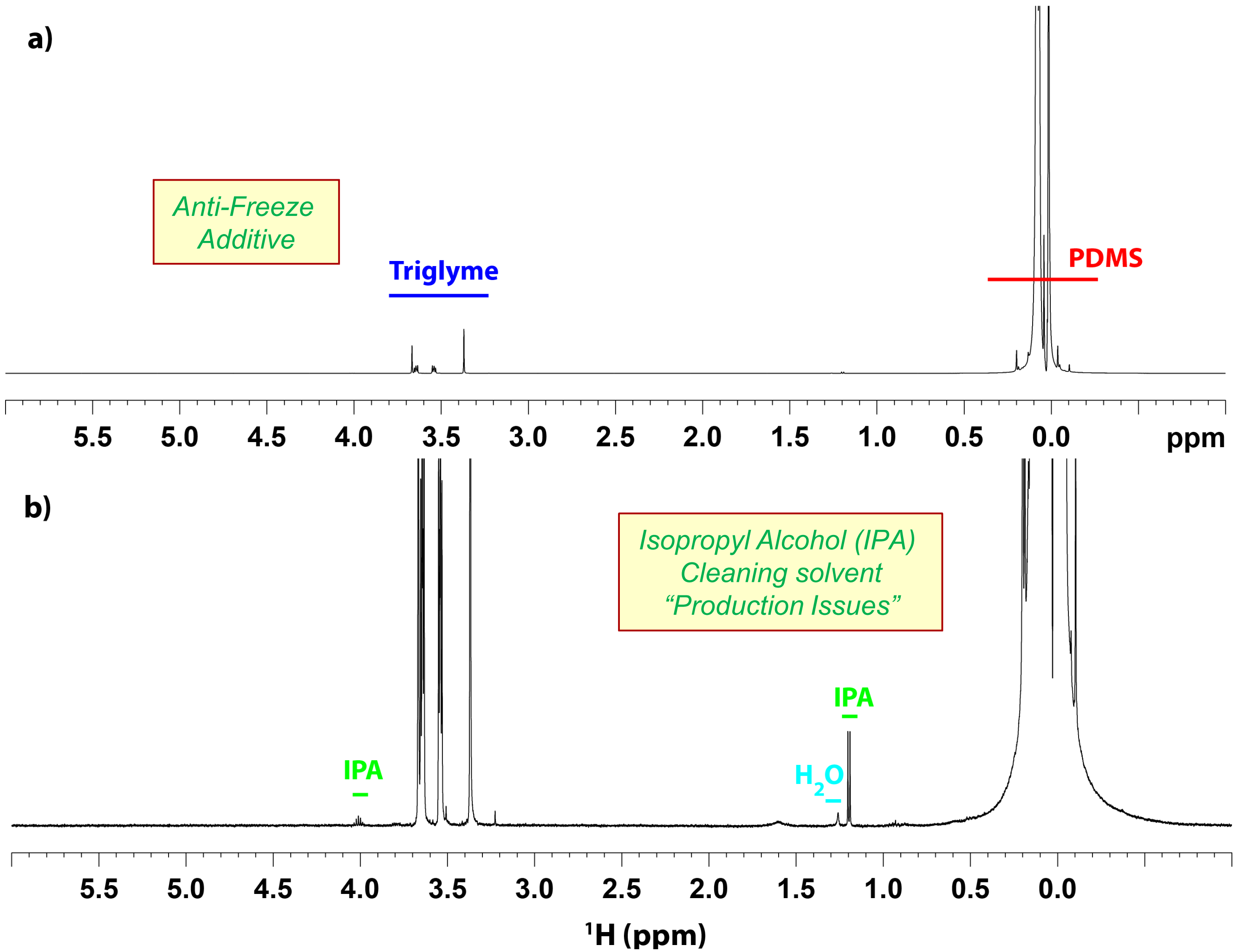
Impurities and Triglyme Additives

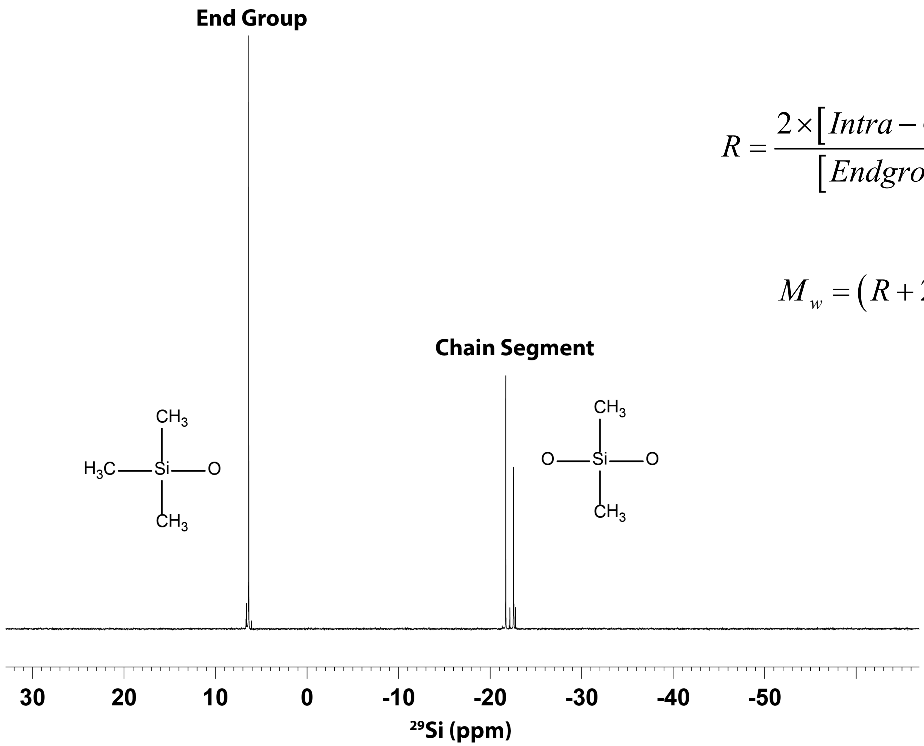
[1]H NMR allows quick survey of PDMS fluids.



Neat Si fluids
500 MHz, ^1H
<25 ppm detection

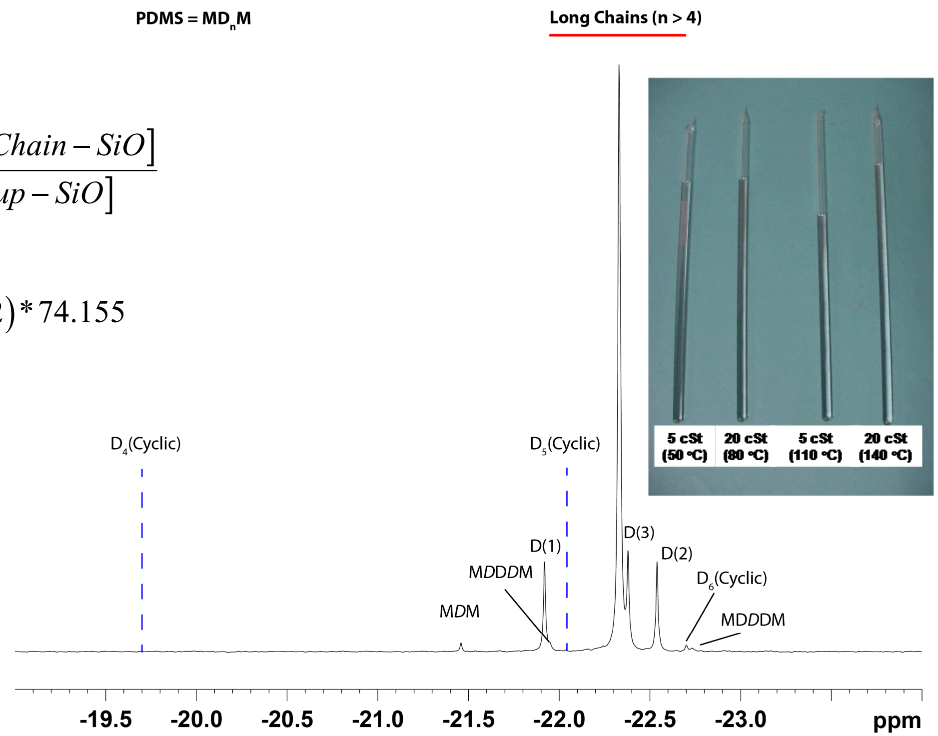
Average Molecular Weight - Structure

^{29}Si NMR allows quick survey of PDMS fluids (Supplements Viscosity).



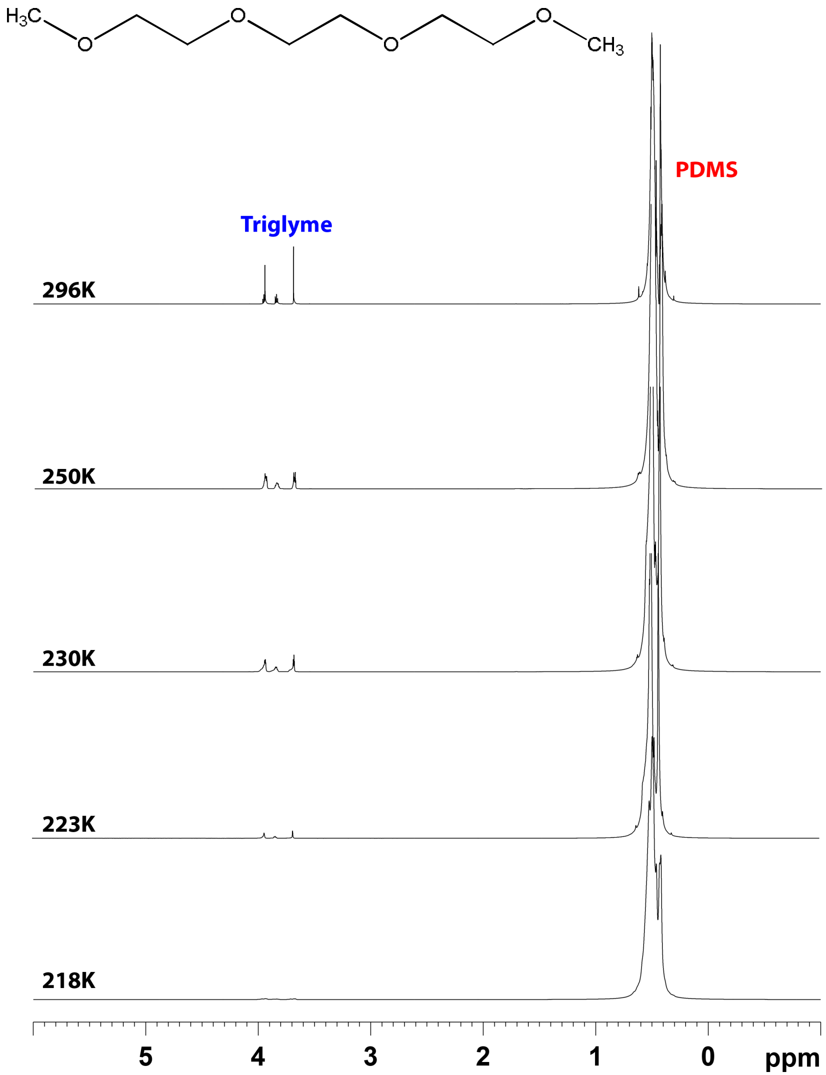
$$R = \frac{2 \times [Intra - Chain - SiO]}{[Endgroup - SiO]}$$

$$M_w = (R + 2) * 74.155$$



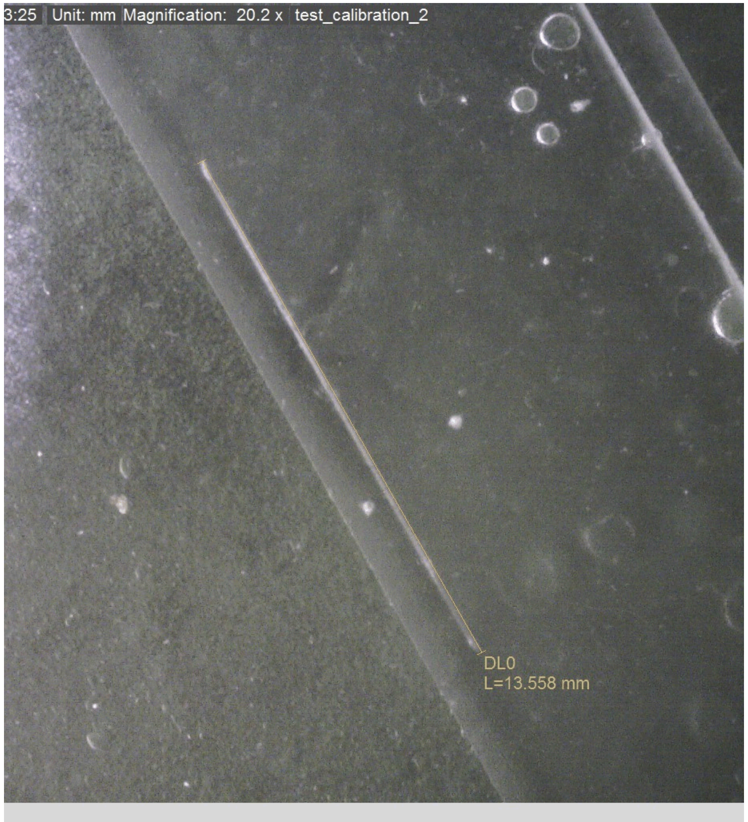
- Have been able to following M_w changes with aging.
- Same small volume (ES&H), sealed samples over 2 -3 years).
- NMR versus “other techniques” for identification of “cyclic PDMS”.

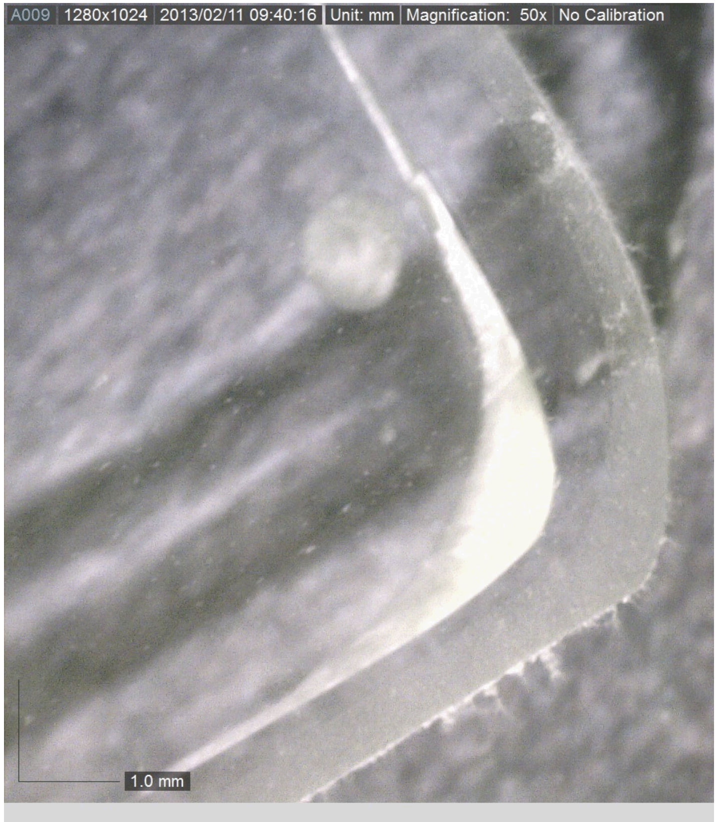
Low Temperature Behavior of Additives



- Triglyme (Triethylene glycol dimethyl ether) added for "antifreeze" protection.
- Electrical contact issues at very low temperatures: originally argued to be trace water effects.
- No visual inspection possible with ESD devices. Required studies of silicone fluid itself.
- Low temperature ^1H NMR revealed issues with the behavior of the triglyme itself.
- Disappearance of triglyme signal at low temperatures.
- NMR perfect for characterizing low temperature effects in these silicone fluids.

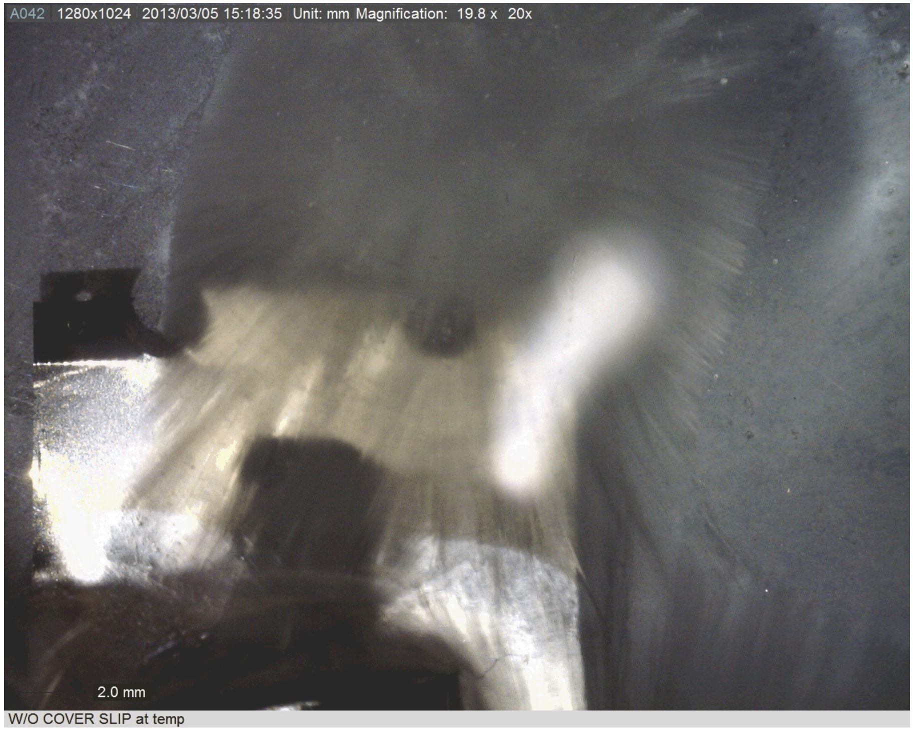
Freezing at Joint Surfaces





- These "freezing effects" could only be visually observed in test cuvettes at joint surfaces.
- Could not be replicated inside the unit (no glass).
- Determined to be an "artifact", and not responsible for change in triglyme behavior.
- Crystal formation observed at low temperatures in NMR tubes.

Triglyme Crystal Formation

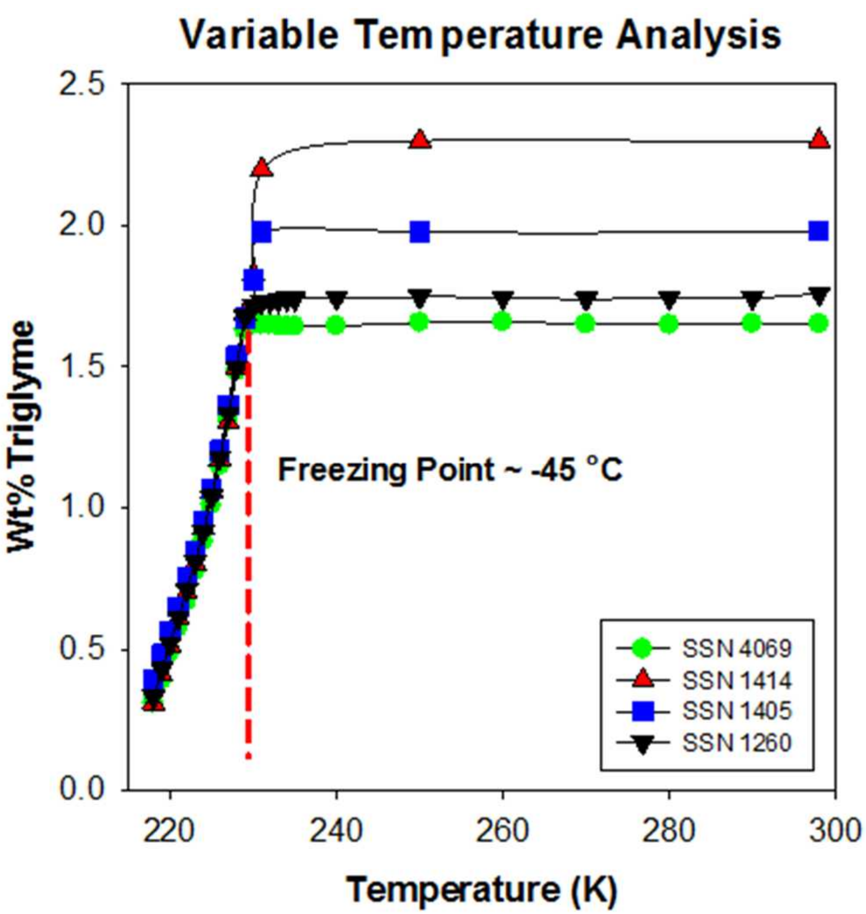


Triglyme Crystals - Pure Triglyme

- Crystals visually observed at low temperatures.
- Effects depends on both the concentration/ temperature.

What is going on?

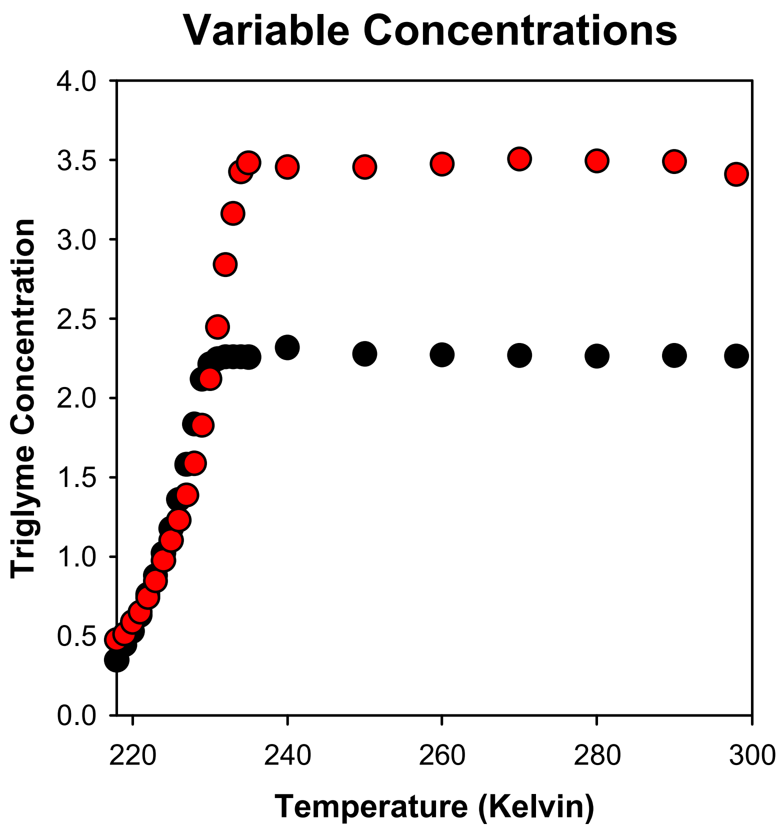
Variable Temperature NMR - Triglyme Studies



- ^{1}H NMR provides a direct measure of the triglyme concentration in solution (within detection coil).
- The variation in triglyme concentration is in contrast to earlier visual estimation (Alam, 2009) of triglyme solubility!
- Triglyme freezes at –46 ^{o}C.
- The reduction on solubility at a given temperature is rapid (~ minutes).
- Extended low temperature at 218K (~ 4 hours) did not further reduce triglyme concentration. This argues against simply freezing effects.
- No clouding was observed as indication of solubility issues, but crystal flocculation can be seen at very low temperatures.

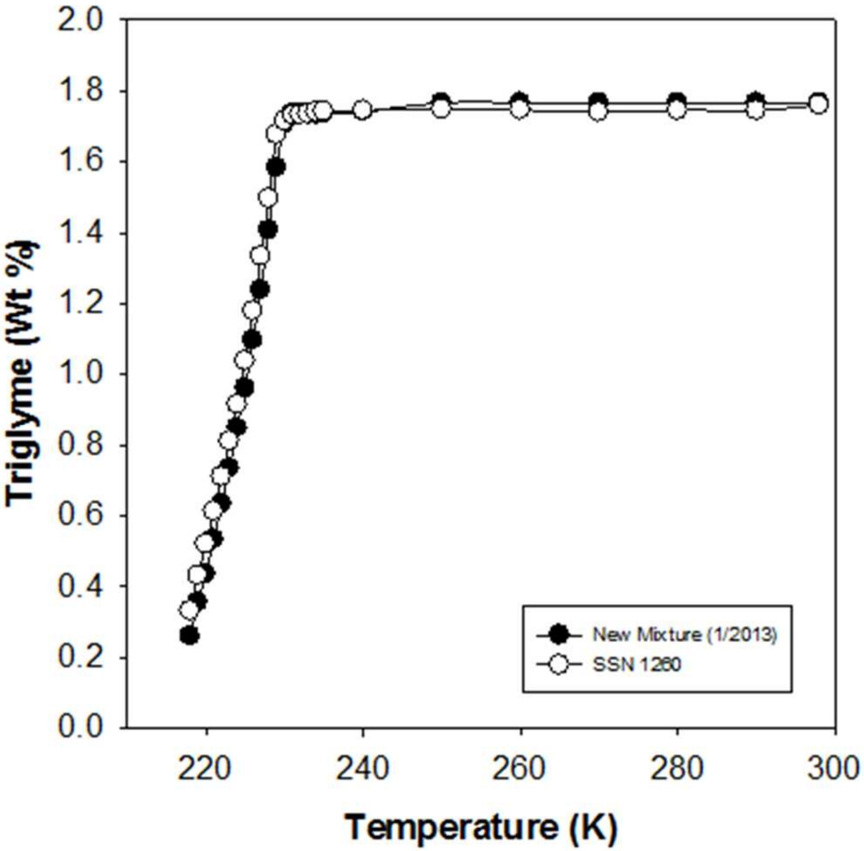
Is this "freezing" or solubility issues - Combination?

Variable Temperature NMR - Triglyme Studies



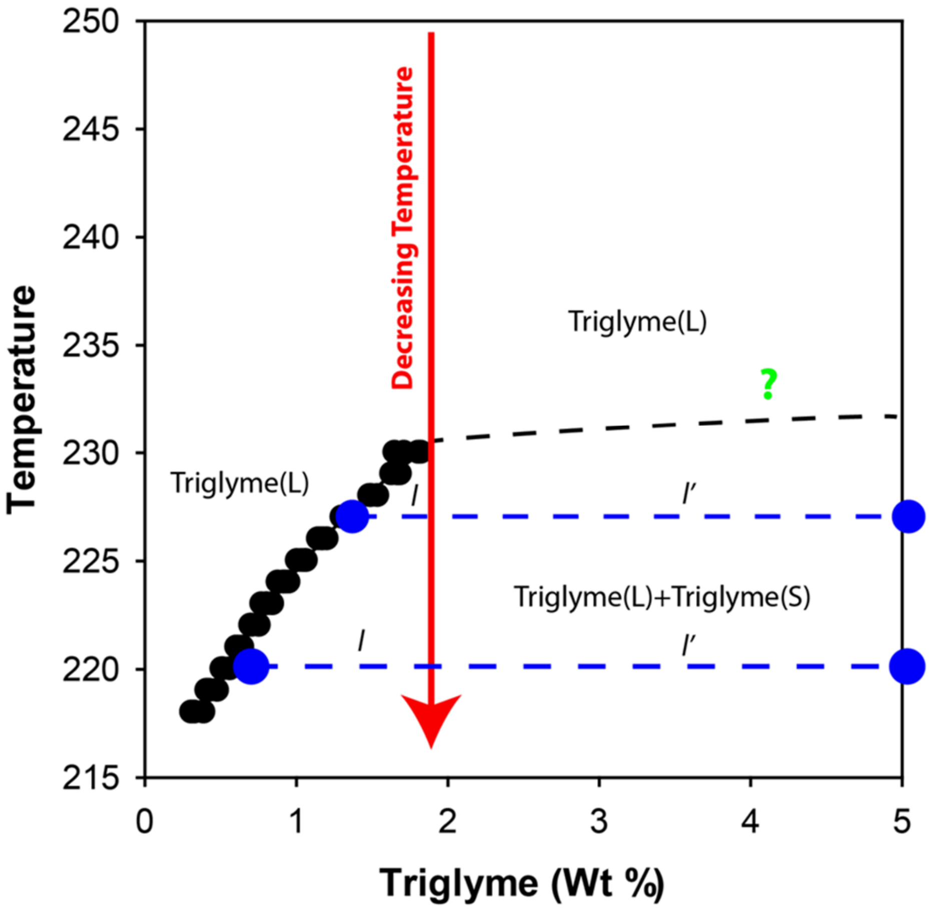
- Note change in the critical temperature with increasing Triglyme concentration.
- This critical concentration is at a higher temperature than the crystallization temperature of Triglyme.
- NMR provided a great tool to map out this solubility issue.

Variable Temperature Triglyme Studies



- Oxidative degradation is known to impact solubility in silicone fluids!
- Oxidation is not expected in sealed units as the O_2 saturation limit is ~ 100 ppm. This would argue that oxidation is O_2 limited – are there are other sources?
- Freezing behavior of triglyme identical for return units (+20 years) and freshly prepared silicone fluid/triglyme mixtures (1/2013).
- Aging does not play a role in this low temperature behavior.

Variable Temperature NMR - Triglyme Phase Diagram



Freezing Behavior of Water in PDMS Fluids

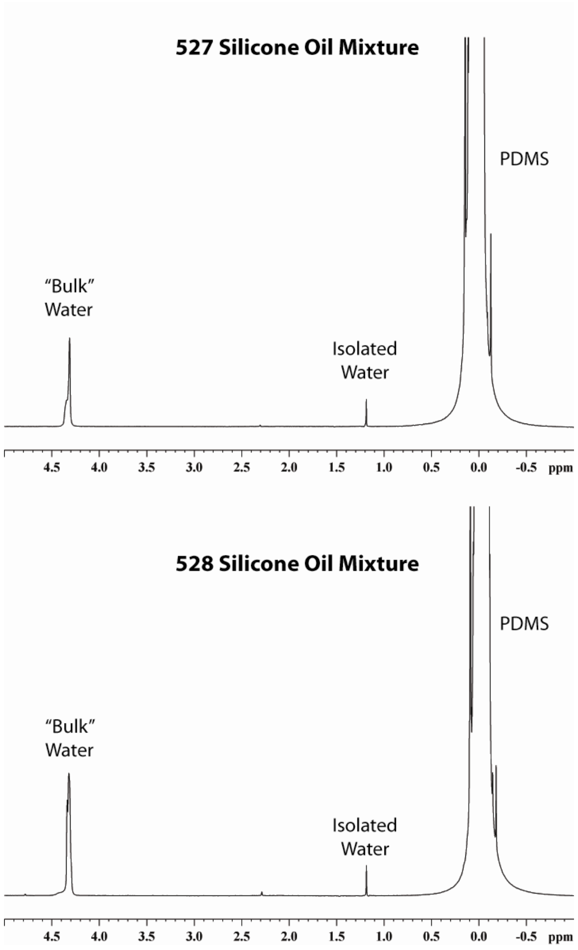
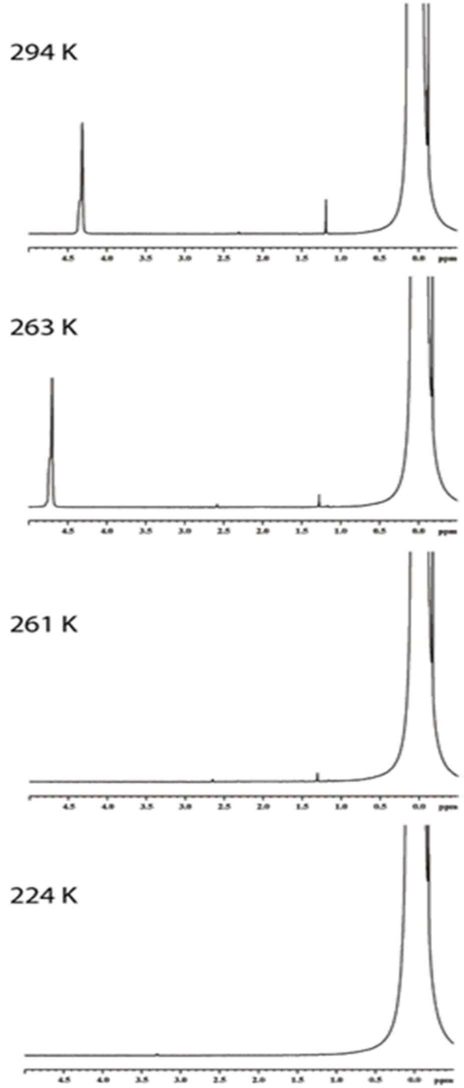


Figure 1: The ^{1}H NMR spectra of silicone fluid mixtures at 294 K.

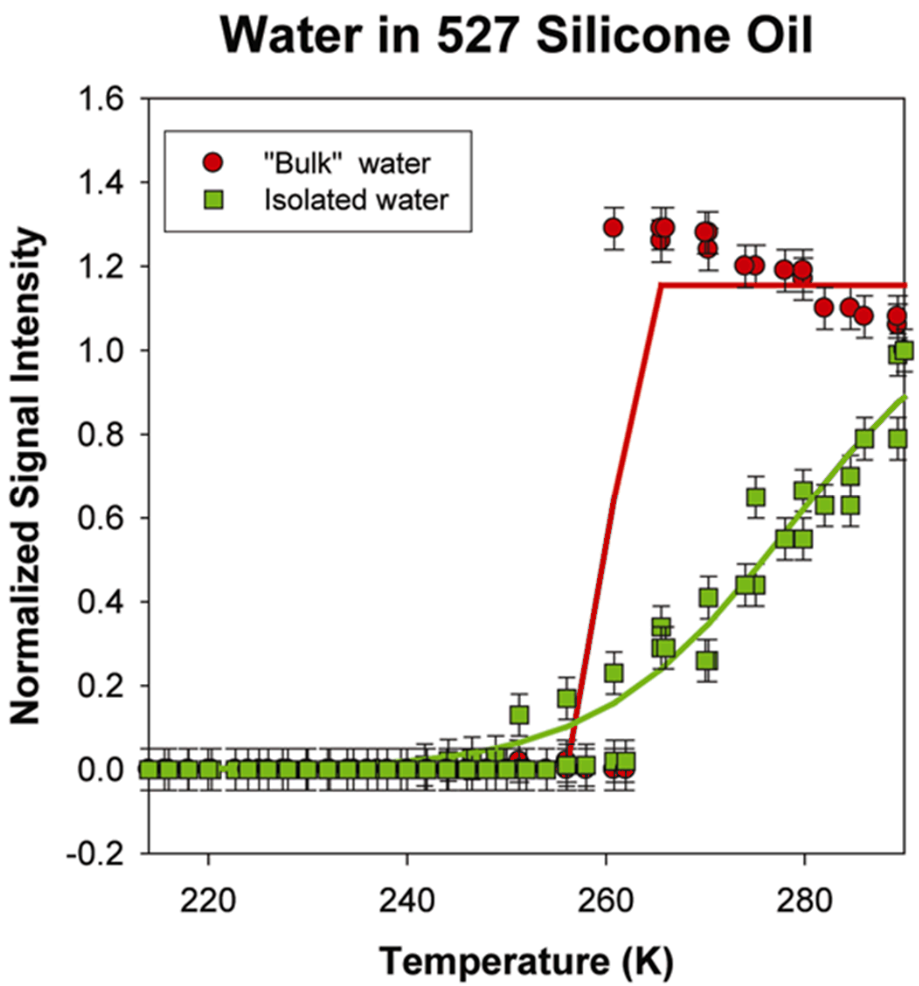
- Different water environments in PDMS fluid can be discerned using ^{1}H NMR.
- Assignments based on "spiking" experiments.
- Observe an isolate water species; no water-water hydrogen bonding.
- Isolated water seen in other organic solvents.
- Concentration consistent with saturation limit (~ 200 ppm), and is supported by Karl Fisher titration.
- "Bulk water" represent phase separated species and the chemical shift suggest hydrogen bonding.

Freezing Behavior of Water in PDMS



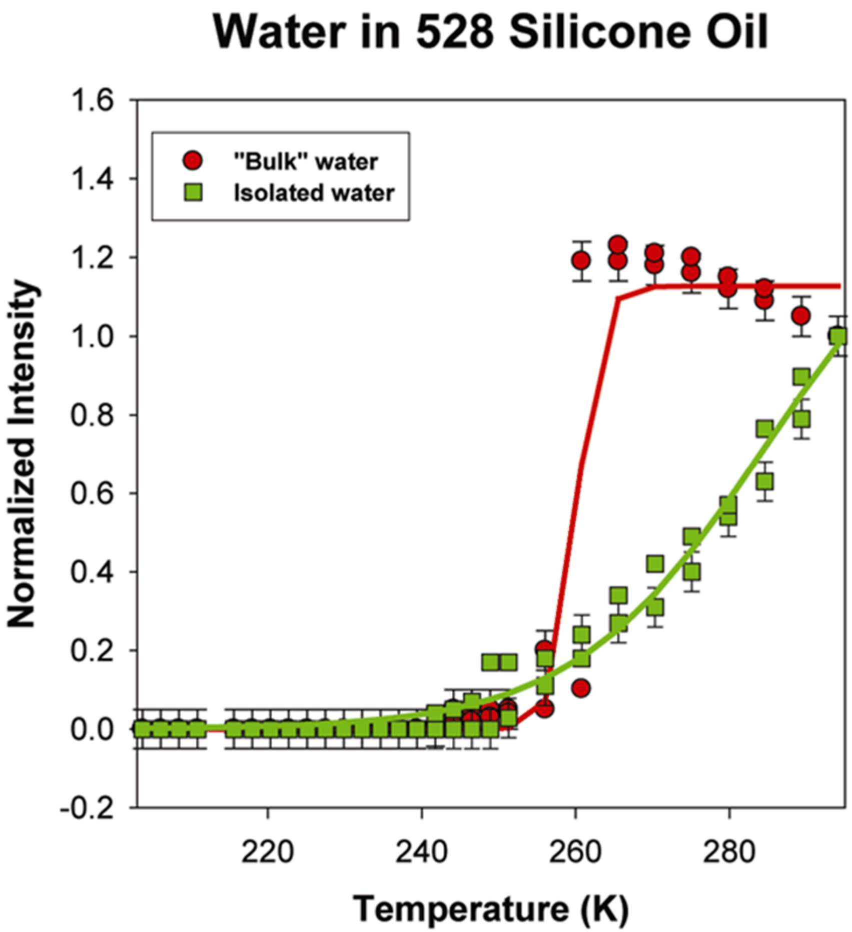
- The high resolution ^{1}H NMR spectra for the silicone fluid mixture as a function of sample temperature allow the low temperature behavior of these different water species to be directly followed.
- Not amendable to Karl Fisher titrations.
- Note the disappearance of both the isolated water species and the “bulk”-like water environment at low temperatures.
- Ice crystals formation within the PDMS fluids are the issue or concern. Need to determine what impact the triglyme/diglyme have on the water freezing properties.
- NMR allows this analysis, cycling and temperature hold experiments.

Freezing Behavior of Water in PDMS



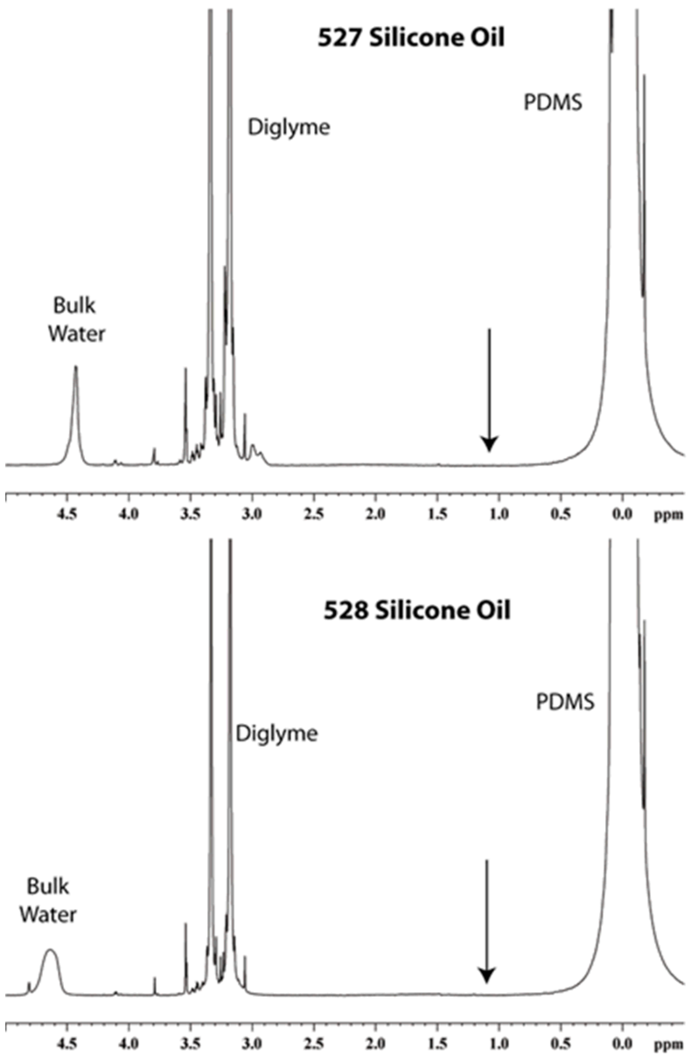
- Both water environments show a “freezing” transition.
- Temperature depressed in PDMS fluids compared to pure water.
- Isolated water species shows a gradual temperature response.
- May reflect solubility changes at lower temperatures.

Freezing Behavior of Water in PDMS



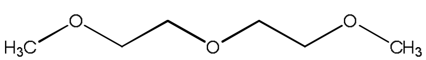
- Similar behavior for different PDMS fluid mixture (different viscosity).
- Note increase in “bulk” environment as the expense of isolated water environment.

The Impact of Glyme Additives

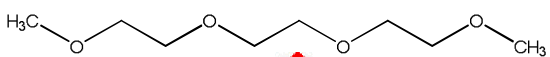


- The high resolution ^{1}H NMR for different silicone fluid mixtures with 2% diglyme additive.
- Note the disappearance (arrow) of the isolated water species in these mixtures.
- Either prevent or increases exchange rate.

Diglyme
Diethylene glycol dimethyl ether



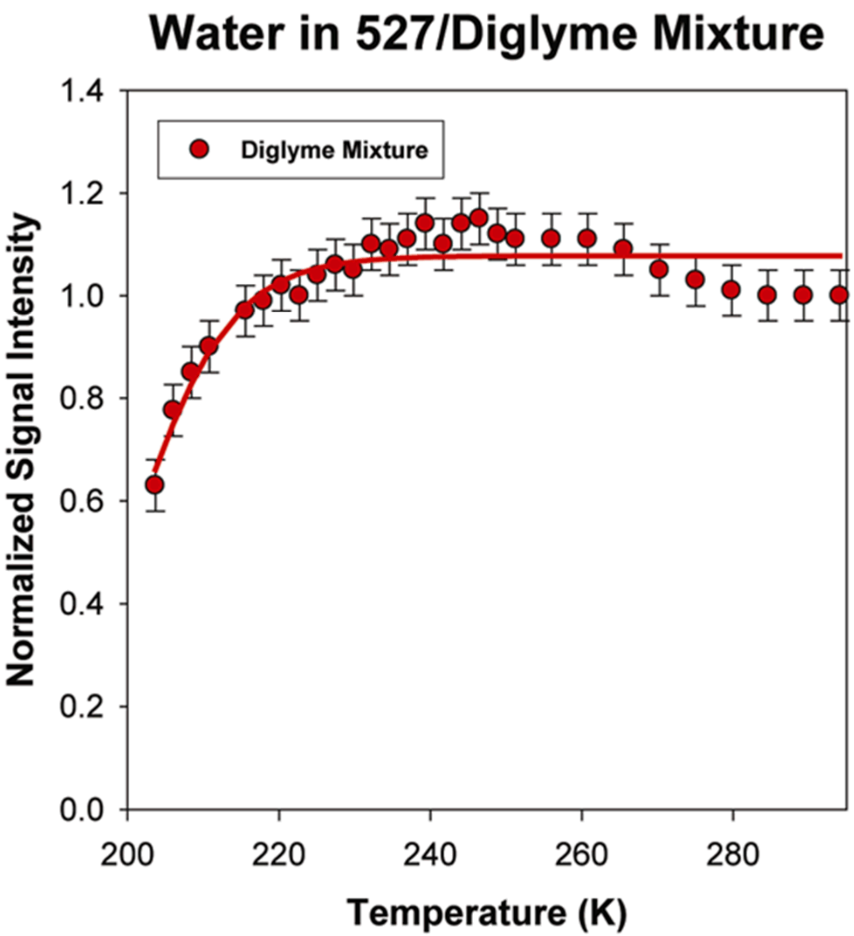
Triglyme
Triethylene glycol dimethyl ether

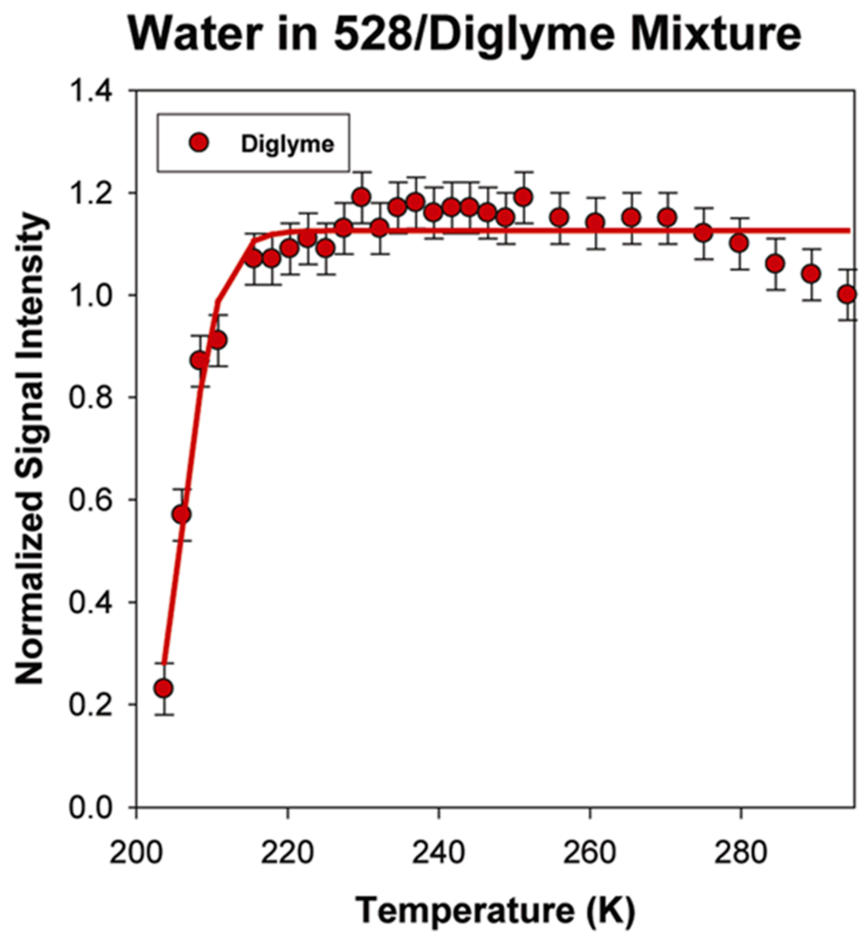


Tetrogenetic
Reproductive toxin

The reproductive toxicity of diglyme is attributed to its minor metabolite 2-methoxyacetic acid, which is generated from 2-methoxyethanol. 2-methoxyacetic acid has shown evidence of accumulation in animals and humans. In humans its half-life was calculated as 77.1h (ECETOC, 1995, WHO, 2002). 2-methoxyacetic acid is also considered to be responsible for the reproductive toxicity of triglyme. A formation of a smaller amount of 2-methoxyacetic acid is however expected to occur in the case of triglyme (in comparison with diglyme).

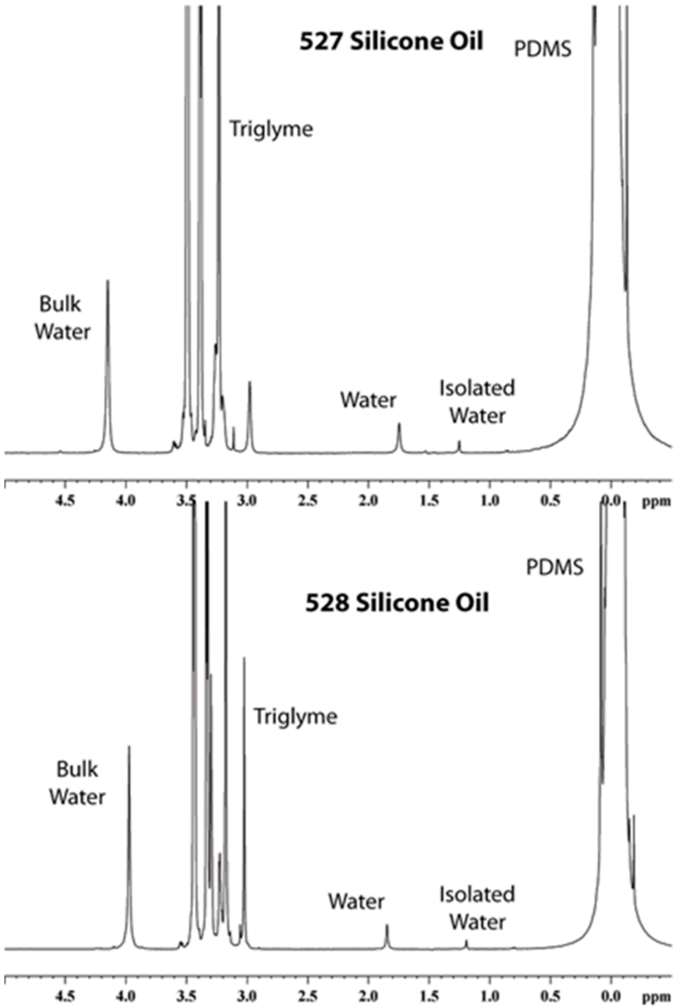
Freezing Behavior of Water in PDMS-Diglyme





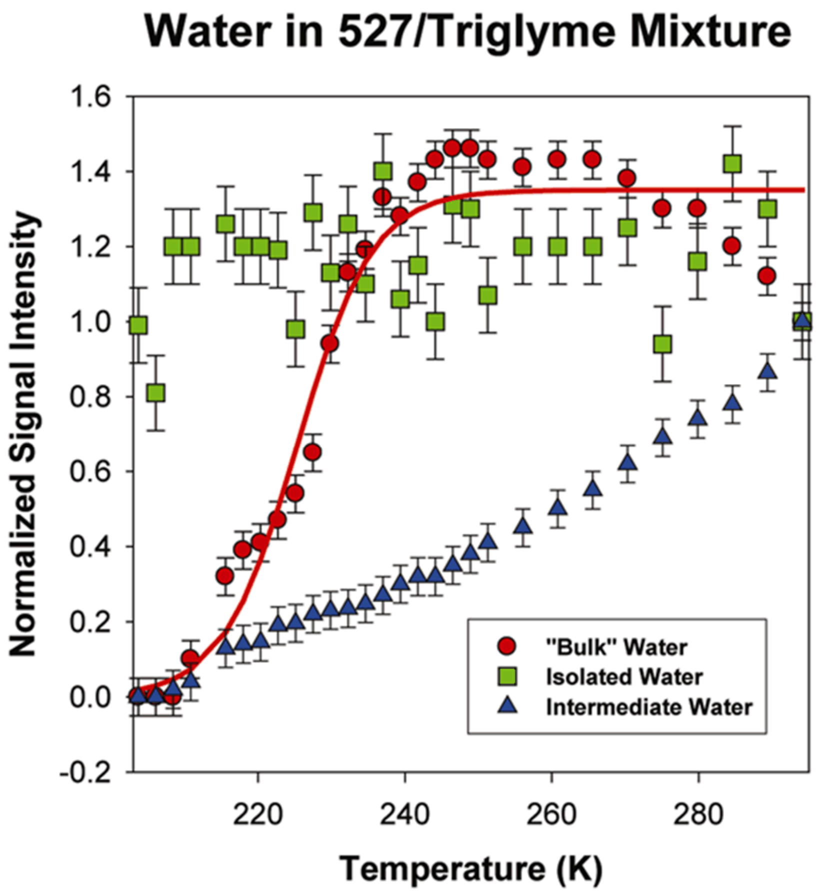
Additive suppresses freezing of "bulk water" in silicone fluids.

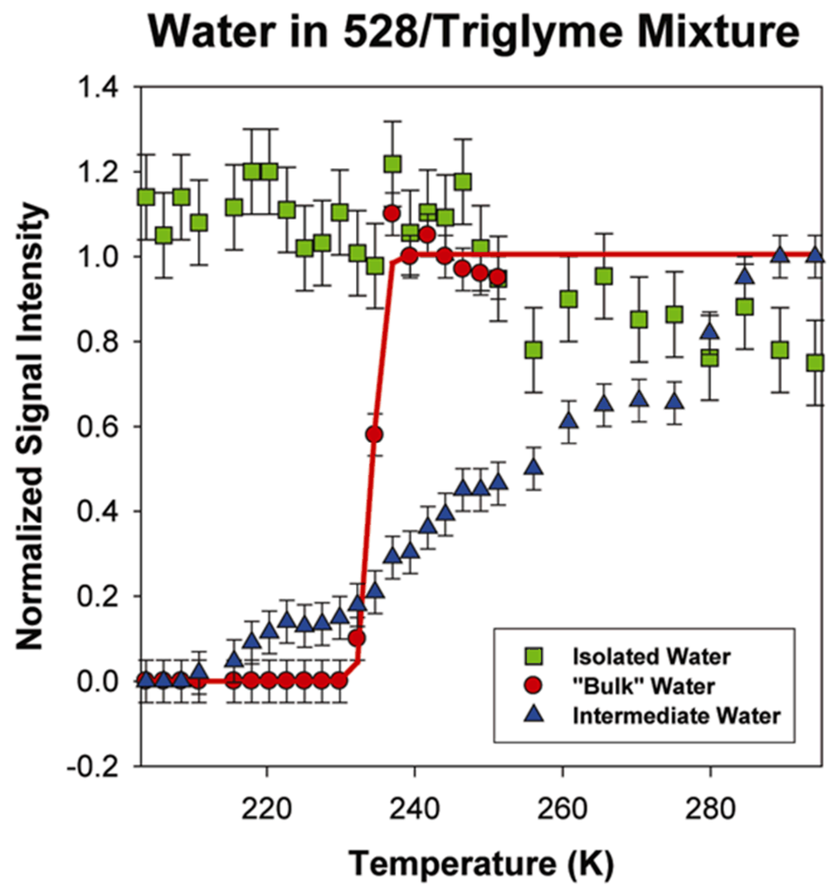
Impact of Triglyme in PDMS



- High resolution ^{1}H NMR spectra of the silicone fluid mixtures containing the triglyme additive.
- Several different water environments are experimentally observed.
- These different environment change with temperature.
- NMR reveals complex differences.

Freezing Behavior of Water in PDMS





- Isolated water remains in the silicone fluid > -50^{o}C
- Design system to maintain low water concentrations: only isolated waters are present.

Conclusions

- NMR provides and powerful to characterize the low temperature behavior of water impurities and additives in silicone fluids.
- Simple 1D NMR experiments in most cases!
- Can follow degradation and Mw for extended accelerated aging periods.
- Able to map out solubility phase diagram for triglyme additive in silicone fluid, and the impact of temperature has on this result.
- Not easily approached with other analytical methods. Especially at variable temperature situations.

Thank the organizers!

Thank you for your attention!