

---

# Rheology of non-Newtonian liquid Mixtures and the Role of Molecular Chain Length

Sean Parlia

Columbia University, Dispersion Technology Inc.

Dr. Ponisseril Somasundaran  
Columbia University

Dr. Andrei Dukhin  
Dispersion Technology Inc.

**Center for Particulate and Surfactant Systems (CPaSS)**  
**Summer 2019 IAB Meeting**  
**Columbia University, New York, NY**  
**August 6-7, 2019**

# Rheology of Non-Newtonian Mixtures

**Research Team:** Sean Parlia, Dr. Andrei Dukhin, Dr. Ponisseril Somasundaran

**Overview:** We employ two methods for studying the rheology of mixtures of nonpolar media mixed with surfactant: Shear Viscosity and Longitudinal Viscosity measurements.



**Technical Information:** Effect of chain length on rheology of nonpolar mixtures; Energy of molecular interactions for short-chain surfactants, volume-based mixing rule for long-chain surfactants, Expanding-collapsing of flexible long-chain surfactant molecules

**Industrial Relevance:** Industrial Relevance: Personal Care, nanotechnology, paints and pigments, food industry, oil industry

# Classical Mixing Rules

- **Arrhenius Mixing Rule (1887):**

$$\ln \eta_m = x_1 \ln \eta_1 + x_2 \ln \eta_2$$

- **Grunberg-Nissan Mixing Rule (1949):**

$$\ln \eta_m = x_1 \ln \eta_1 + x_2 \log \eta_2 + x_1 x_2 d$$

- **Katti-Ghaudhri Mixing Rule (1964):**

$$\ln \eta_m V_m = x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2$$

## Symbols

$\eta$  – viscosity

$x$  – mole fraction

$V$  – molar volume

**Molecular energy  
relating to structure**



# Classical Mixing Rules, Continued

## Symbols

R – gas constant

T – absolute temp.

E – intermolecular energy between components

- **Excess Activation Energy of the Viscous Flow:**

$$\Delta G = \sum_i \sum_j x_i x_j E_{ij}$$

- **Eyring's Representation of Liquid Viscosity:**

$$\ln \eta_m V_m = \sum_i^N x_i \ln \eta_i V_i + \frac{\Delta G}{RT}$$

- **Combining above equations for 2-component mixture:**

$$\ln \eta_m V_m = x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2 + x_1 x_2 \frac{E_{12}}{RT}$$

# Materials and Measurements

## Materials -

### Newtonian Liquid:

- **Toluene**
  - Molecular Weight: 92.14 g/mol

### Non-Newtonian Liquids:

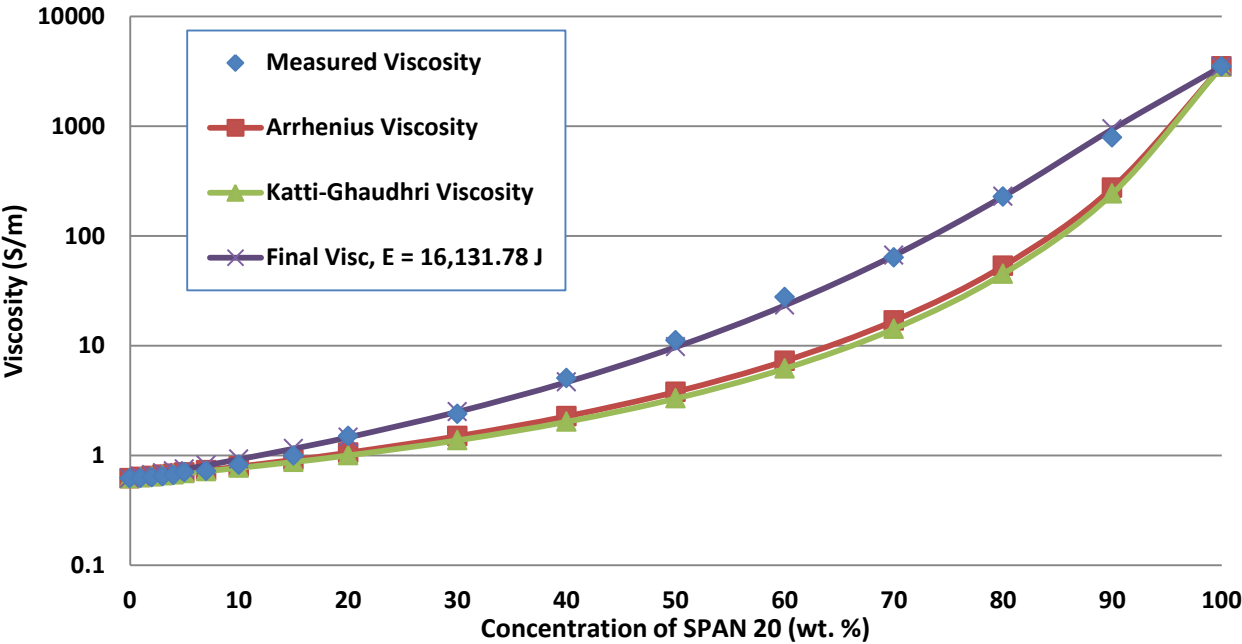
- Short Chain Surfactants:
  - **Sorbitan Monolaurate (SPAN 20)** –
    - Molecular Weight: 346.5 g/mol
  - **Sorbitan Monooleate (SPAN 80)**-
    - Molecular Weight: 428.6 g/mol
- Long Chain Surfactants:
  - **Xiameter OFX-5098**
    - Molecular Weight: 3,255.9 g/mol
  - **Xiameter OFX-0400-**
    - Molecular Weight: 3,101.1 g/mol

## Measurements

- **Shear Viscosity** – Translational & Oscillational\* Motion
- **Longitudinal Viscosity** – Oscillational Motion

# Shear Rheology – Short Chain Surfactant

Theoretical vs Measured Viscosity of SPAN 20/Toluene Mixtures

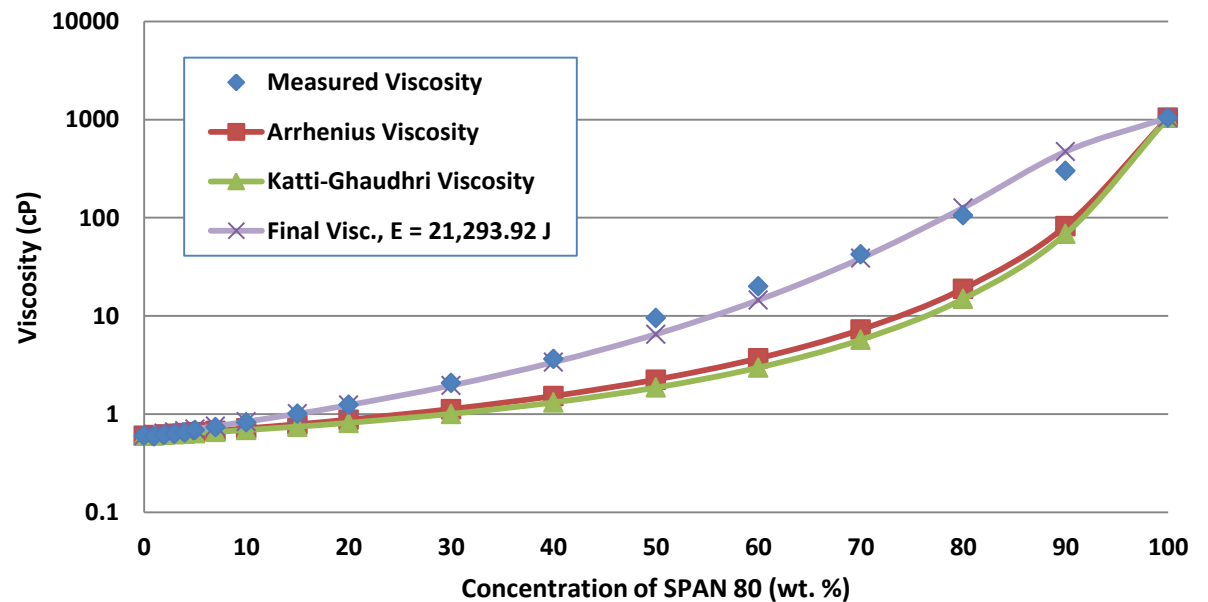


- Simple Mixing Rules Fail
- Excess Activation Energy Mixing Rule fits data
  - Indicates strong intermolecular interactions

## $E_{12}$ Values:

- SPAN 20: 16,131 J
- SPAN 80: 21,293 J

Theoretical vs Measured Viscosity of SPAN 80/Toluene Mixtures



# Intermolecular Forces $E_{12}$ Consistent with HLB

## HLB Numbers:

- **SPAN 20 – 8.6**
- **SPAN 80 – 4.3**
  
- **SPAN 80 is more hydrophobic than SPAN 20, so it has higher affinity for nonpolar Toluene.**
- **$E_{12}$  is higher for SPAN 80 than SPAN 20, confirming higher affinity for toluene.**

## $\Delta G$ Values (at 50% Surfactant concentration):

**SPAN 20 : 4040 J**

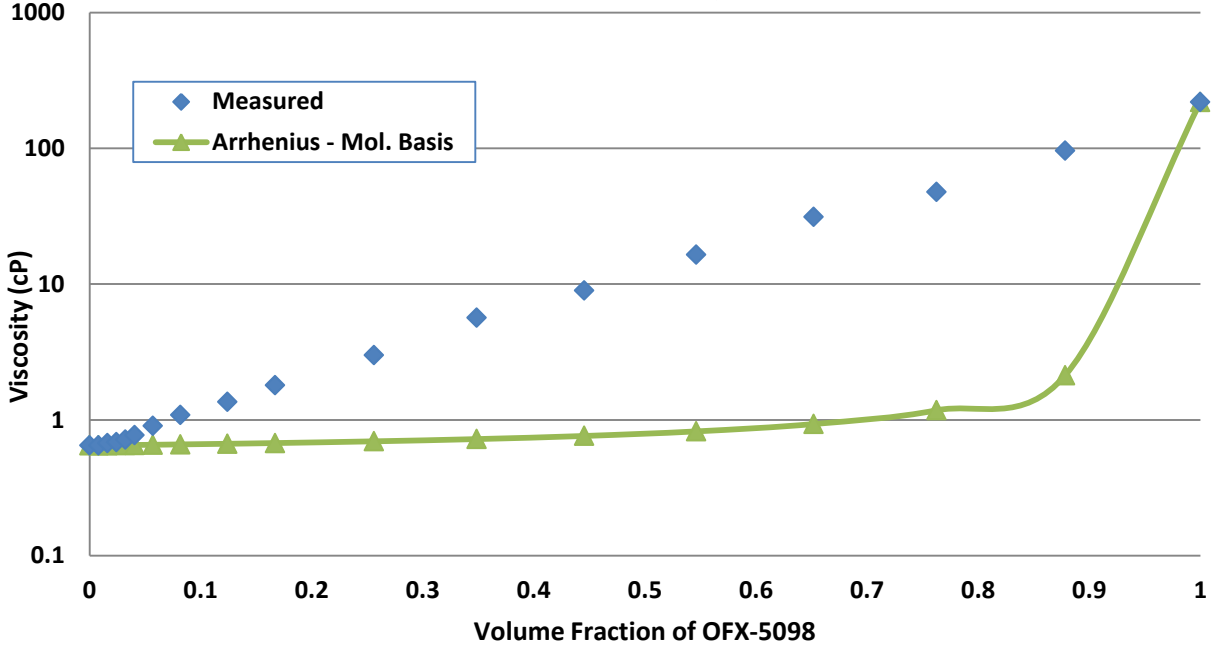
**SPAN 80: 5040 J**

**These values are ~2x higher than values reported by Monsalvo<sup>[1]</sup> for mixtures of 1,1,1,2-tetrafluoroethane (HFC-134a) with tetraethylene glycol dimethylether**

[1] - Monsalvo M.A., Baylaucq A., Reghem P., Quinones-Cisneros S.E., Boned C. “Viscosity measurements and correlations of binary mixtures: 1,1,1,2-tetrafluoroethane (HFC-134a) + tetraethylene glycol dimethylether (TEGDME), J. Fluid Phase Equilibria, 233, 1-8 (2005)

# Classic Mixing Rules Fail for Long Chains

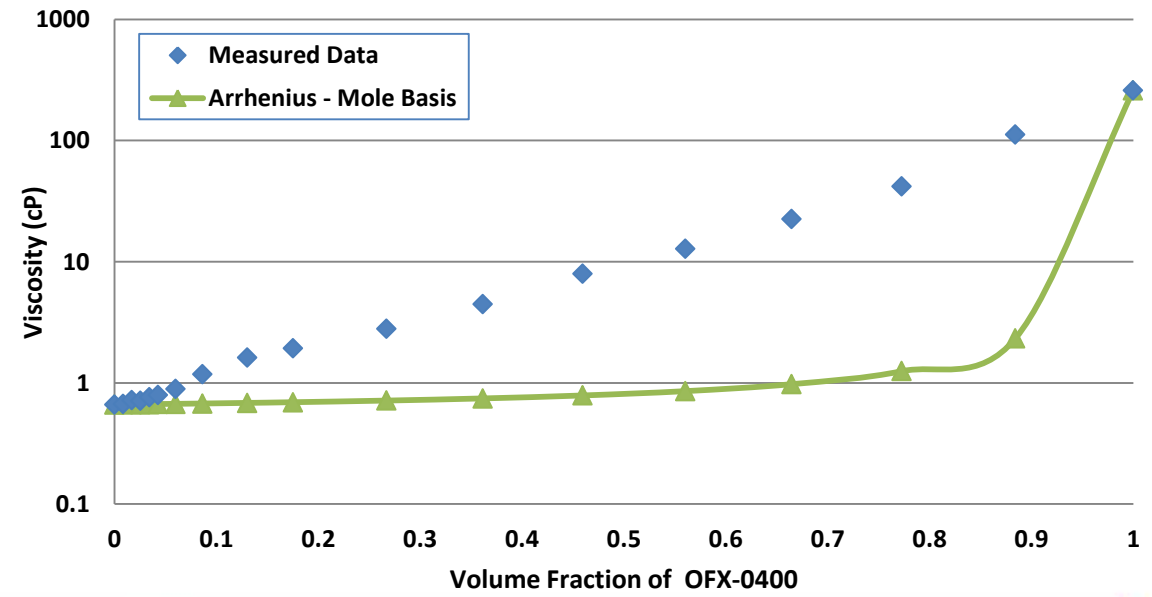
### Theoretical vs Measured Viscosity of OFX-5098 Mixtures



- Standard mixing rules, based on mole fractions, fail in all cases

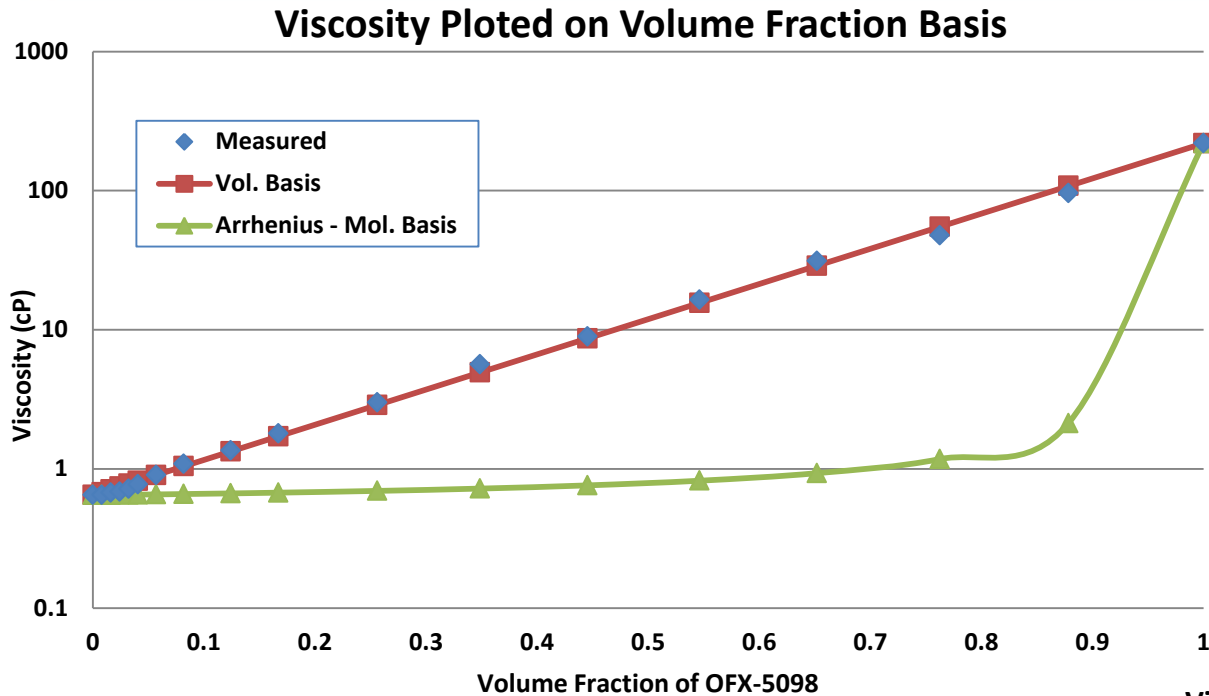
- Even when considering excess activation energy, theories still fail.

### Theoretical vs Measured Viscosity of OFX-0400 Mixtures





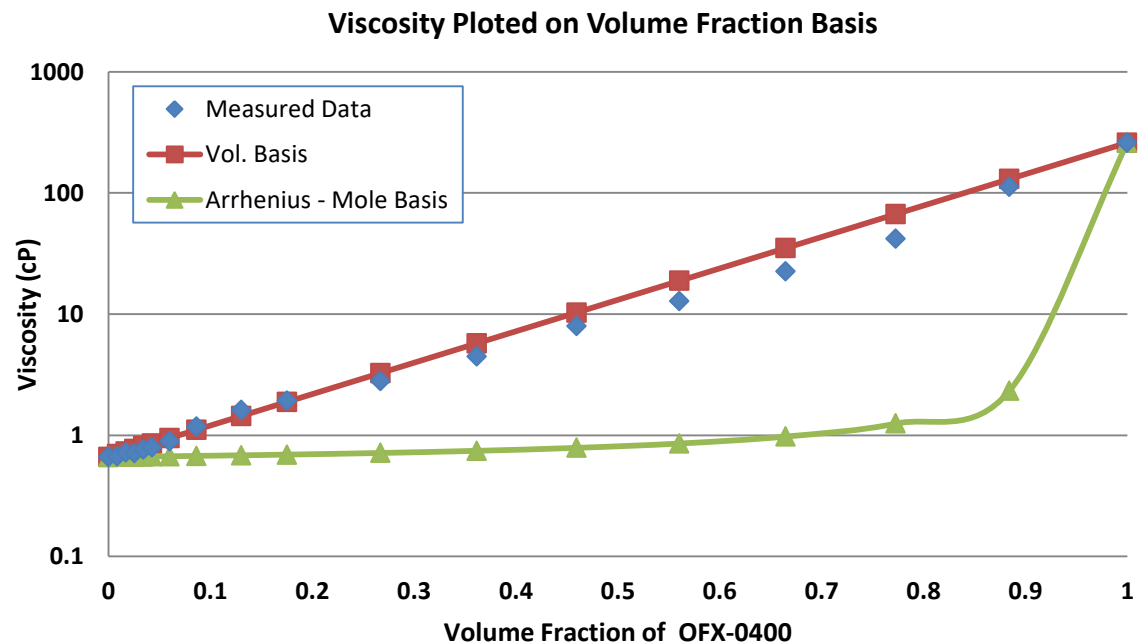
# Vol. Fraction Based Rule Works for Long Chains



Volume fraction-based mixing rule:

$$\ln \eta_m = (1 - \varphi) \ln \eta_1 + \varphi \ln \eta_2$$

Why does this theory work, but not the others?



# Hypothesis for Long Chain Surfactants

Distance



Initial State

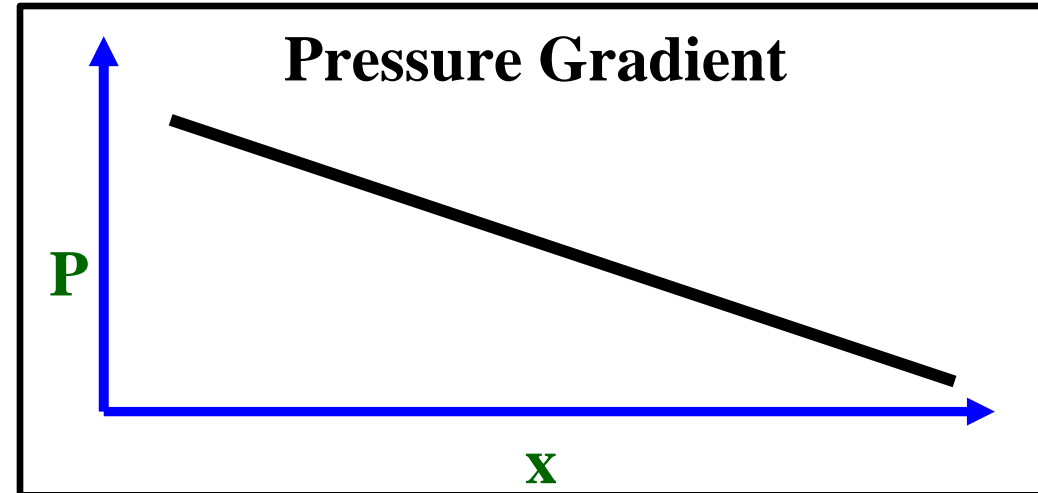


Expansion under longitudinal stress



Stress

Return to initial state, moved translationally



- Surfactant is initially bound in place to nonpolar media (toluene)
- Under stress the molecule stretches
- When molecule is sufficiently stretched, it can release from initial molecule, and return to original shape in new position, moving translationally.
- Longitudinal rheology data used for exploring this hypothesis

# Hypothesis for Long Chain Surfactants

- **Think: Slinky**



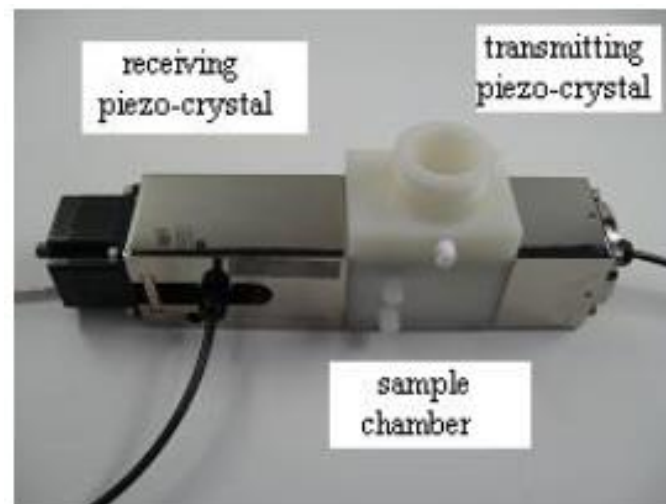
- Molecule experiences consecutive cycles of expansion and collapsing. In addition, it progresses forward driven by the stress.
- Such motion can be presented as superposition of oscillation and translation.
- Consequently, the two degrees of freedom that are involved translational and oscillational.
- According to this model, viscosity of the mixture depends solely on the amount of the non-Newtonian surfactant, hence:

$$\ln \eta_m = (1 - \varphi) \ln \eta_1 + \varphi \ln \eta_2$$

# Longitudinal Rheology: Role of Oscillation

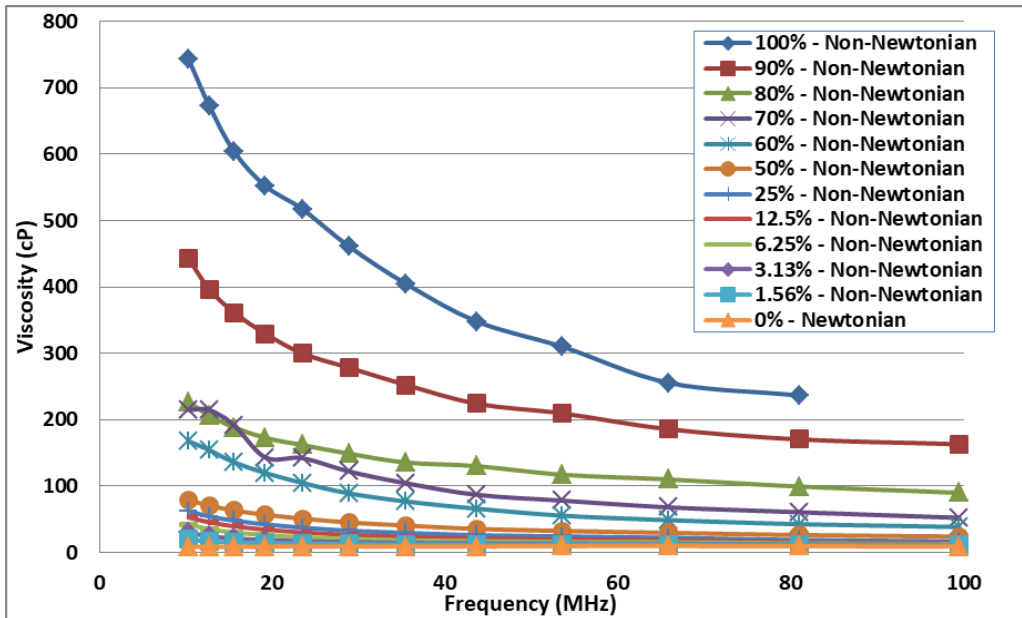
## Longitudinal ultrasound-based rheometer:

- Measures attenuation at multiple frequencies from 1 – 100 MHz:
- Molecules undergo mostly oscillational motion when such device is employed.
- This would allow us to characterize this degree of freedom individually, separately from the translational degree of freedom.
- Also can use to characterize mixtures as Newtonian or Non-Newtonian:
  - Newtonian liquid viscosity is independent of frequency.



# Short-Chain Surfactants always Non-Newtonian

## SPAN 20



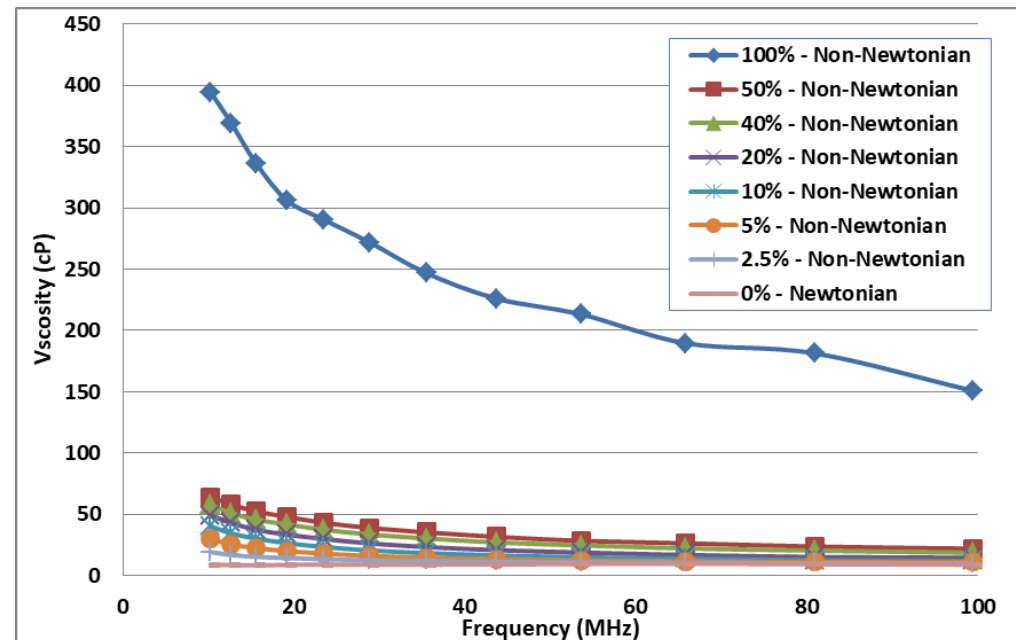
- Short-chained surfactants (SPAN) form non-Newtonian liquid mixtures even at very low concentrations
- Only at VERY low concentrations do the mixtures transition to Newtonian (below 1%)

←

Longitudinal Viscosity vs. Frequency Plots

↓

## SPAN 80

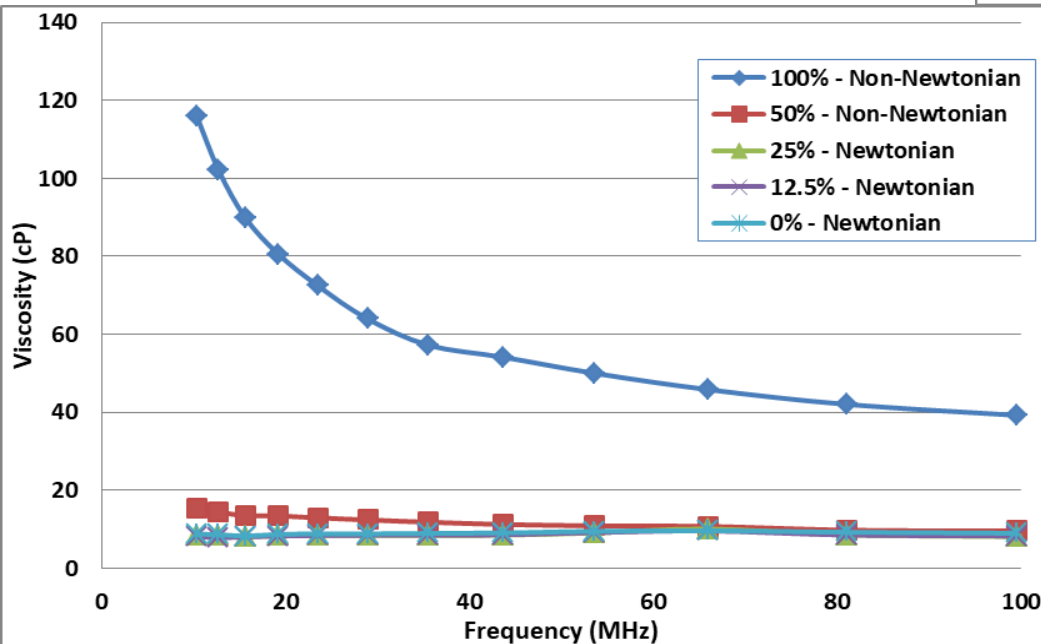


# Long-Chain Surfactants: Unique Behavior

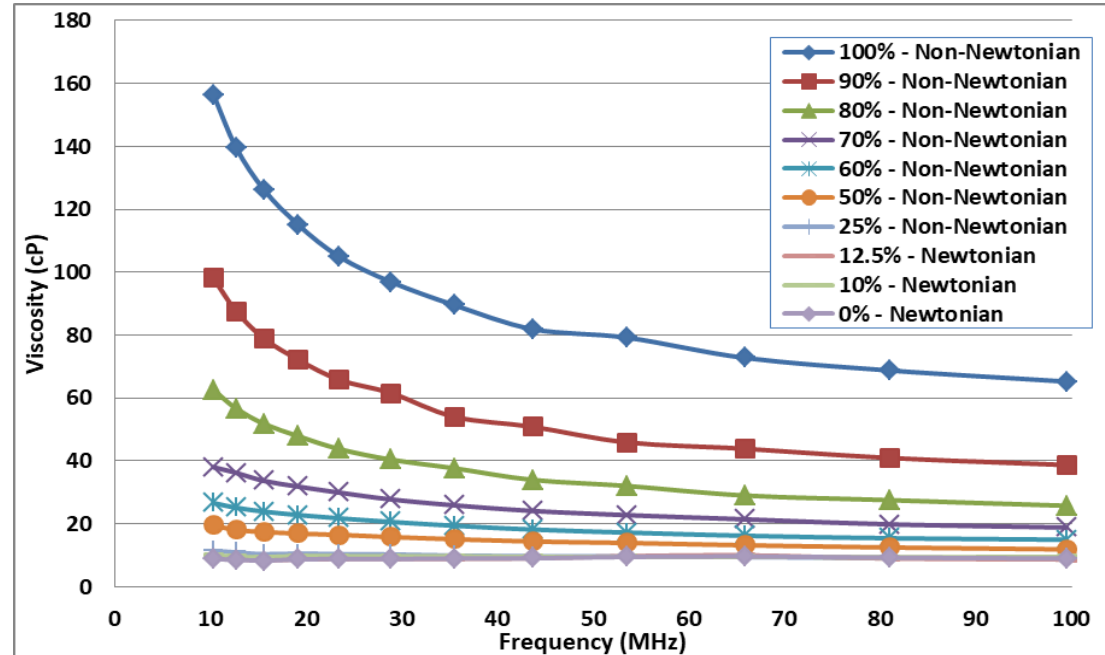
Long-chain surfactant mixtures become Newtonian at MUCH higher concentrations:

- OFX-5098 – Below 12.5 %
- OFX-0400 – Above 25 %

## OFX-0400



## OFX-5098



Oscillation of long-chained molecules in an ultrasound wave does not contribute to the longitudinal viscosity

- indicates that the long chained molecules that we study here are practically purely elastic.

Their oscillation is thermodynamically reversible and does not lead to energy dissipation.

# Conclusions

---

- **Classic Mixing rules successfully model viscosity for mixtures with short-chain surfactants**
  - **Allows for calculation of excess activation energy between surfactant and toluene**
- **Volume-fraction based mixing rule succeeds in predicting viscosity data**
- **Hypothesized that energy dissipation for long-chained surfactants caused by expanding-collapsing of flexible long-chain surfactant molecules (slinky)**
- **Longitudinal rheology data implies that oscillational motion does not result in energy dissipation for long-chain surfactants**
  - **Molecules are effectively elastic**
  - **All energy dissipation comes from translational motion**

# Acknowledgements

---

This material is based upon work supported by the National Science Foundation under Grant No. 0749481/1362060 and by CPaSS industry members.

## Thanks to:

- **Dr. Andrei Dukhin, Dispersion Technology Inc.**
- **Dr. Ponisseril Somasundaran, Columbia University**
  - **Members of Dr. Somasundaran's Lab Group.**

## Disclaimer

Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation/Sponsors.