Rheological Investigations of Latex, Associative Thickener, and Surfactant Interactions

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Overview

- Introduction
- Materials
- Procedure
- Results and Related Models
- Summary
- Further Work
- Acknowledgements

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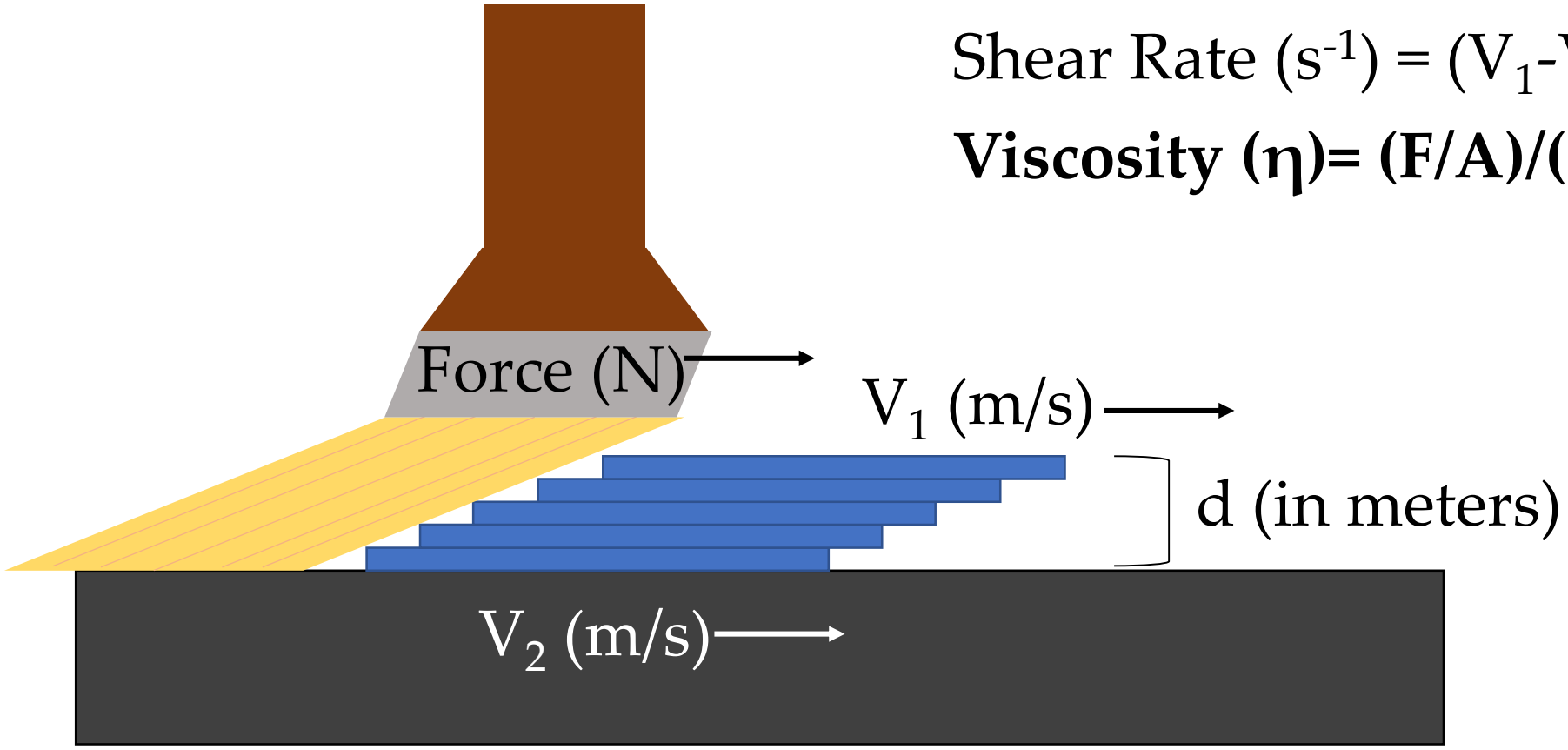
Shear and Flow

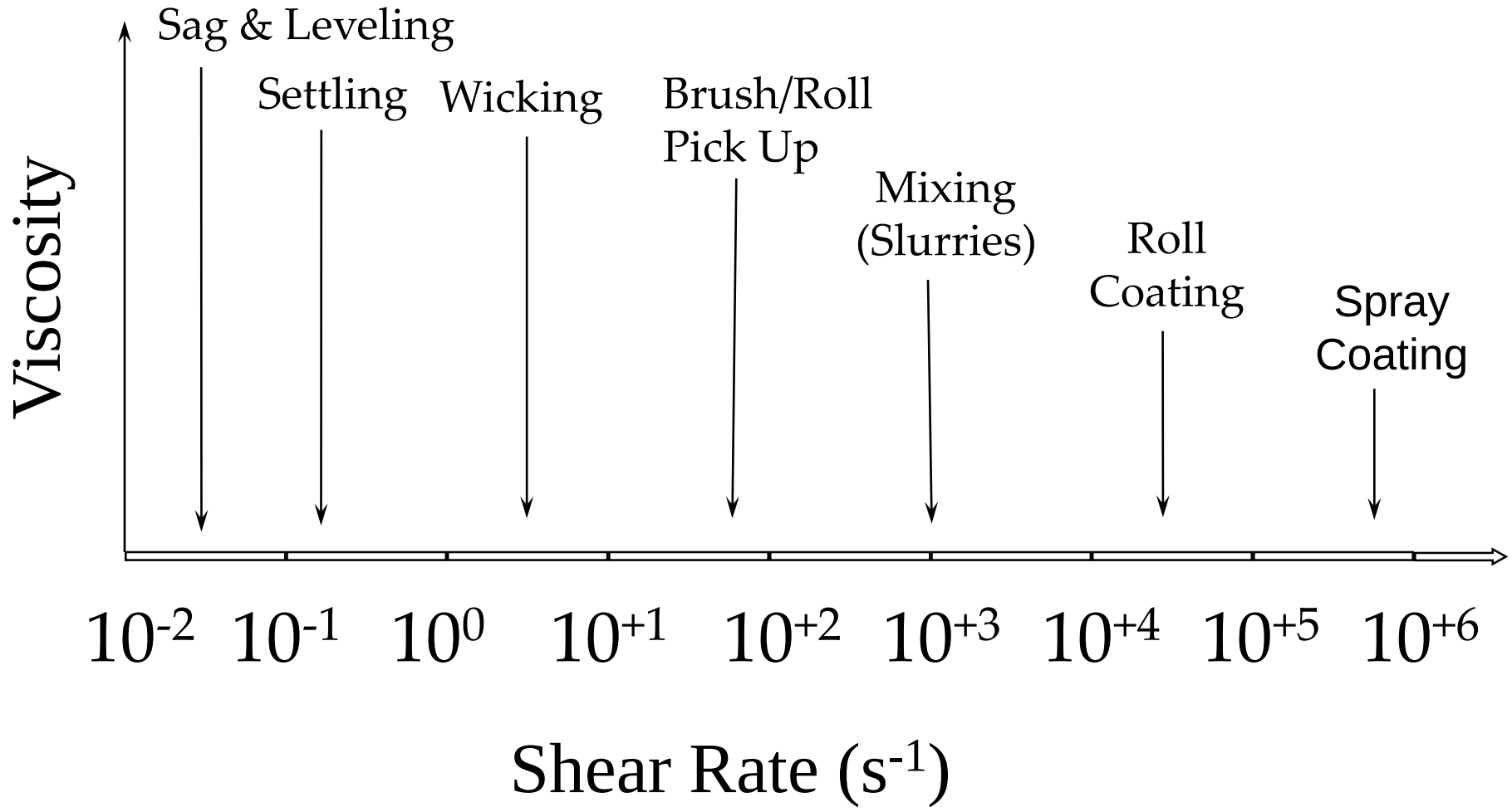
A = Area of Liquid

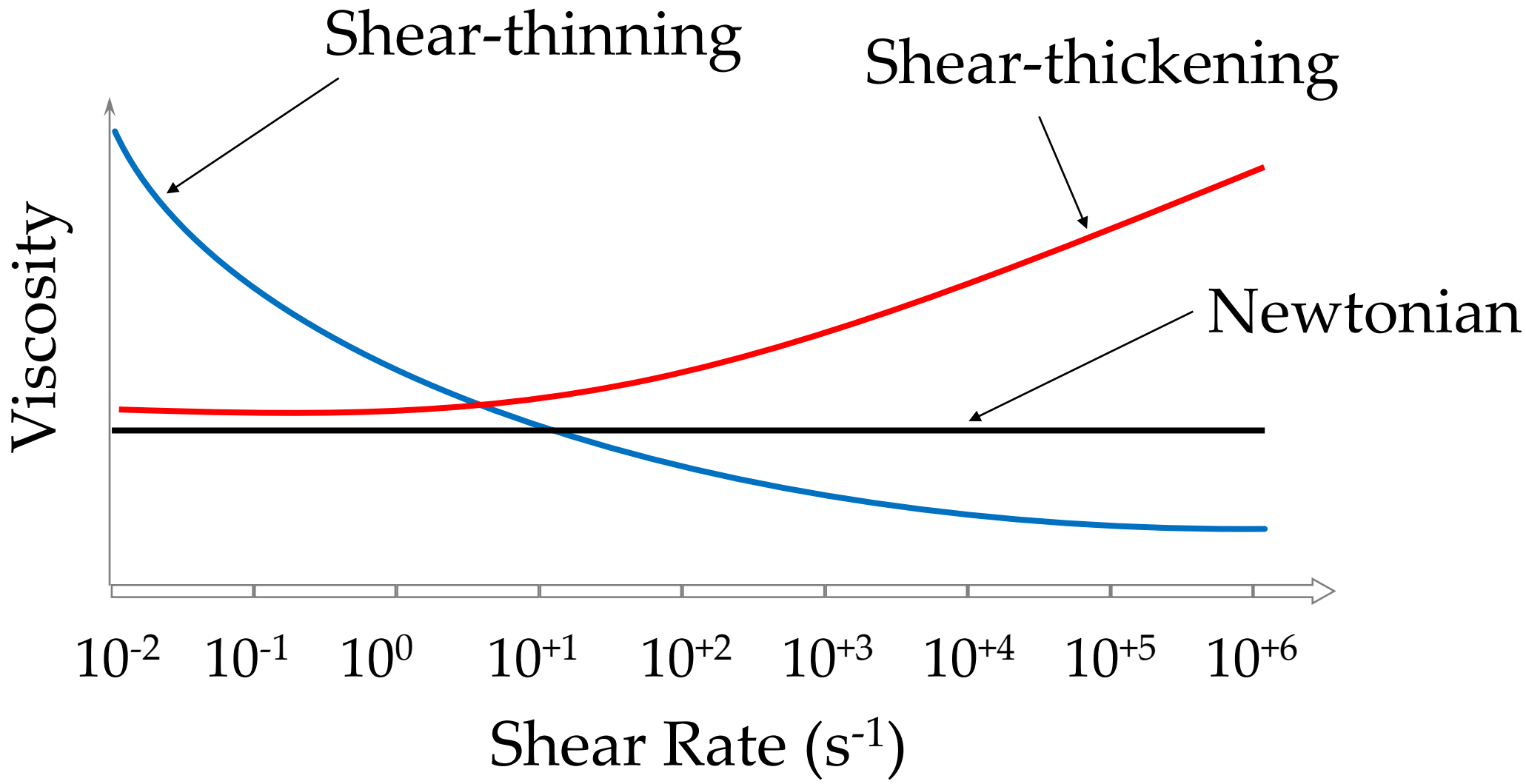
Shear Stress (N/m^2) = F/A

Shear Rate (s^{-1}) = $(V_1-V_2)/d$

Viscosity (η)= (F/A)/(ΔV/d)

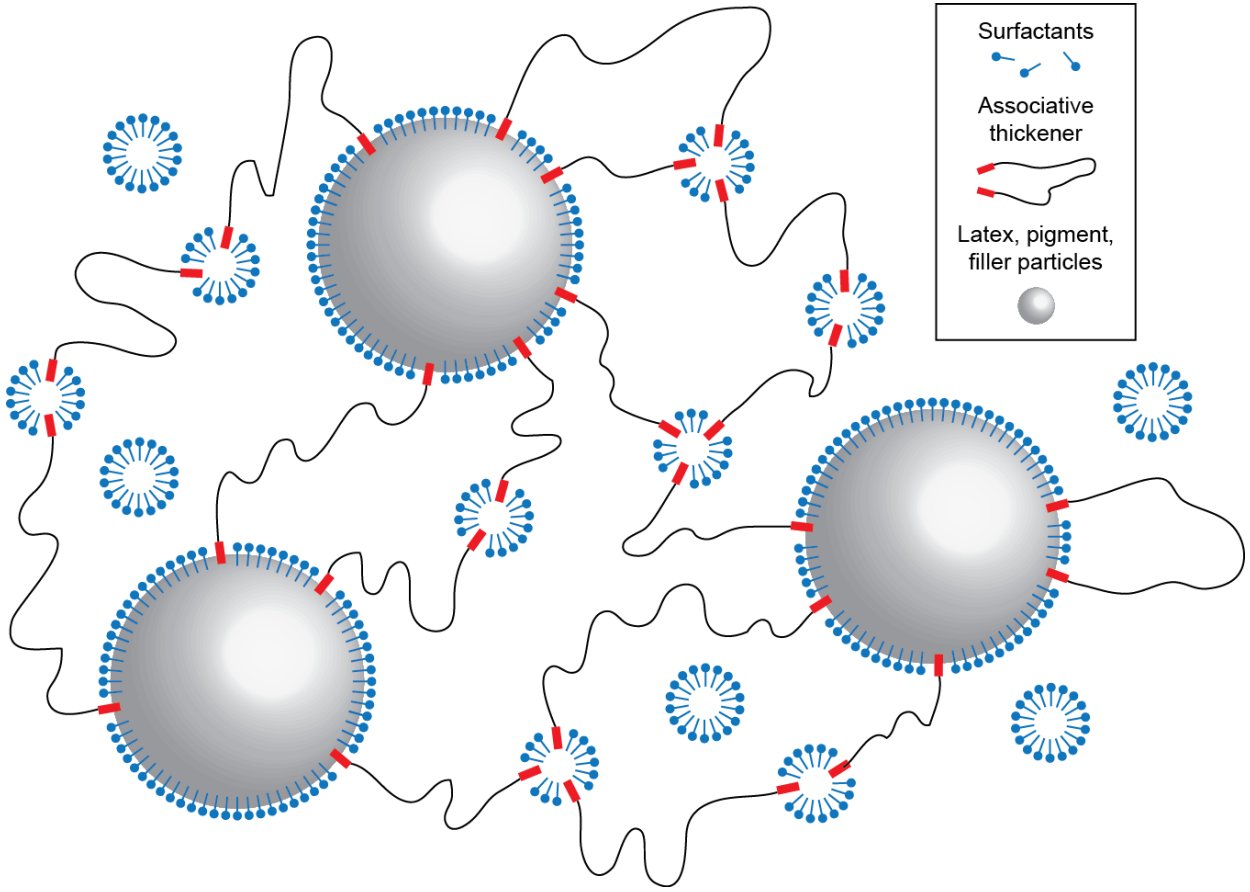



Sag & Leveling
Settling
Wicking
Brush/Roll
Pick Up
Mixing
(Slurries)
Roll
Coating
Spray
Coating
Viscosity
10-2
10-1
100
10+1
10+2
10+3
10+4
10+5
10+6
Shear Rate (s-1)


Shear-thinning
Shear-thickening
Newtonian
Viscosity
10-2
10-1
100
10+1
10+2
10+3
10+4
10+5
10+6
Shear Rate (s-1)

Coating Formulation Ingredients

- Polymeric Binder
  - Waterborne Latex Particles
    - Stabilized with SDS from synthesis
- Surfactants
  - Surface Active Agents
  - Anionic, cationic, or non-ionic
- Thickeners
  - HEC, HASE, and HEUR
- Pigments
- Additives



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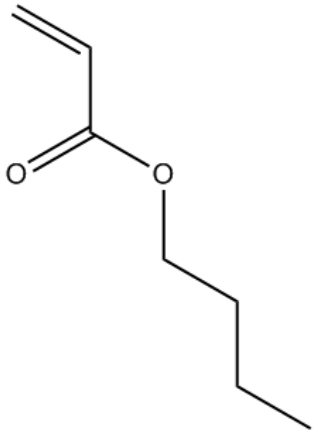
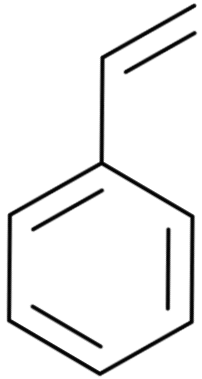
BA/STY Experimental Latex

- Composition:
  - 55% Butyl Acrylate units
  - 43% Styrene units
  - 2% Methacrylic Acid end functionalization



n-Butyl Acrylate (BA)

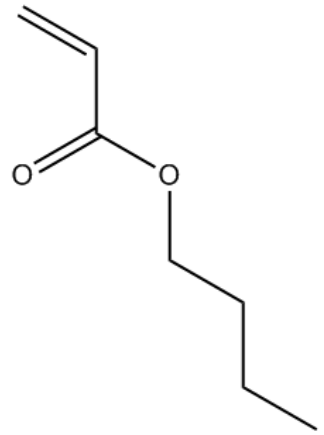


Styrene (STY)

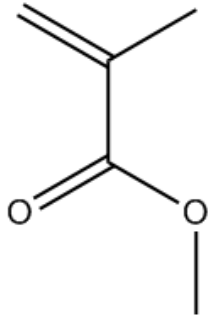
- Relatively Hydrophobic
- Glass Transition Temperature:
  - 14°C
- Initial 45% solids
  - Diluted to 25% volume solids in samples
- Average Particle Diameter:
  - 123 nm
- pH:
  - 9.6
- pKa:
  - 8.5

BA/MMA Experimental Latex

- Composition:
  - 55% Butyl Acrylate units
  - 43% Methyl Methacrylate units
  - 2% Methacrylic Acid end functionalization



n-Butyl Acrylate (BA)

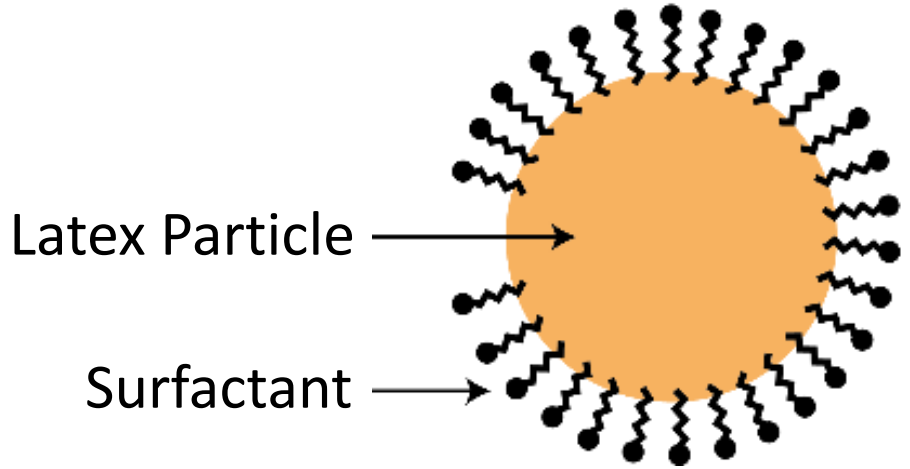


Methyl Methacrylate (MMA)

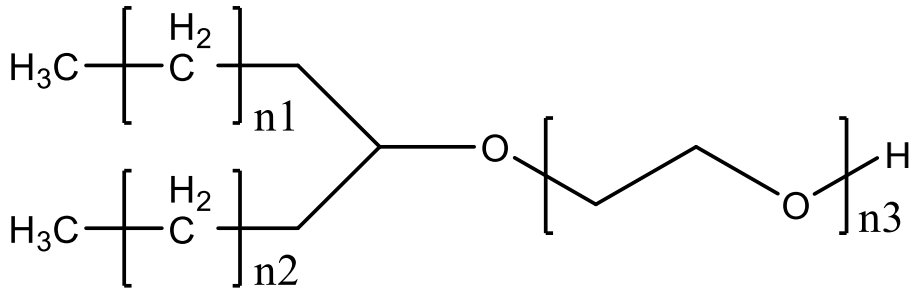
- Relatively Hydrophilic
- Glass Transition Temperature:
  - 10°C
- Initial 45% solids
  - Diluted to 25% volume solids in samples
- Average Particle Diameter:
  - 126 nm
- pH:
  - 9.3
- pKa:
  - 8.3

Surfactants being investigated

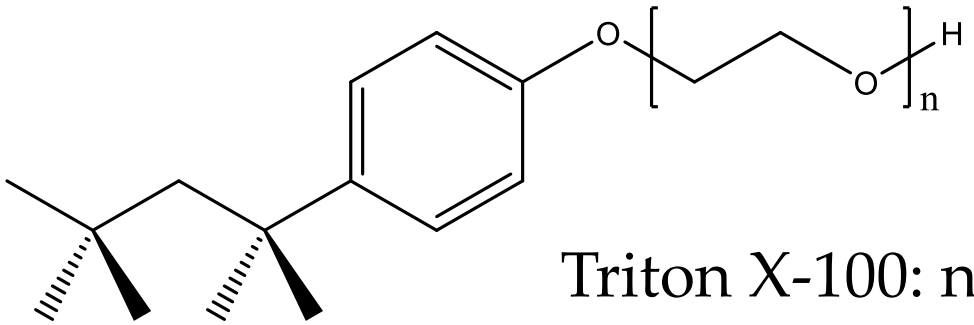
- Surface Active Agents:
  - Alkyl Chain:
    - Sodium dodecyl sulfate (anionic)
  - Ethylene Glycol Chain:
    - TSP-16 (non-ionic)
    - Tergitol 15-S-40 (non-ionic)
    - Triton X-100 (non-ionic)
    - TSP-16S (anionic)
    - TSP-16PE-30 (anionic)



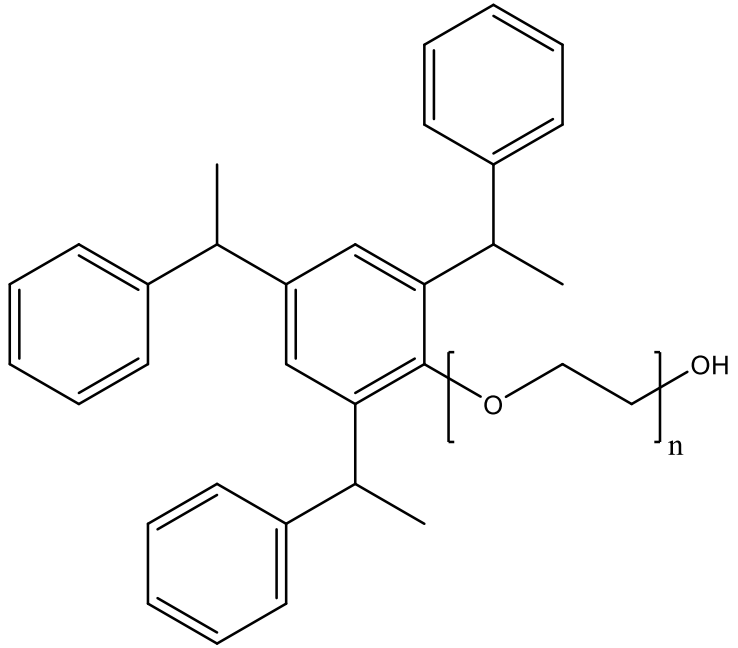
Surfactant Structures (Nonionic)



Tergitol 15-S-40:
(n1+n2=11-15, n3=41)

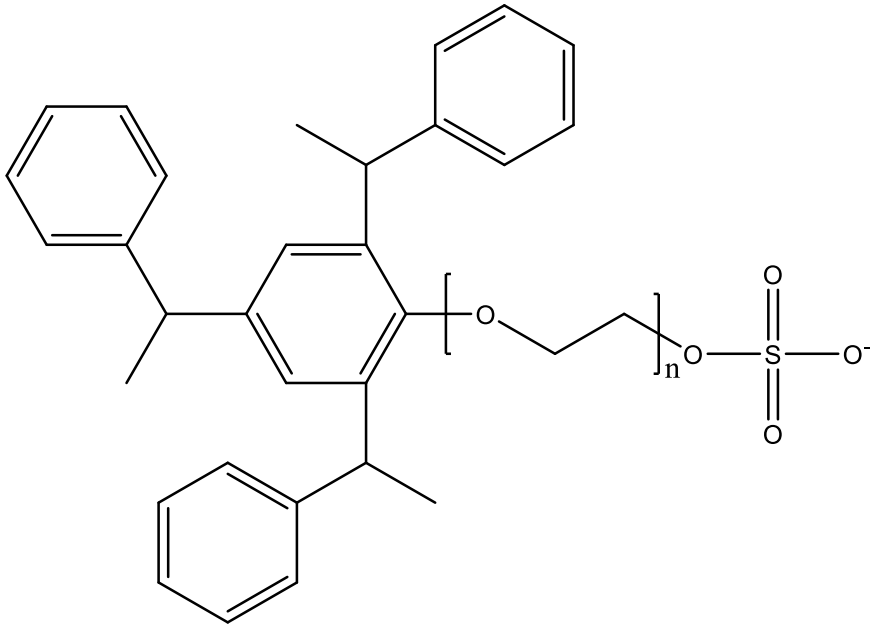


Triton X-100: n= ~9.5

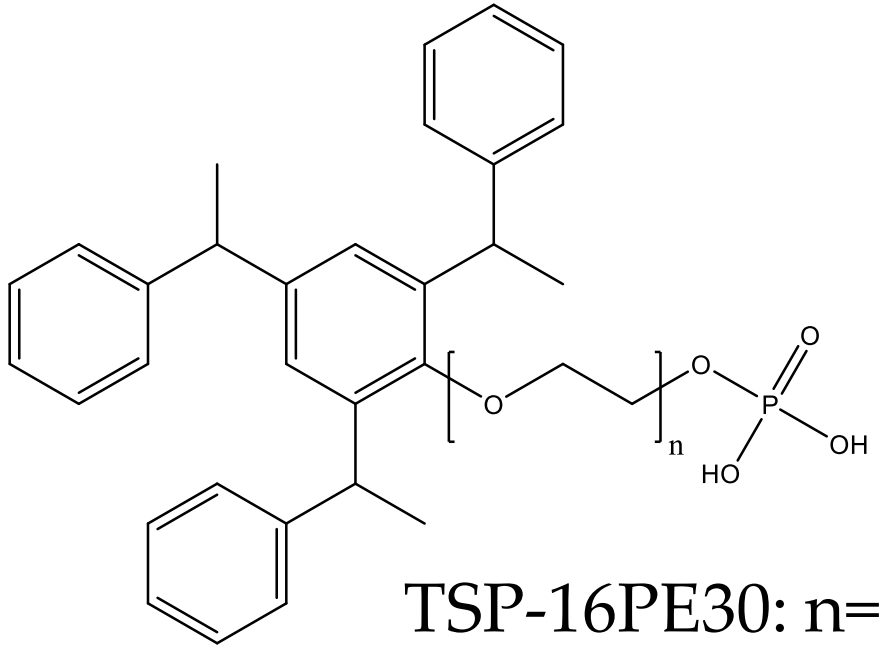


TSP-16: n=16

Surfactant Structures (Anionic)

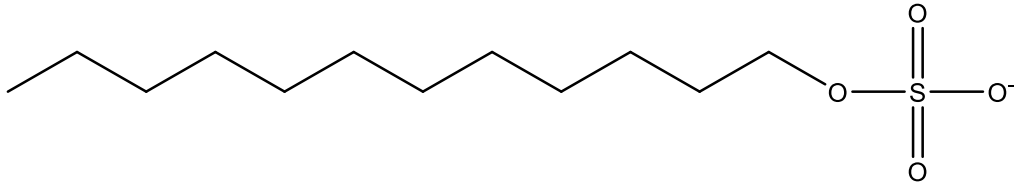


TSP-16S: n=16



TSP-16PE30: n=16

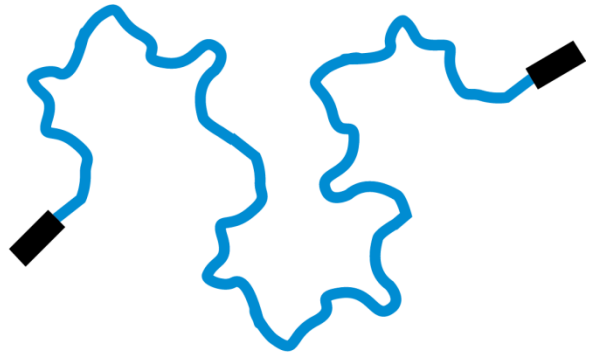
pH=1-2.5

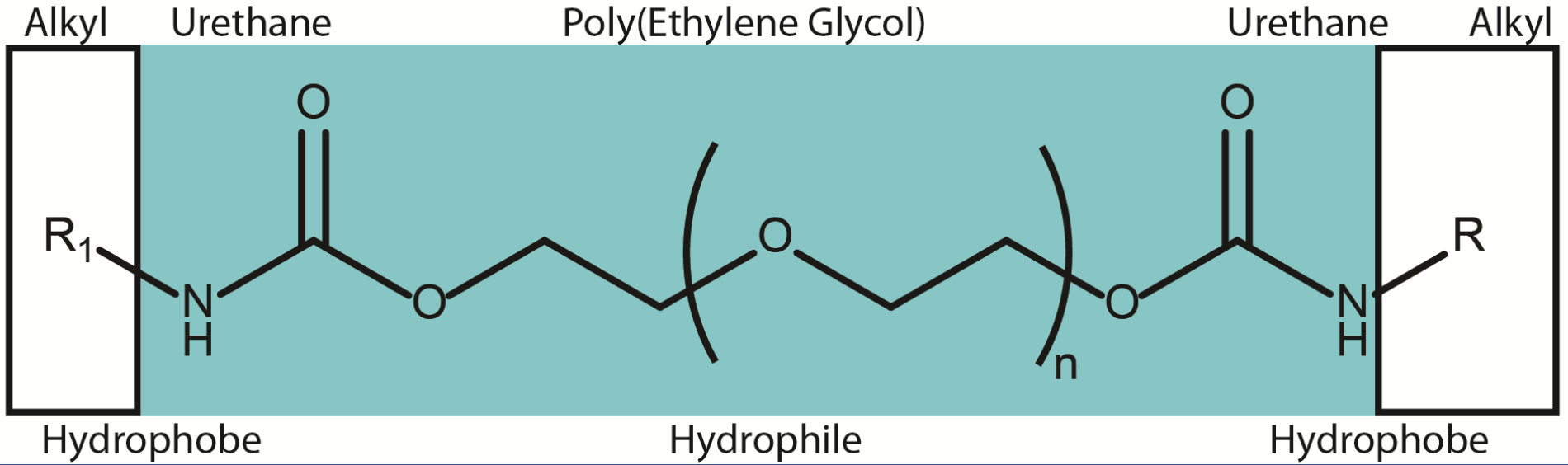


SDS

C18-EO795 Experimental HEUR

- R Group: 18 Carbon Alkyl
- PEG Length: 795 ethylene oxide (EO) units
- M_n: 26.8 kg/mol





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Flow Sweep Procedure

- 30 second hand mix
- 2 min pre-shear step
- Geometry: 40 mm, 2° Cone
- Range: 0.001-1000 s^{-1}
- Logarithmic Scale
- 10 points per decade
- Constant Temperature: 25°C
- 1 minute per data point
  - 15 second averaging time

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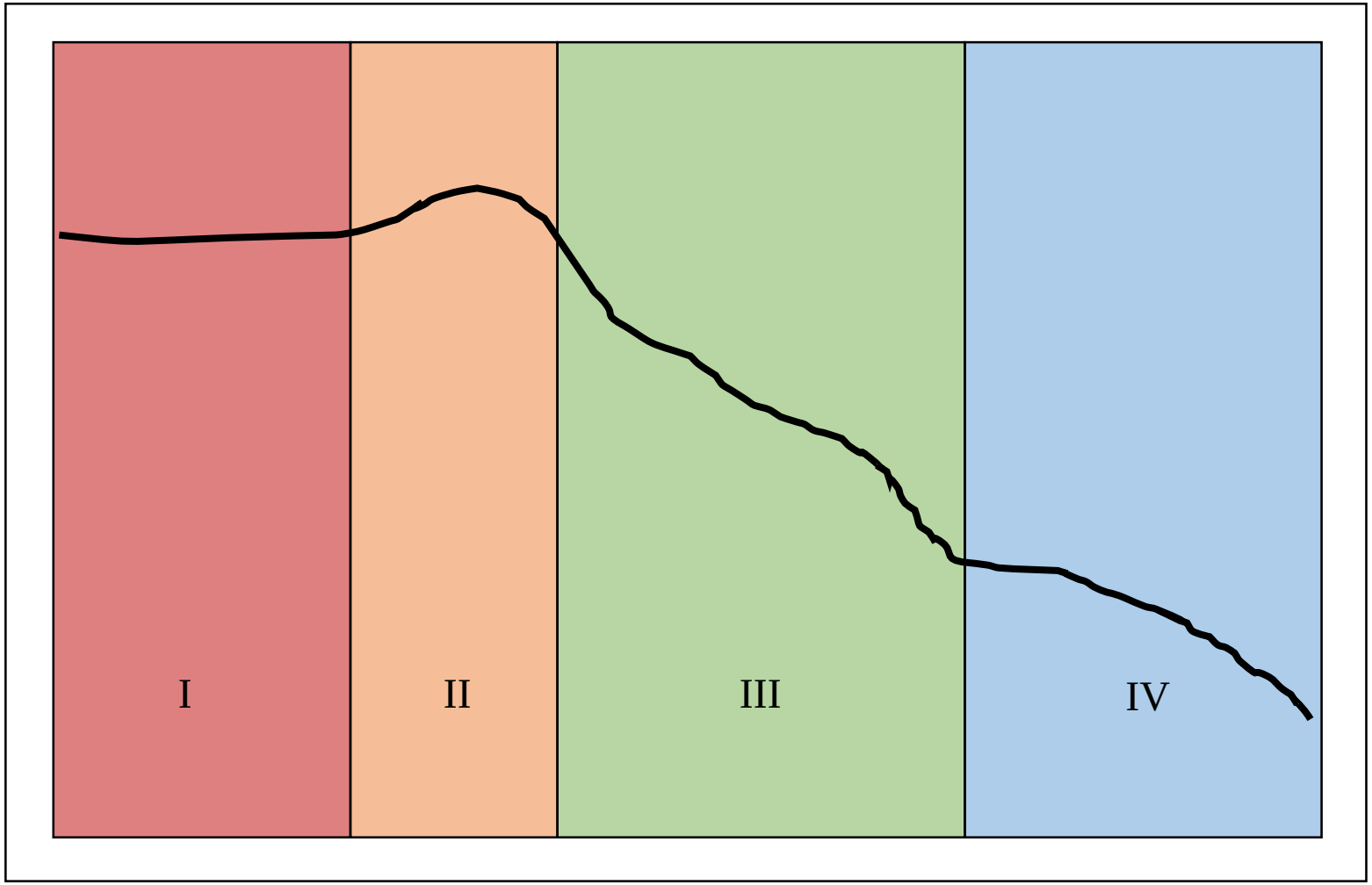
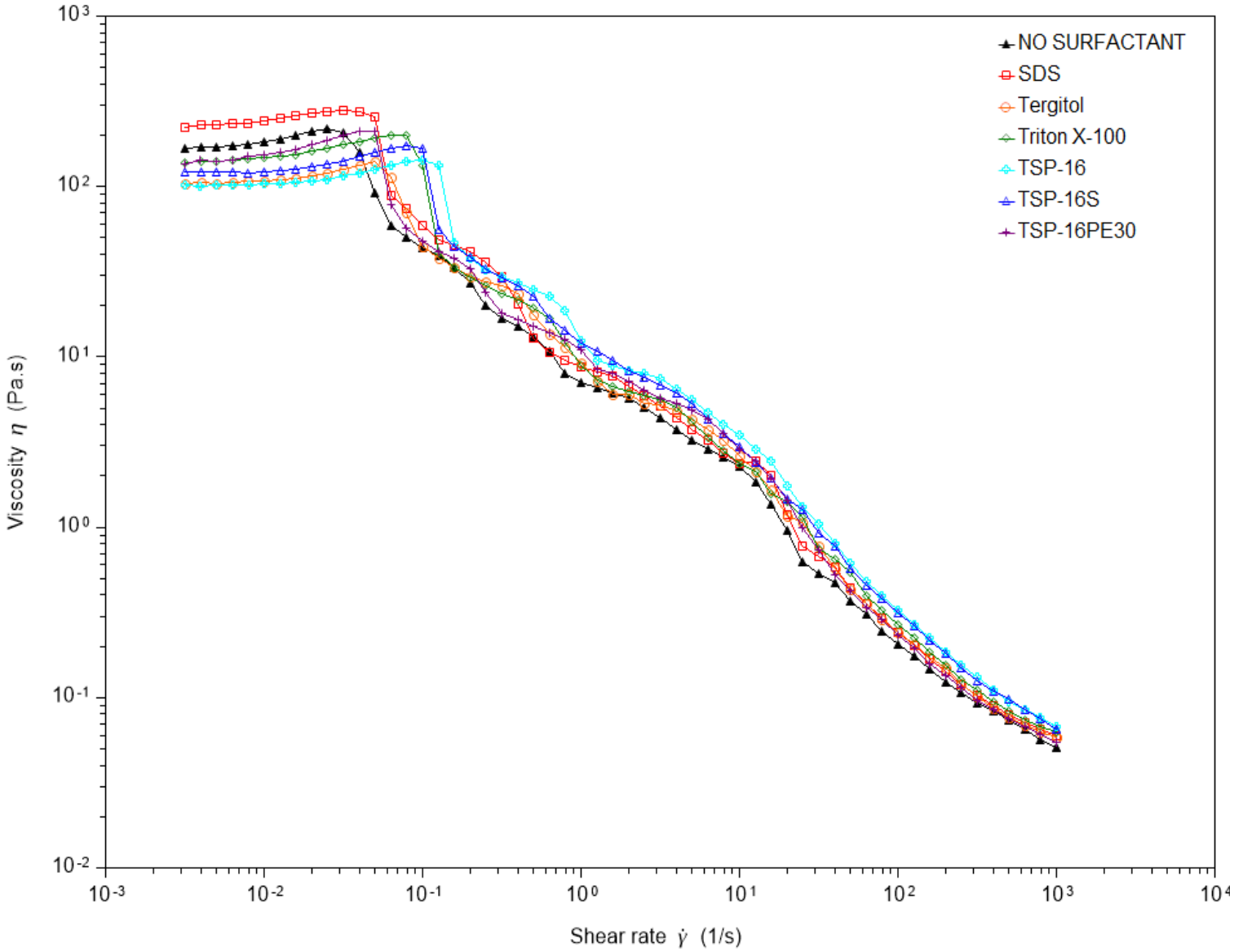
Latex-HEUR-Surfactant Systems

- Flow sweep rheological profiles demonstrate 4 major regimes:
  - Regime I: Newtonian-like Plateau
  - Regime II: Shear-thickening region
  - Regime III: Complex step-like region
  - Regime IV: High shear rate region (100-1000 s^{-1})

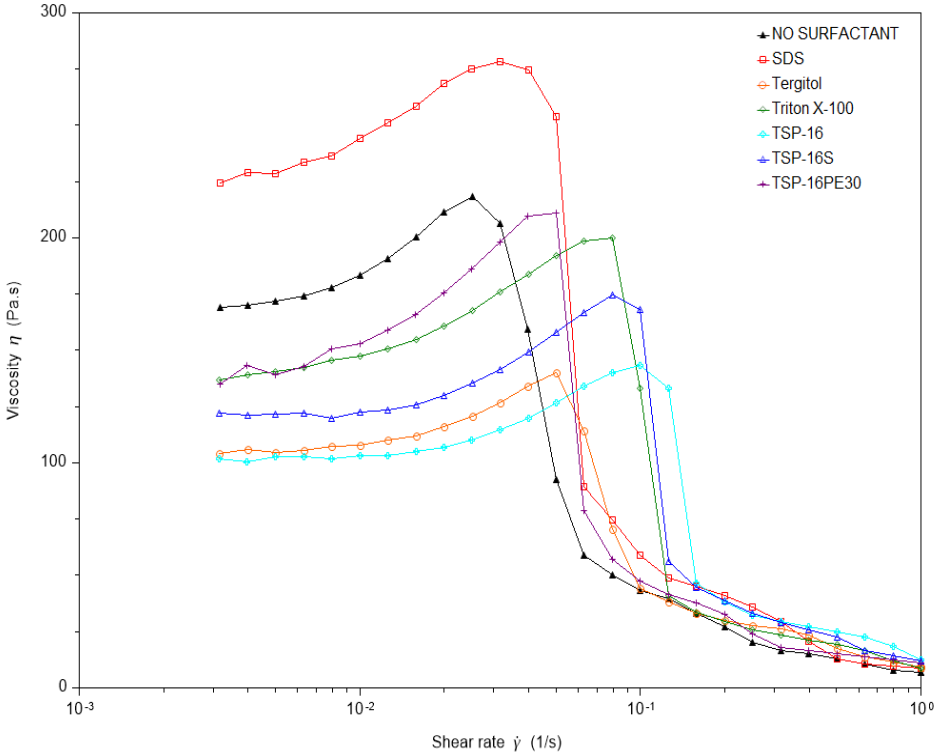
Representative Flow Sweep



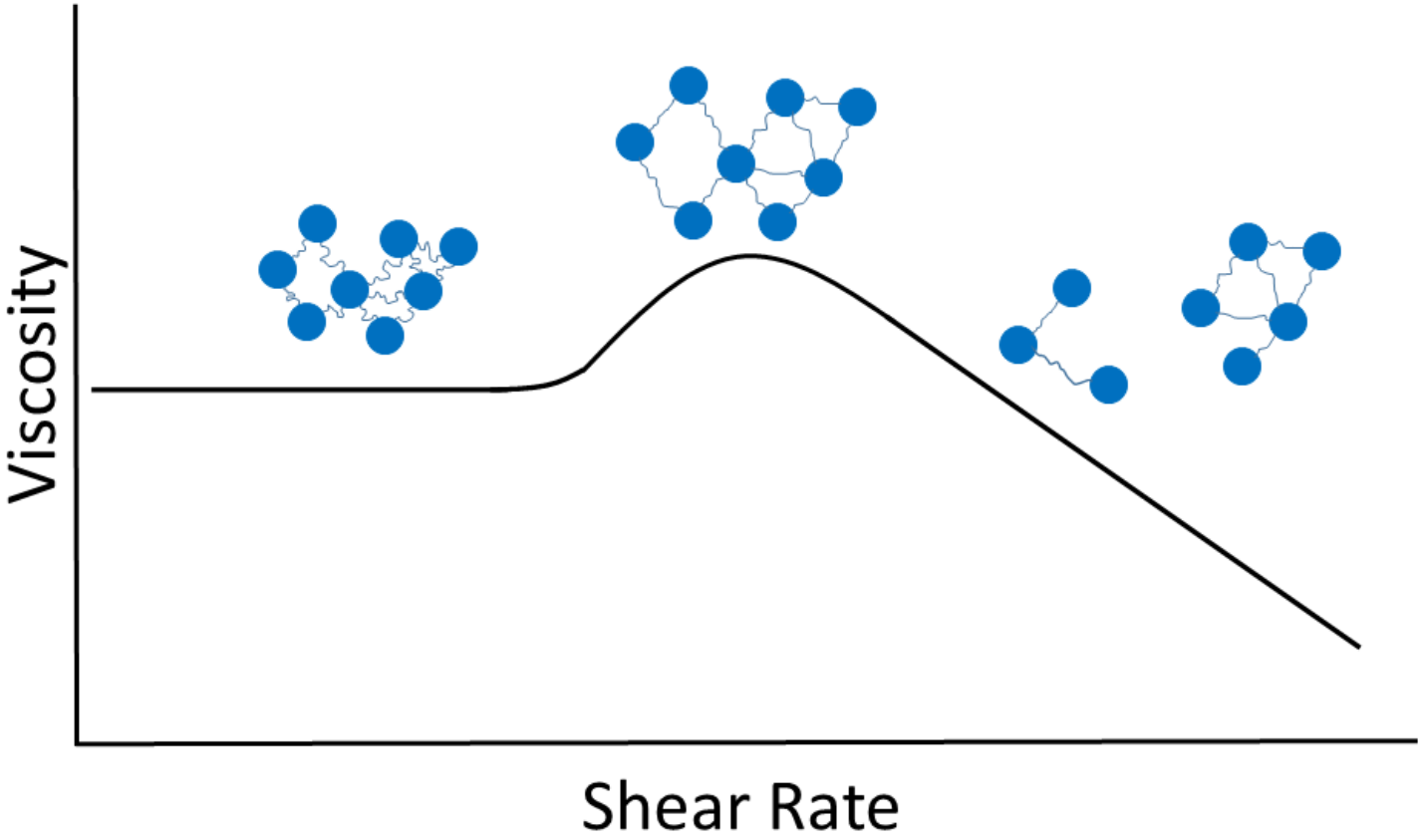


Flow Sweep Overlay:

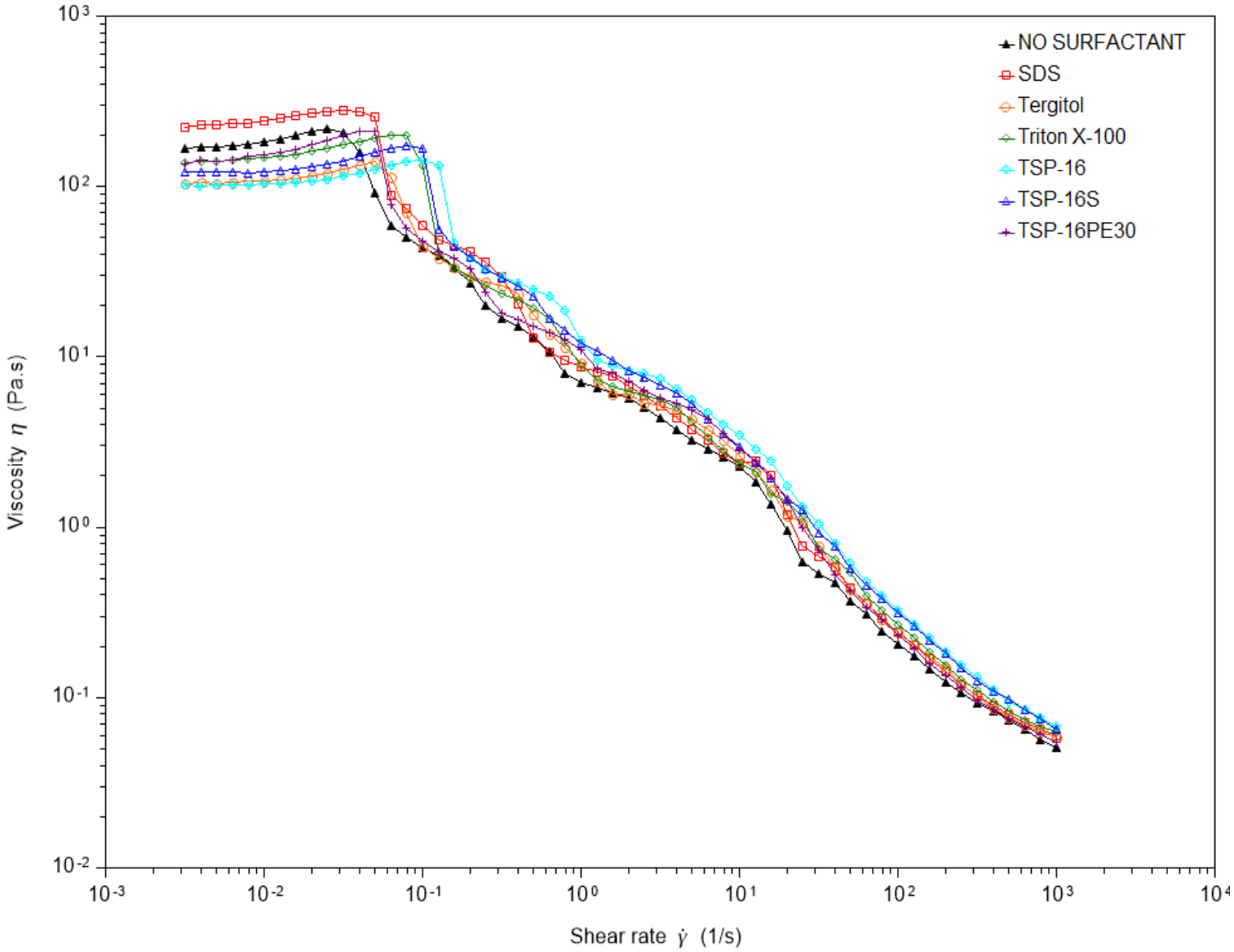
- BA/STY Latex at 25 vol. %
- EO795 thickener at 0.5 wt%
- **Surfactant at 0.1 wt. %**



Shear-Thickening Model



Horigome, *Langmuir*, 18, 1968 (2002)
Santos, *Journal of Coatings Technology and Research*, 14, 57 (2017)



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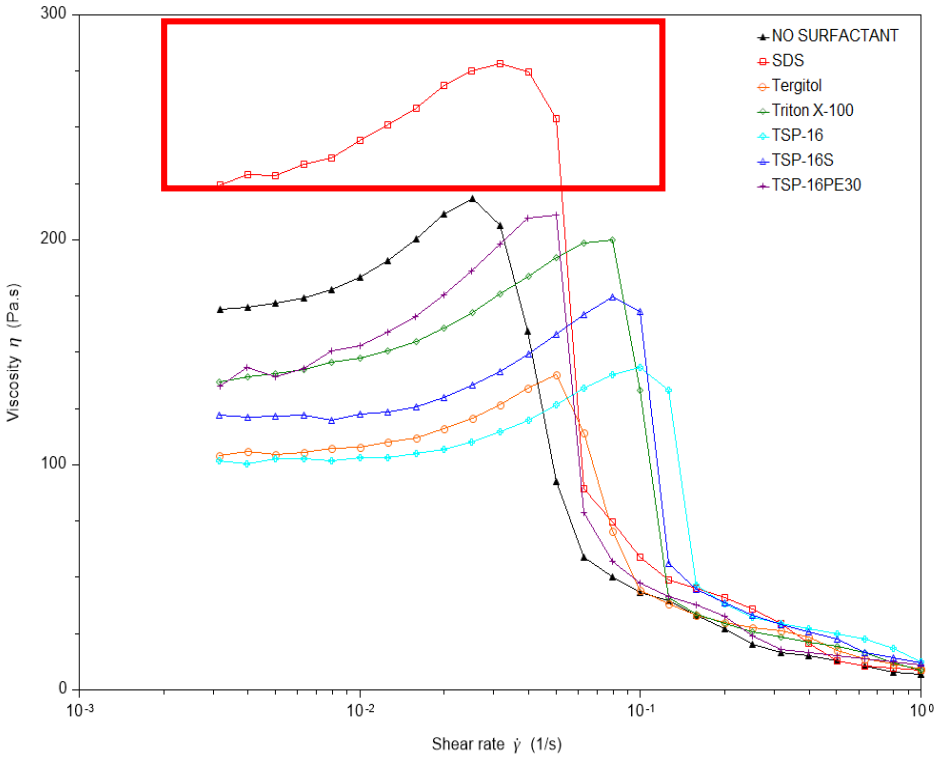


SDS-PEG Complexation

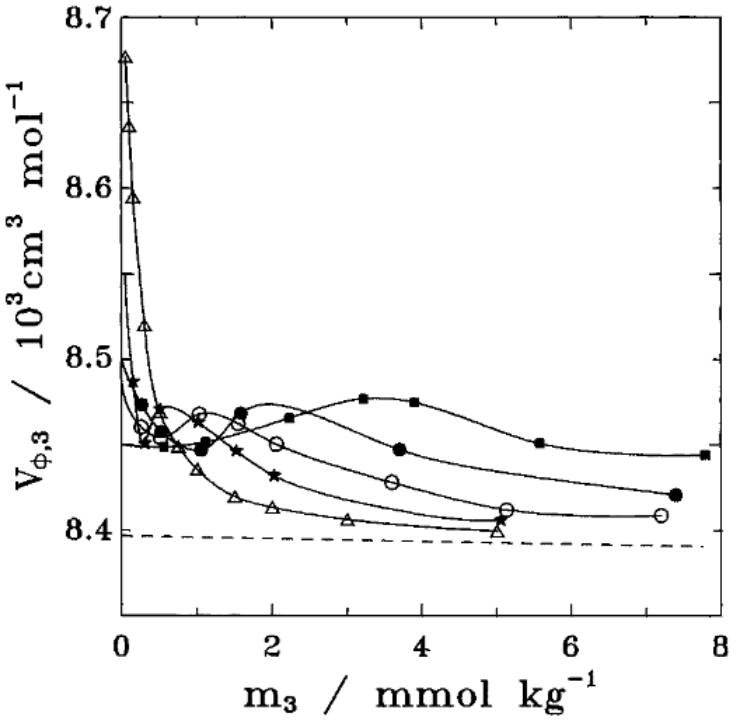


Figure 1. Apparent molar volumes of PEG 10000, $V_{\phi,3}$, versus its molality (m_3) at different concentrations of SDS (m_2): △, 0.01; ★, 0.05; ○, 0.1; ●, 0.2; ■, 0.4; dotted line, pure water.

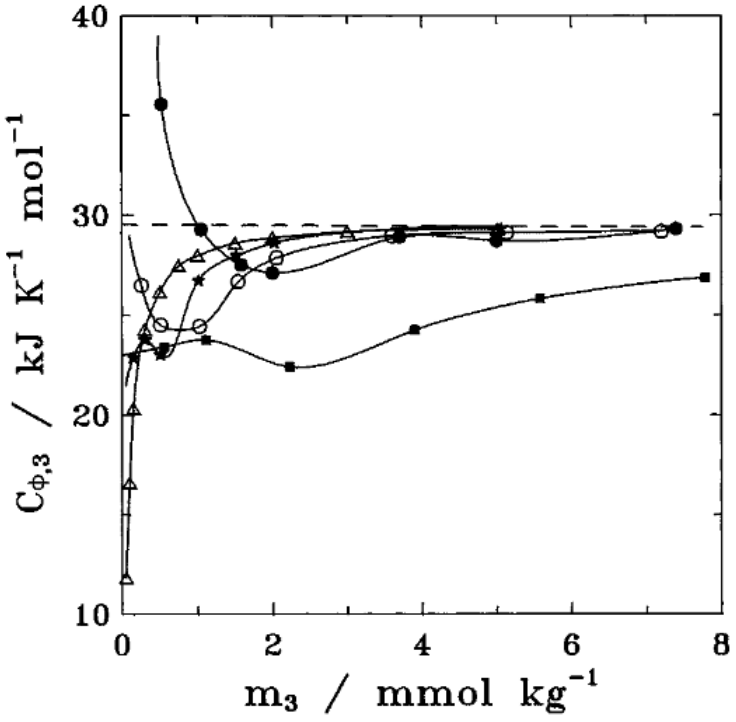
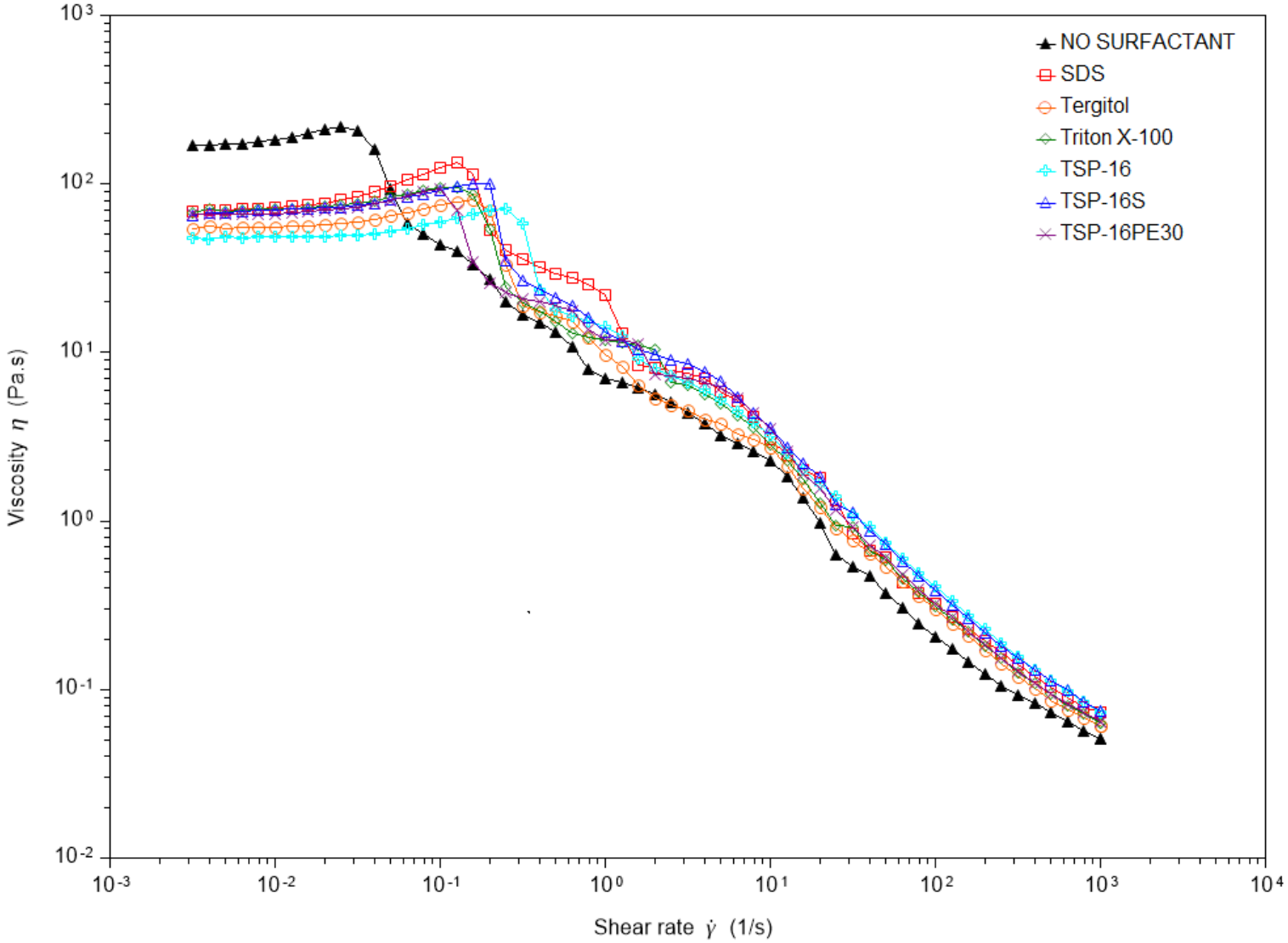


Figure 2. Apparent molar heat capacities of PEG 10000, $C_{\phi,3}$, versus its molality (m_3) at different concentrations of SDS (m_2): △, 0.01; ★, 0.05; ○, 0.1; ●, 0.2; ■, 0.4; dotted line, pure water.

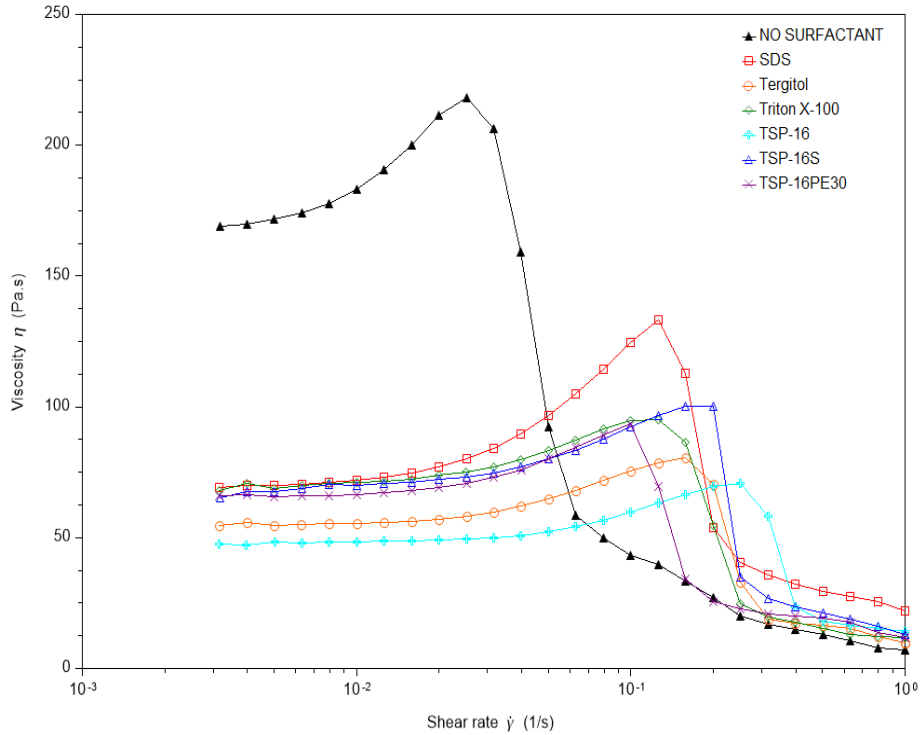
- SDS was found to complex with poly(ethylene glycol) at a ratio of PEG:SDS of approximately 2.3:1.0 as was determined by apparent molar volume and molar heat capacity experiments

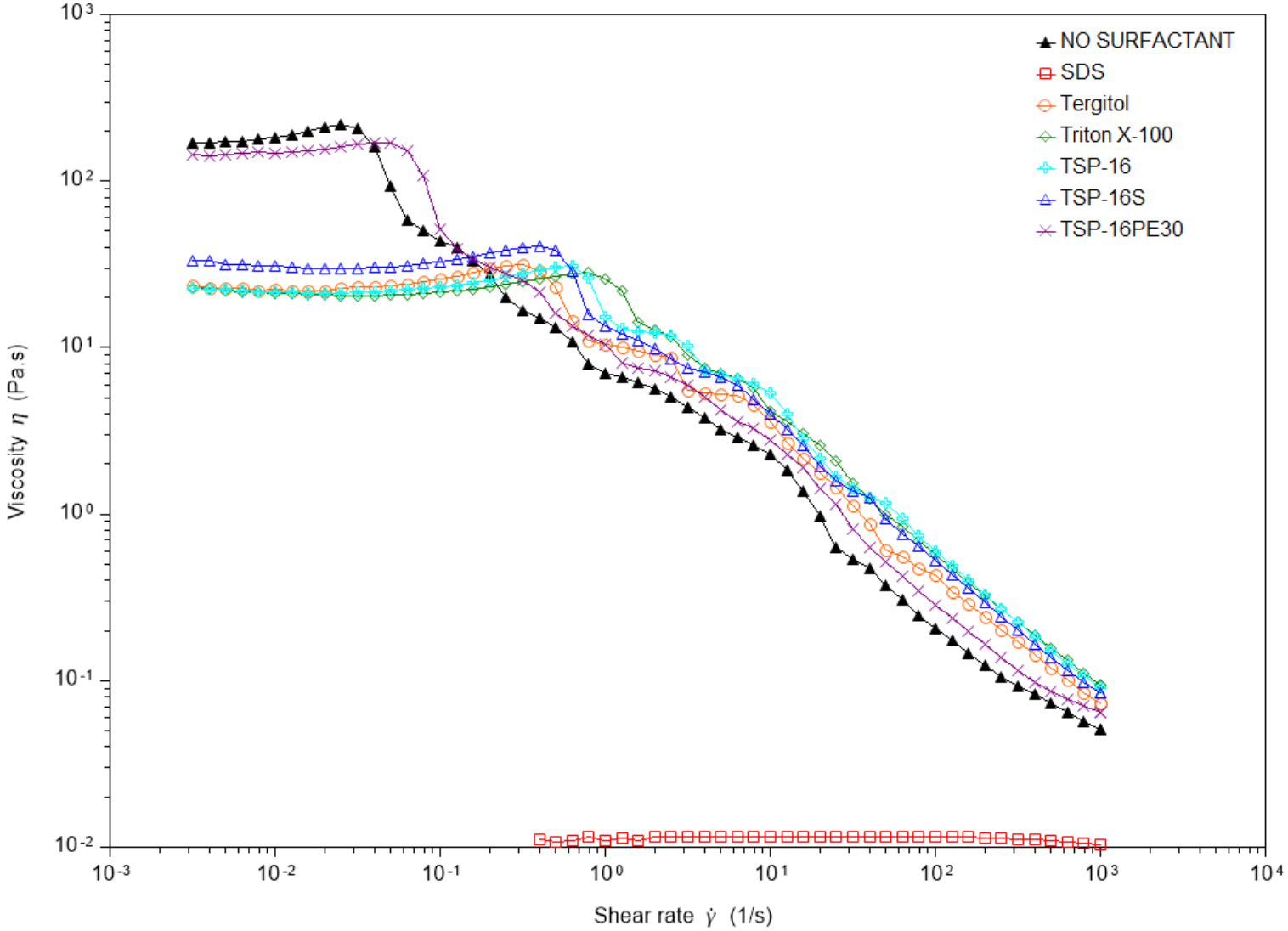
Ballerat-Busserolles, *Langmuir*, 13, pages 1946-1951, 1997.



Flow Sweep Overlay:

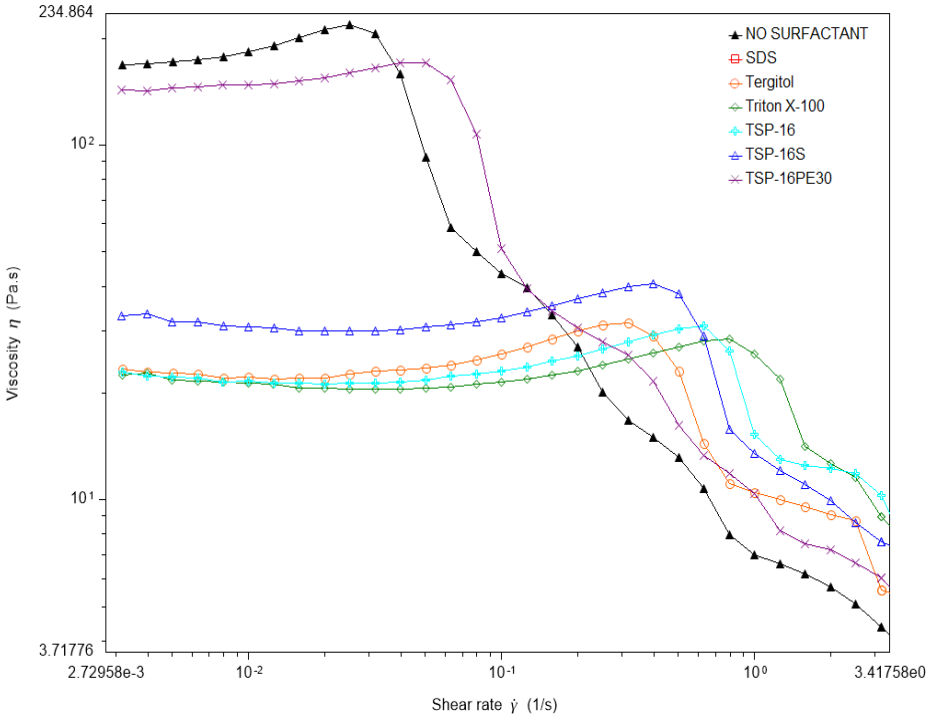
- BA/STY Latex at 25 vol. %
- EO795 thickener at 0.5 wt%
- **Surfactant at 0.25 wt. %**

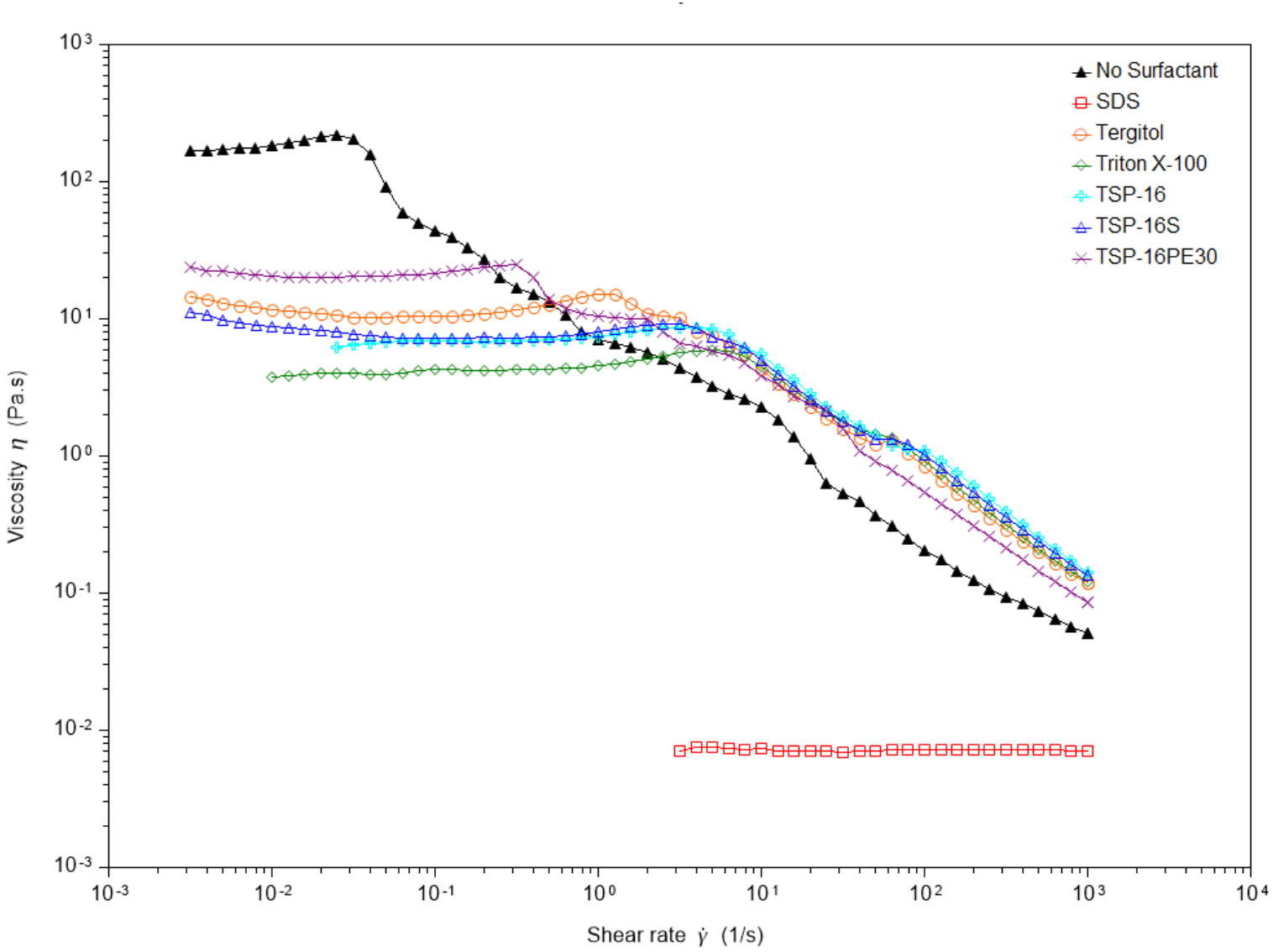




Flow Sweep Overlay:

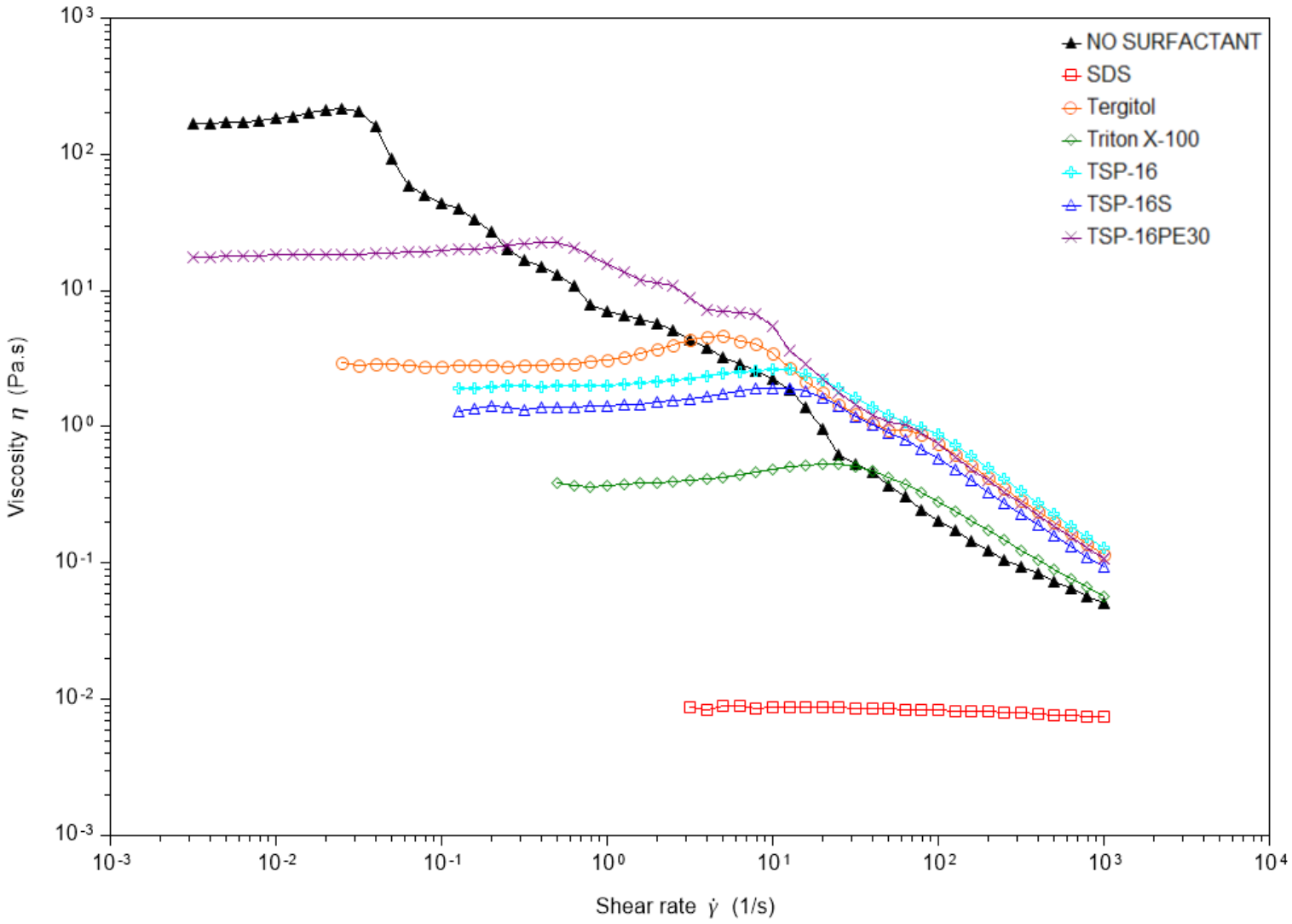
- BA/STY Latex at 25 vol. %
- EO795 thickener at 0.5 wt%
- **Surfactant at 0.50 wt. %**





Flow Sweep Overlay:

- BA/STY Latex at 25 vol. %
- EO795 thickener at 0.5 wt%
- **Surfactant at 0.75 wt. %**

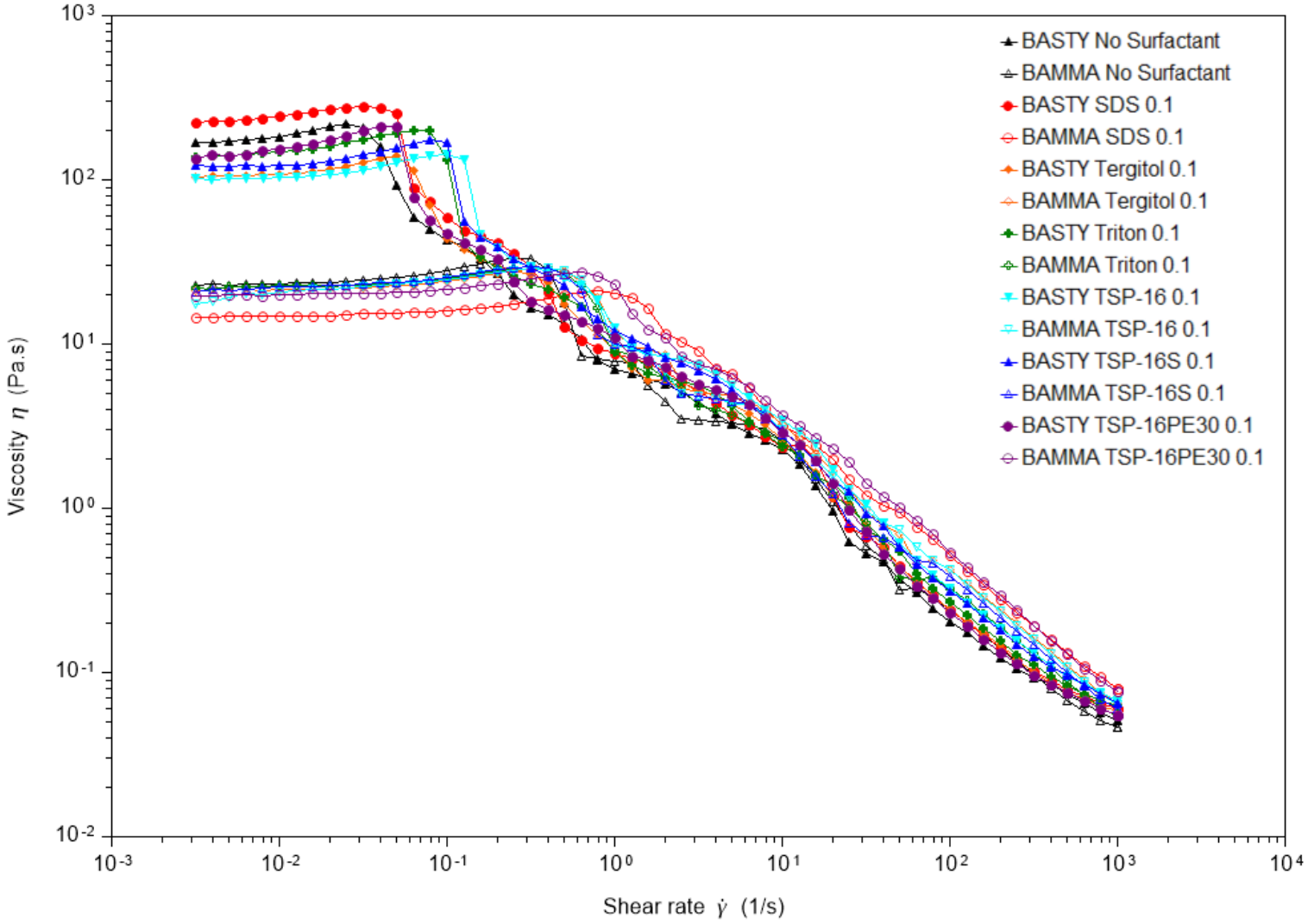


Flow Sweep Overlay:

- BA/STY Latex at 25 vol. %
- EO795 thickener at 0.5 wt%
- **Surfactant at 1.0 wt. %**

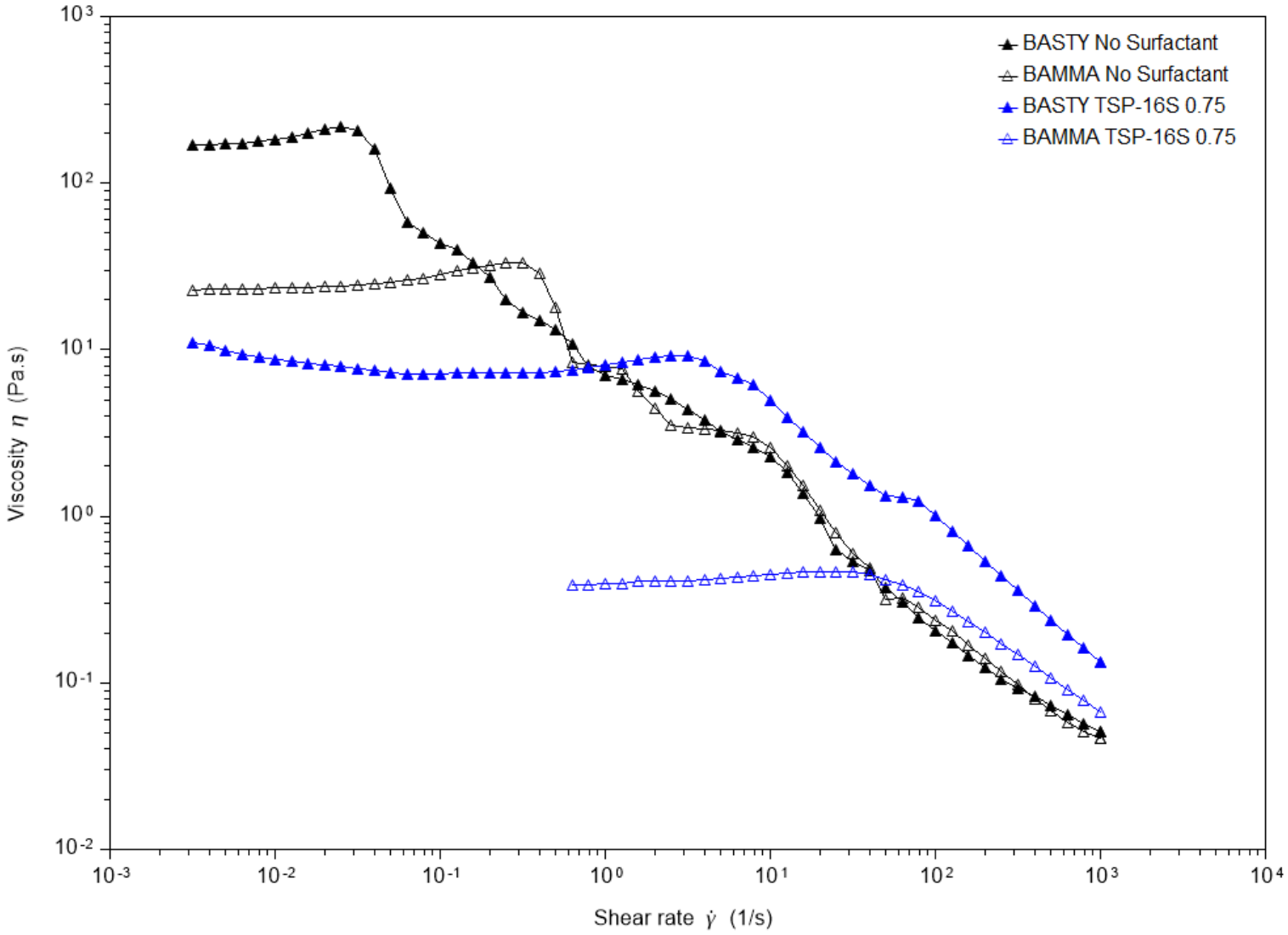
BA/STY and BA/MMA Comparison

- Key Things:
  - BA/STY is hydrophobic
  - BA/MMA is hydrophyllic
  - The HEUR associative ends are hydrophobic
  - Surfactants have hydrophobic tails and hydrophyllic heads
    - High mobility
    - Small size



Flow Sweep Comparison:

- Latex at 25 vol. %
- EO795 thickener at 0.5 wt%
- **TSP-16S at 0.10 wt. %**



Flow Sweep Comparison:

- Latex at 25 vol. %
- EO795 thickener at 0.5 wt%
- **TSP-16S at 0.75 wt. %**

Summary

- Surfactants play a major role in these systems:
  - Increases in surfactant concentration led to more surfactant molecules occupying surface area of the latex particles
    - Surfactants interfered through competitive association
    - Total number of transient bridges that would be associated at any given time decreased, decreasing viscosity
  - All tested surfactants more readily associated with the BA/MMA latex compared to the BA/STY, decreasing viscosity in all regimes
  - Sufficient surfactant concentrations can completely disrupt the associative thickener mechanism in either of the latex systems studied

Further Work

- Observation of surfactant effects in fully formulated paint systems
  - Relating this fundamental work to effects seen in more complex systems
- Probing with Diffusing Wave Spectroscopy (X-Ray Laser)
  - Micro-Rheology, Brownian Motion, Particle Sizing, Time-Dependent Phenomena
- Thixotropy testing (Moduli vs. Time and Stress vs. Shear Rate)
  - The shearing of microstructures to determine how the networks rebuild in absence of stress

Acknowledgements

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- Kenneth N. Edwards Western Coatings Technology Center
- Dow Chemical Company
    - Dr. Gary W. Dombrowski – Senior Research Scientist
    - Dr. John J. Rabasco – Principal Research Scientist
    - Dr. Patrick E. Hartnett – Senior Scientist
- Dr. Raymond H. Fernando
- Fellow Team Members
    - Travis Smith – University of Akron, PhD Program
    - David Chisholm – MS Internship at Behr
    - Abby Cheng – New BS+MS Candidate