Rheological-based approach to gel curve analysis of alcohol ethoxylates

2022 AOCS Annual Meeting & Expo

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May 3, 2022

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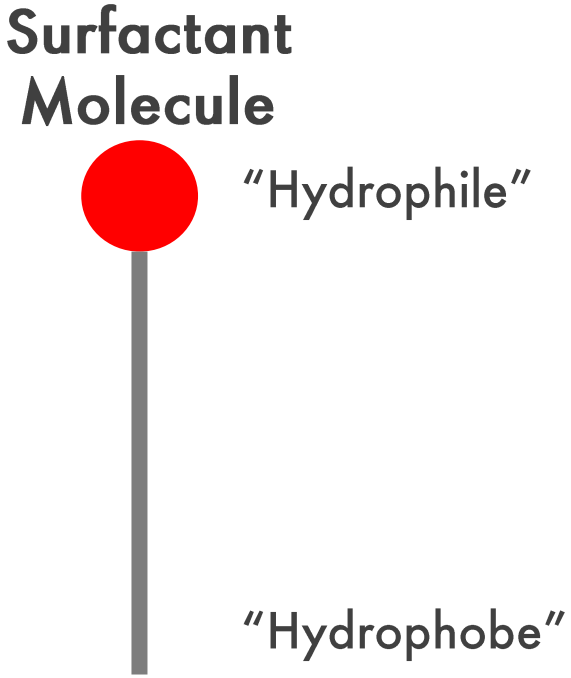
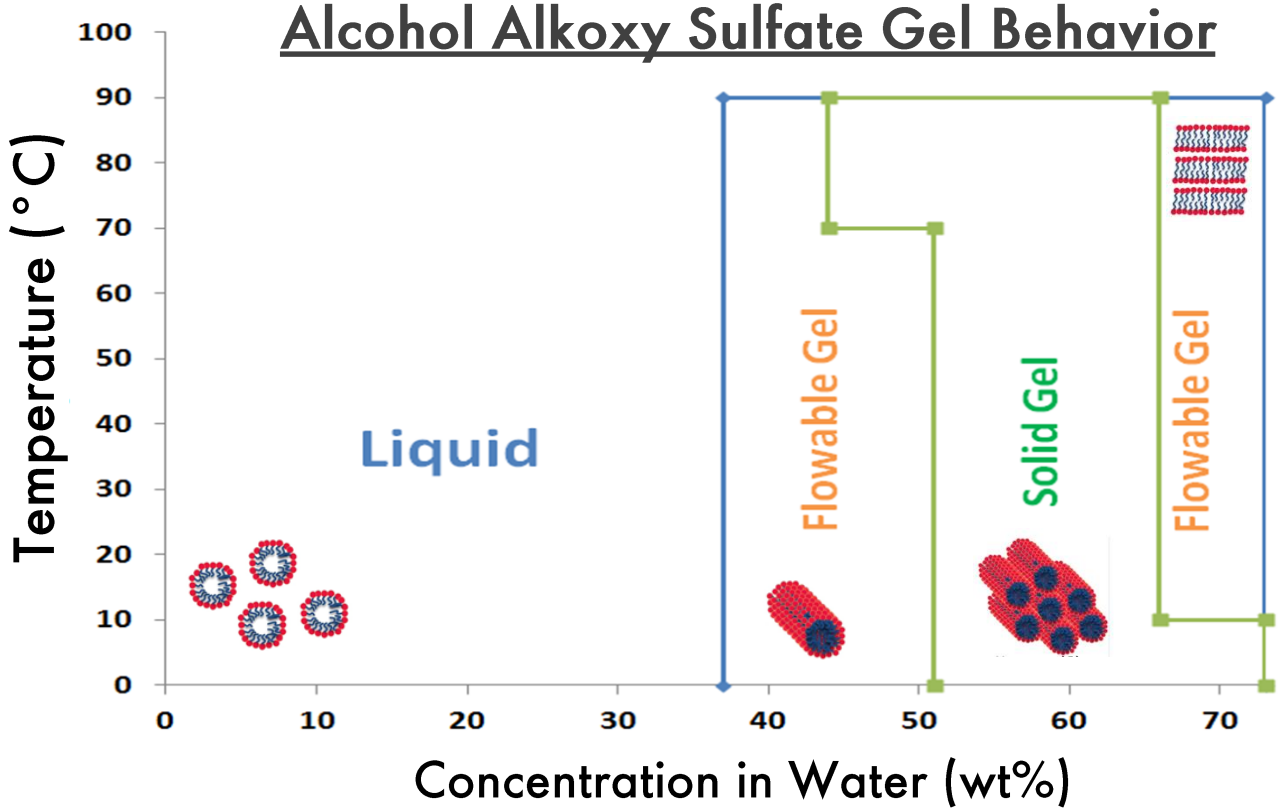
Outline

- Background on Gels
  - Why do gels matter?
- Visual-based (former) method
- Rheology-based (new) method
- Alcohol Ethoxylate gel results
  - Comparison to visual-based results
  - Structure-Property relationship (carbon and EO numbers)
- Summary and Future Work

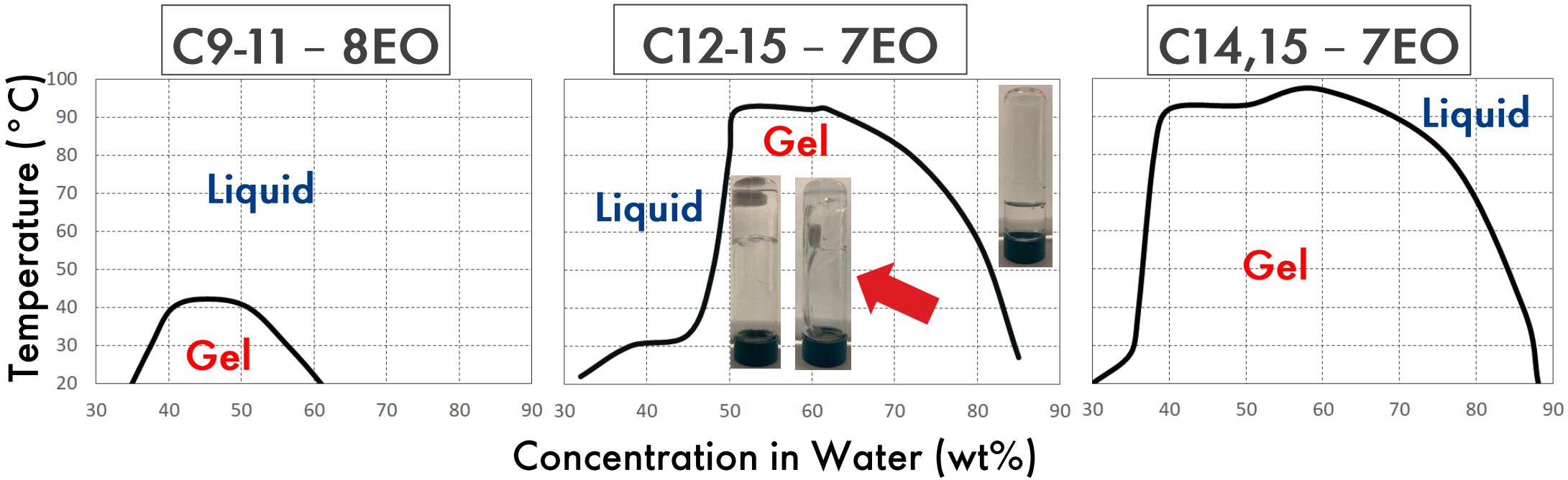
Gel formation

- Undesirable, viscous gels (**microstructures**) may quickly form on dilution of concentrated surfactants
  - Depends on concentration and temperature
  - Not all gels are equal (in viscosity)



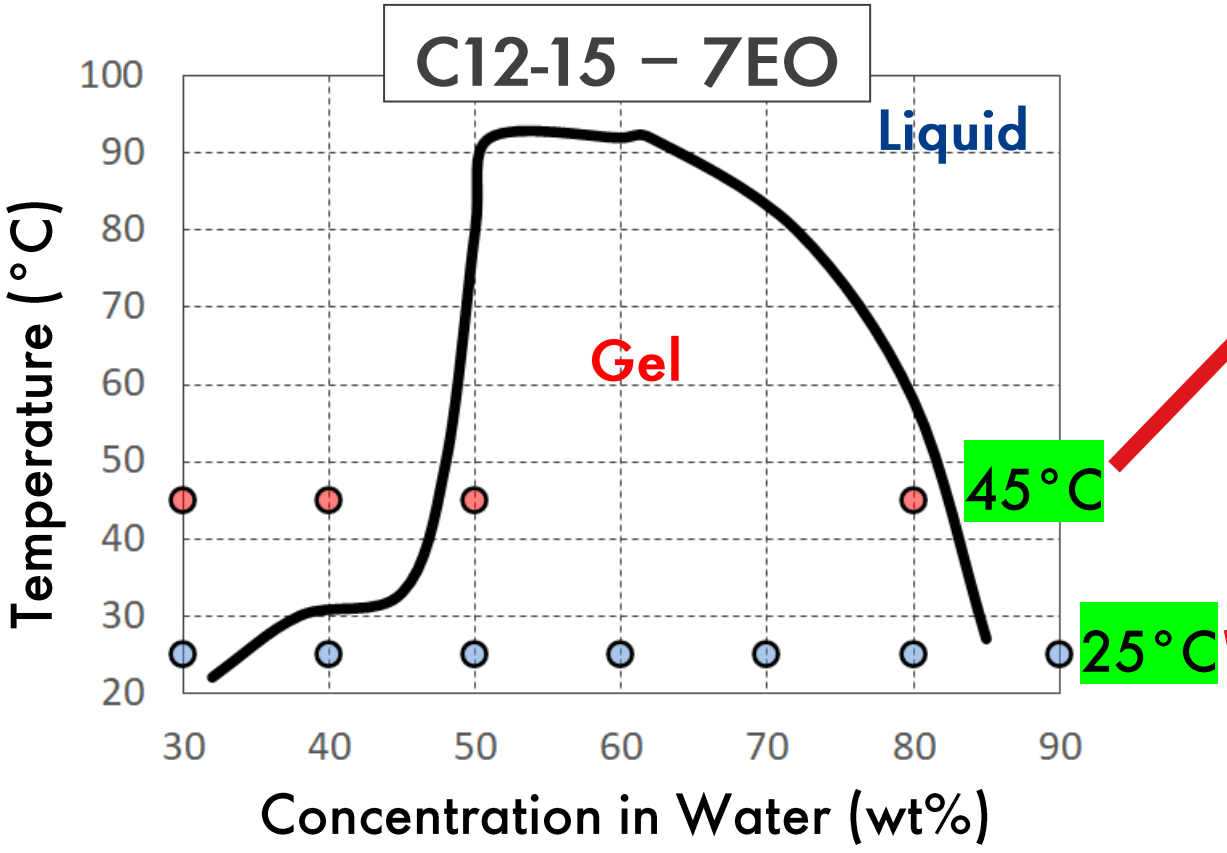


Gel behavior of Alcohol Ethoxylate surfactants



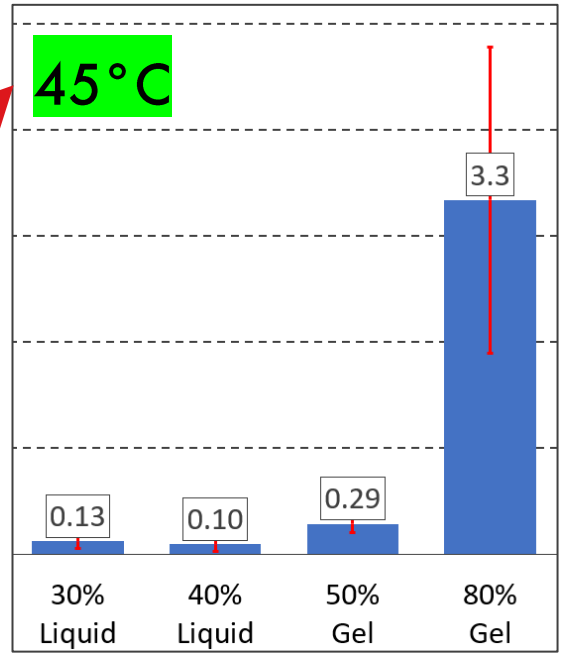
- Why is understanding gel behavior important?
  - **Large scale**: Influences process handleability
  - **Dilution of compact liquids**: Trend to reduce water content
  - **Performance**: Long dissolution time is undesirable

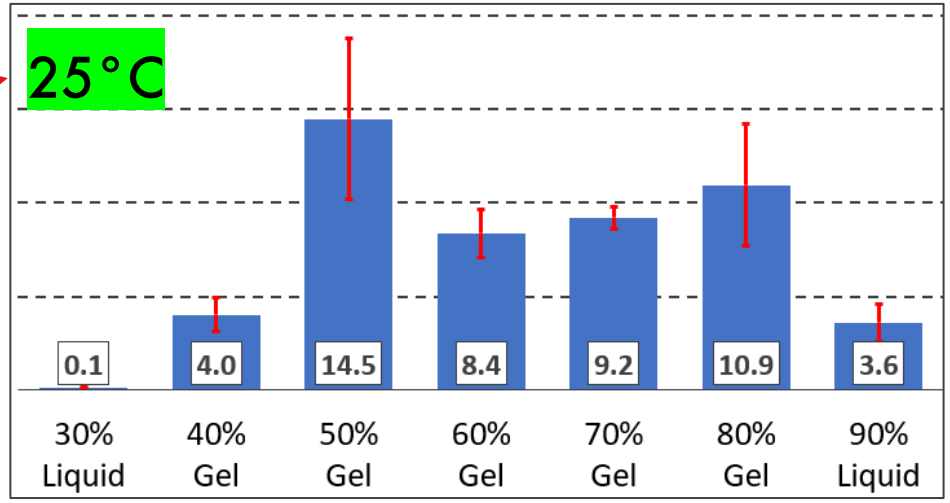
Gels increase dissolution (dissolving) time



Dissolution Time (min)

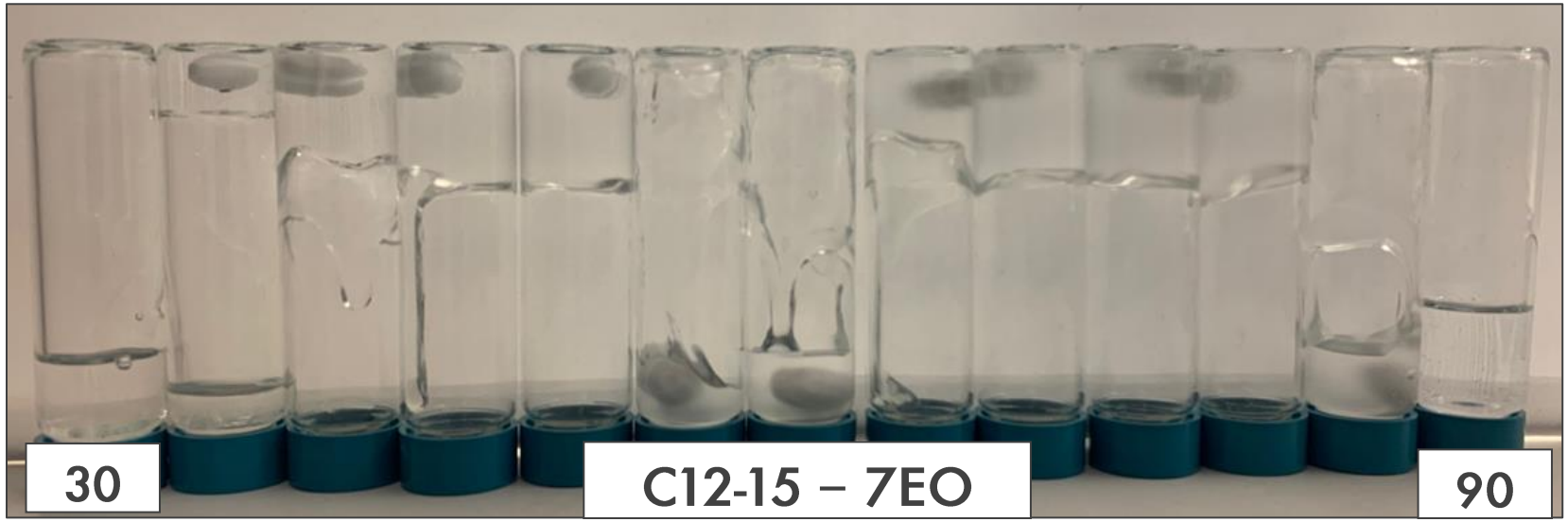
Error bars represent 95% CI

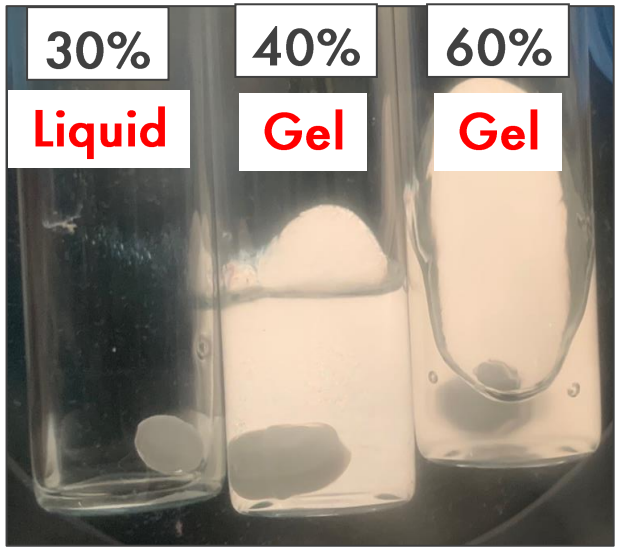




(Former) visual-based gel methodology

- This judges a) appearance under natural and polarized light, and b) flow behavior at different temperatures
  - Very subjective (operator-dependent) and time consuming

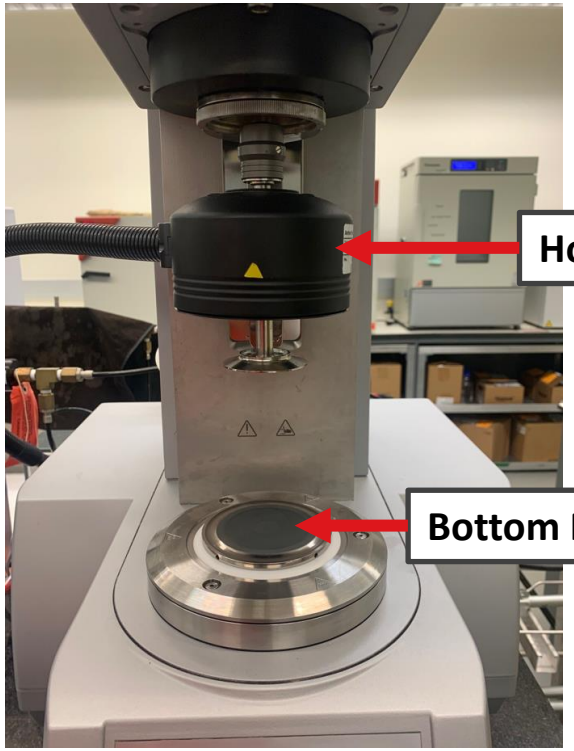


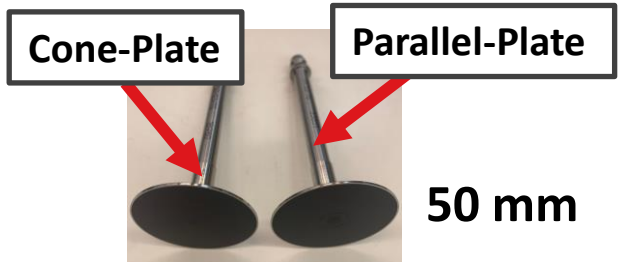


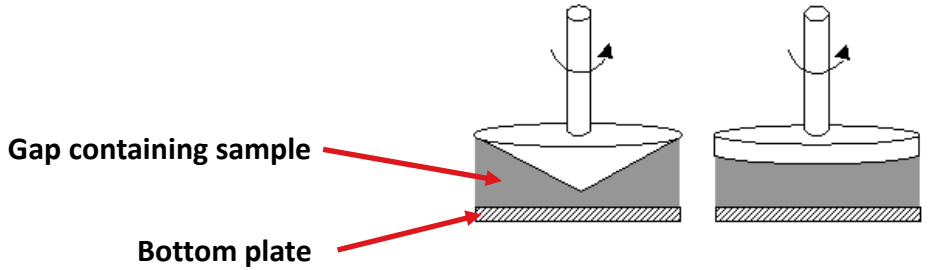
- (New) approach to reduce subjectivity and increase speed
  - Use rheological properties for gel characterization

(New) rheometry-based gel methodology

- Since gels are micro-structures, they exhibit viscous and elastic behavior ("viscoelastic")
- On a rheometer, an oscillatory sweep is used to infer how strong the microstructure in response to stress
  - Keeping microstructure intact
  - Very accurate temperature control
  - Automated

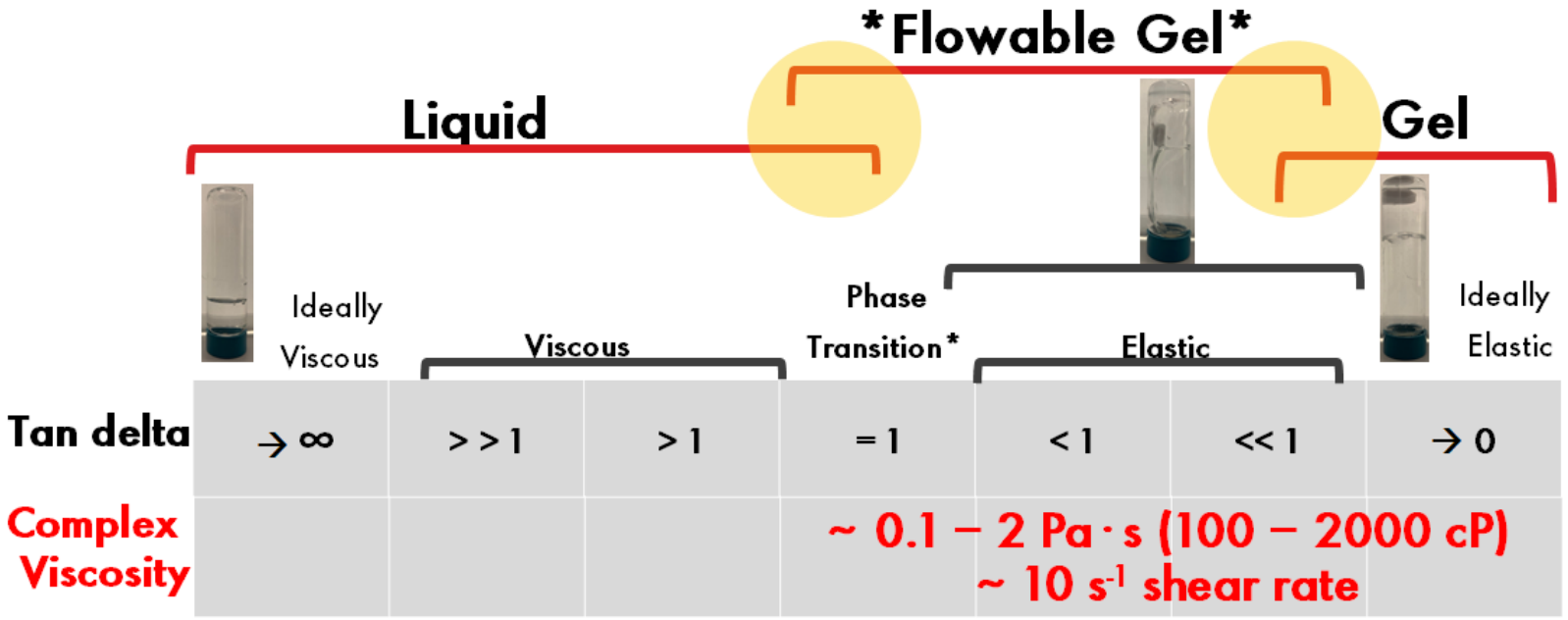






Rheological Gel Characterization

- Perturbation of microstructure:
  - Viscous (liquid) response is the loss modulus (G'') and elastic response is the storage modulus (G')
  - Ratio G''/G' is known as tan delta (damping factor) and can help with gel identification
- Complex viscosity provides insight on viscosity direction (oscillatory frequency is equivalent to shear rate)



Reference: Mezger, T.G., Applied Rheology. 2015: Anton Paar GmbH. PP. 98-100 (ISBN: 978-3-9504016-0-8)

Gel maps

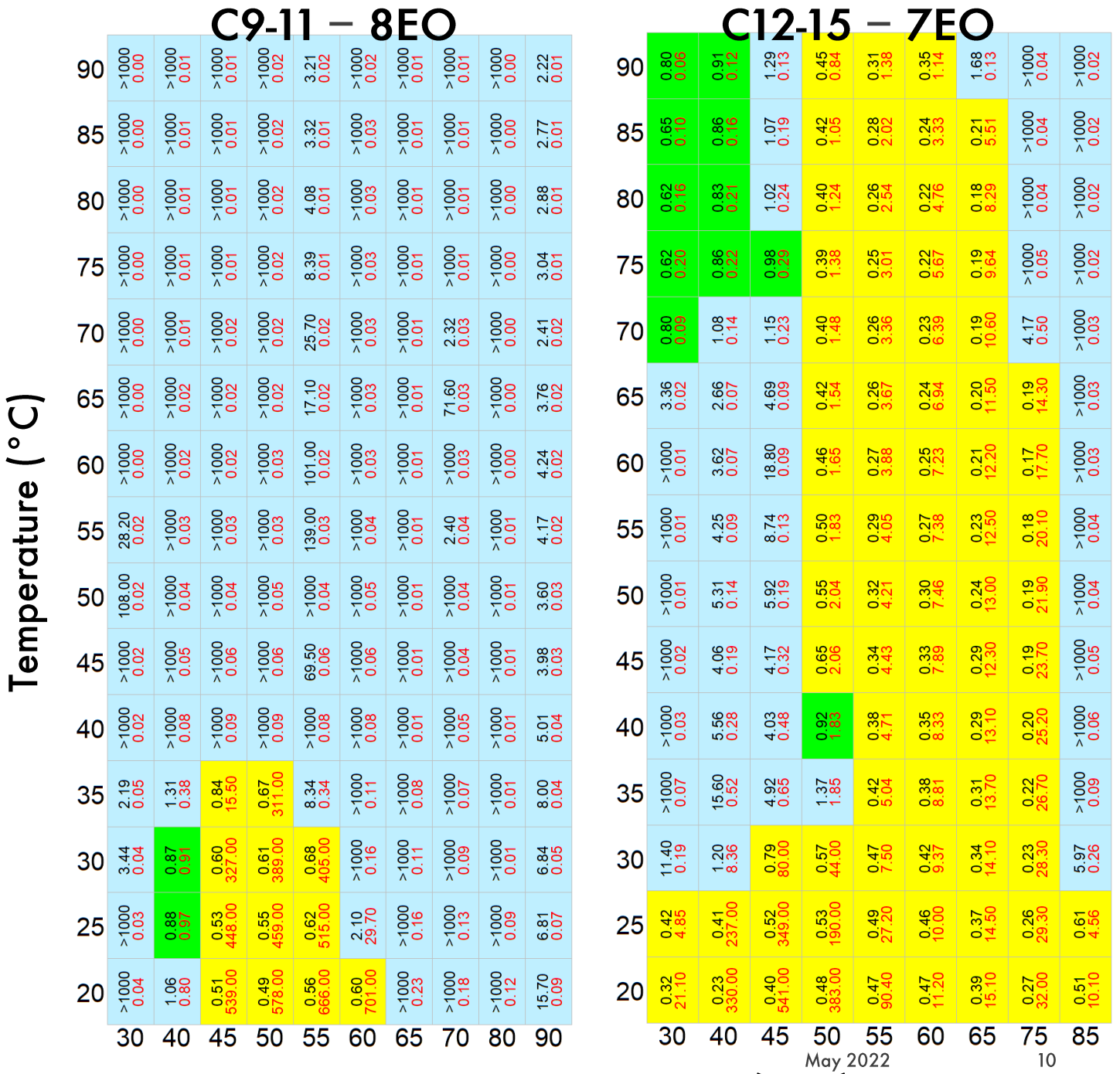
- Different categories of flowable gels
- Gel curves are generated

Tan Delta

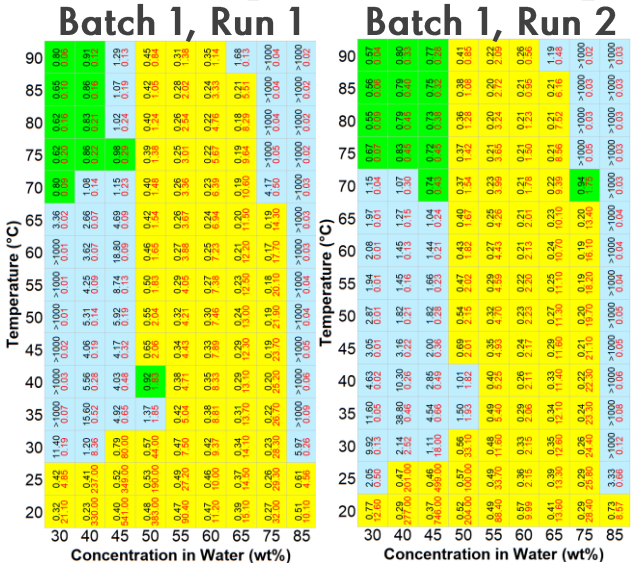
Complex Viscosity (Pa · s)

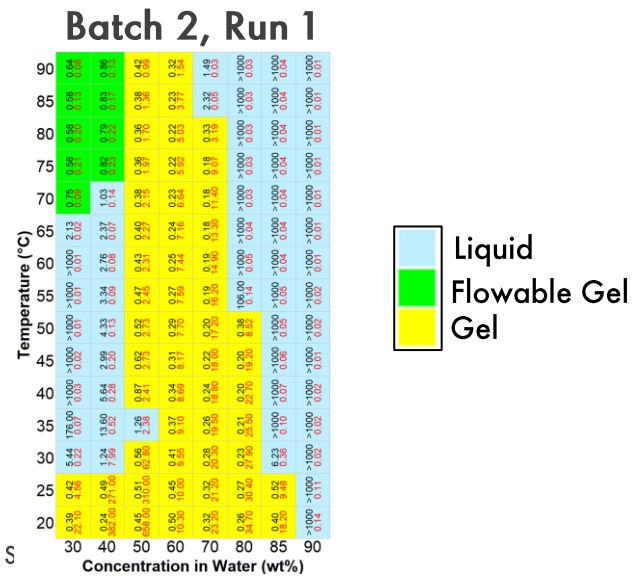
mPa · s = cP = 1000 x Pa · s

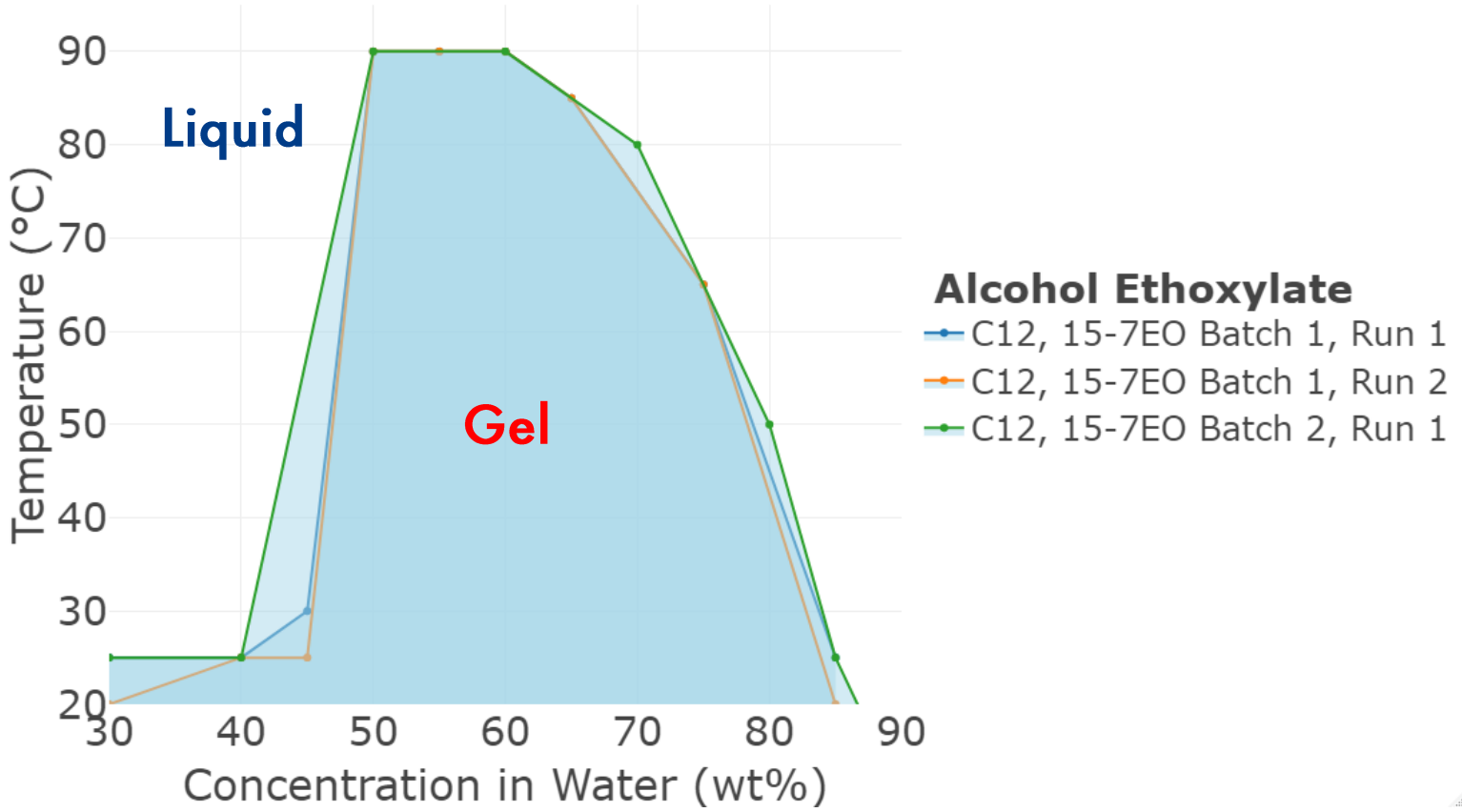
Liquid
Flowable Gel
Gel



Excellent repeatability with C12-15 – 7EO



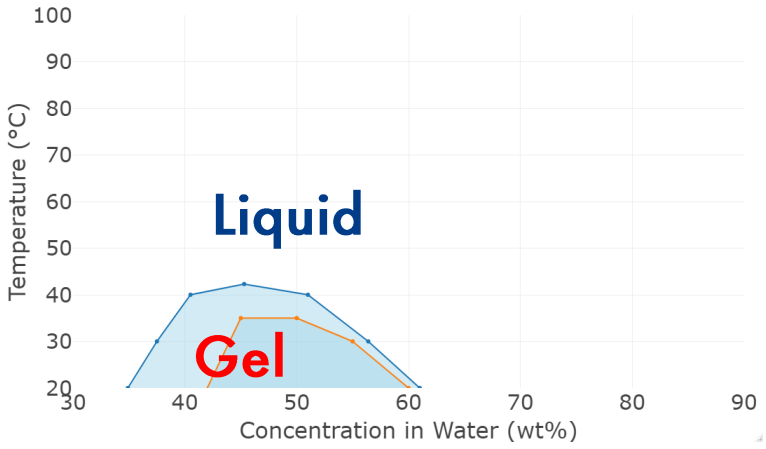




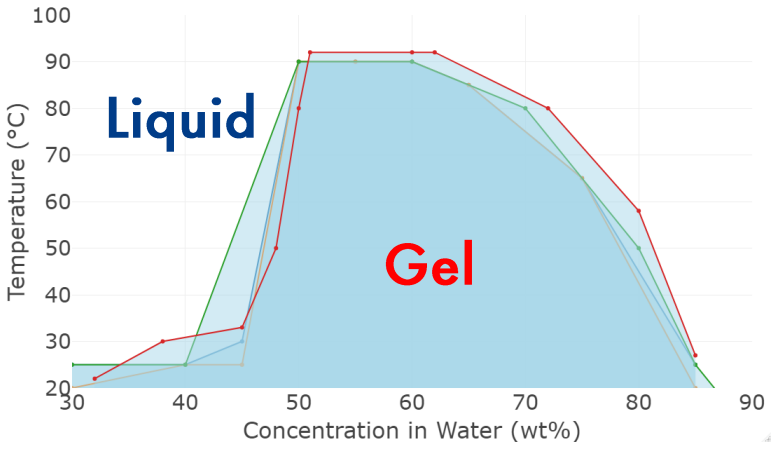
Former vs. New gel curve comparison

- How do the rheology-based gel curves compare to the former gel curves?

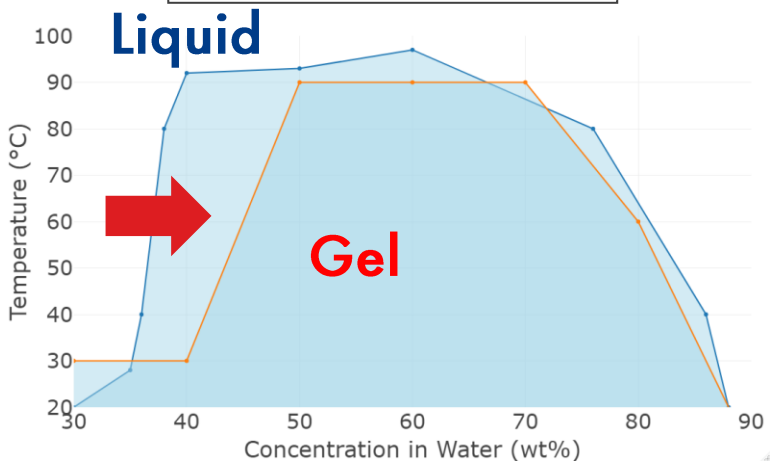
C9-11 – 8EO



C12-15 – 7EO



C14,15 – 7EO



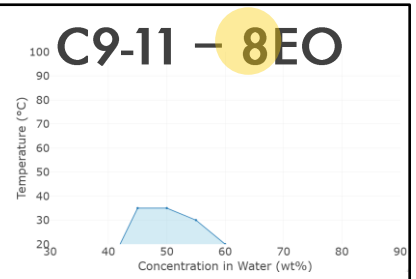
New method: Alcohol ethoxylates Structure-Property Relationship

Average Carbon Number →

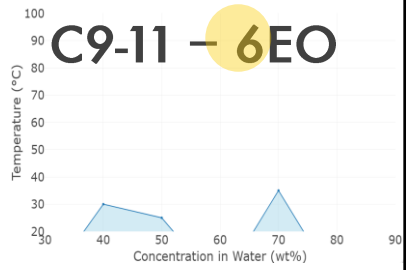
EO Number ↑

10.2

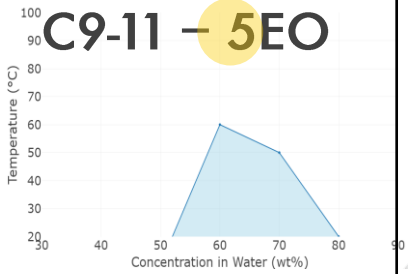
C9-11 – 8EO



C9-11 – 6EO

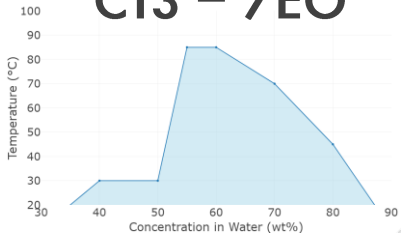


C9-11 – 5EO



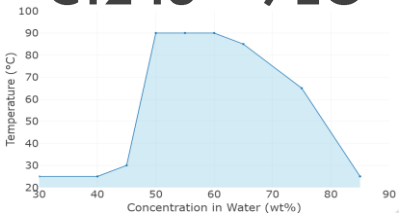
13.0

C13 – 7EO

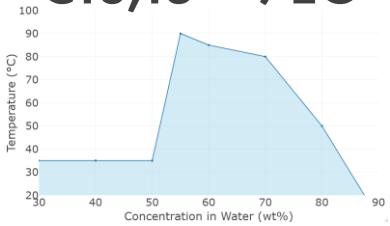


13.6

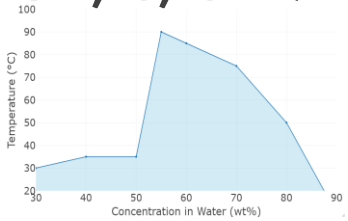
C12-15 – 7EO



C13,15 – 7EO

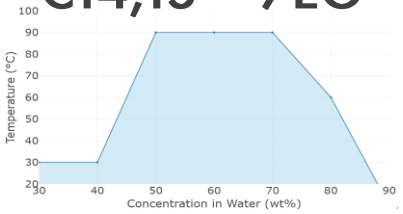


C11,13,15 – 7EO



14.5

C14,15 – 7EO



Summary

- Rheometry-based gel identification method is:
  - Fast
  - Comparable to our (former) visual-based method
  - Not subjective, gives numbers
- Allows linkage of structure to gel formation

Future Work

- Expand the method to other Alcohol Ethoxylate grades
- Application to Alcohol Ethoxy Sulfates

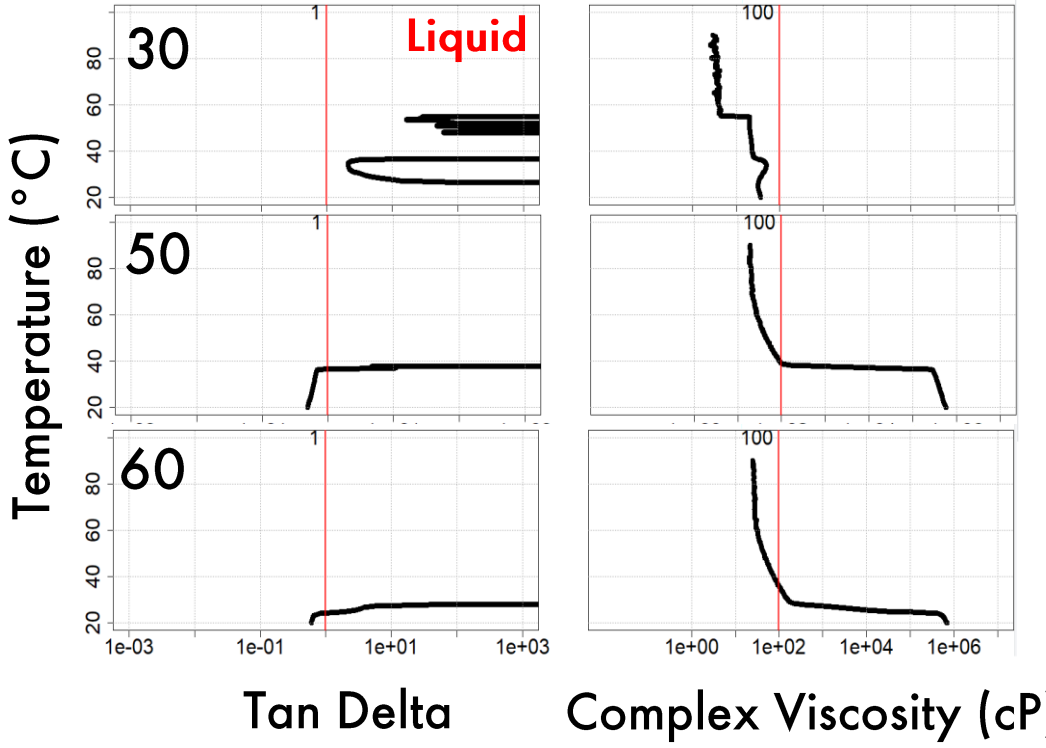
Thank You Audience, Organizers, and Shell!

Presentation Backup Slides

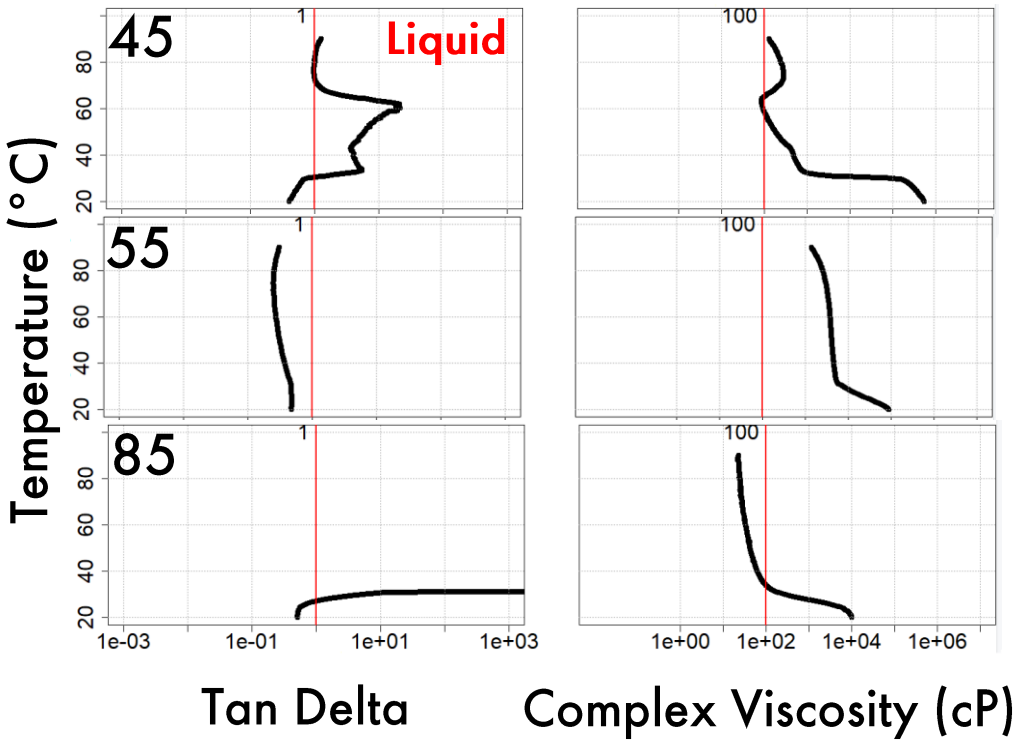
Oscillatory Testing at Each Concentration

- Tan delta and complex viscosity measurements were performed at various concentrations (30 to 90 wt%) while temperature was ramped to 90°C

C9, 11-8EO Concentration (wt%)



C12, 15-7EO Concentration (wt%)



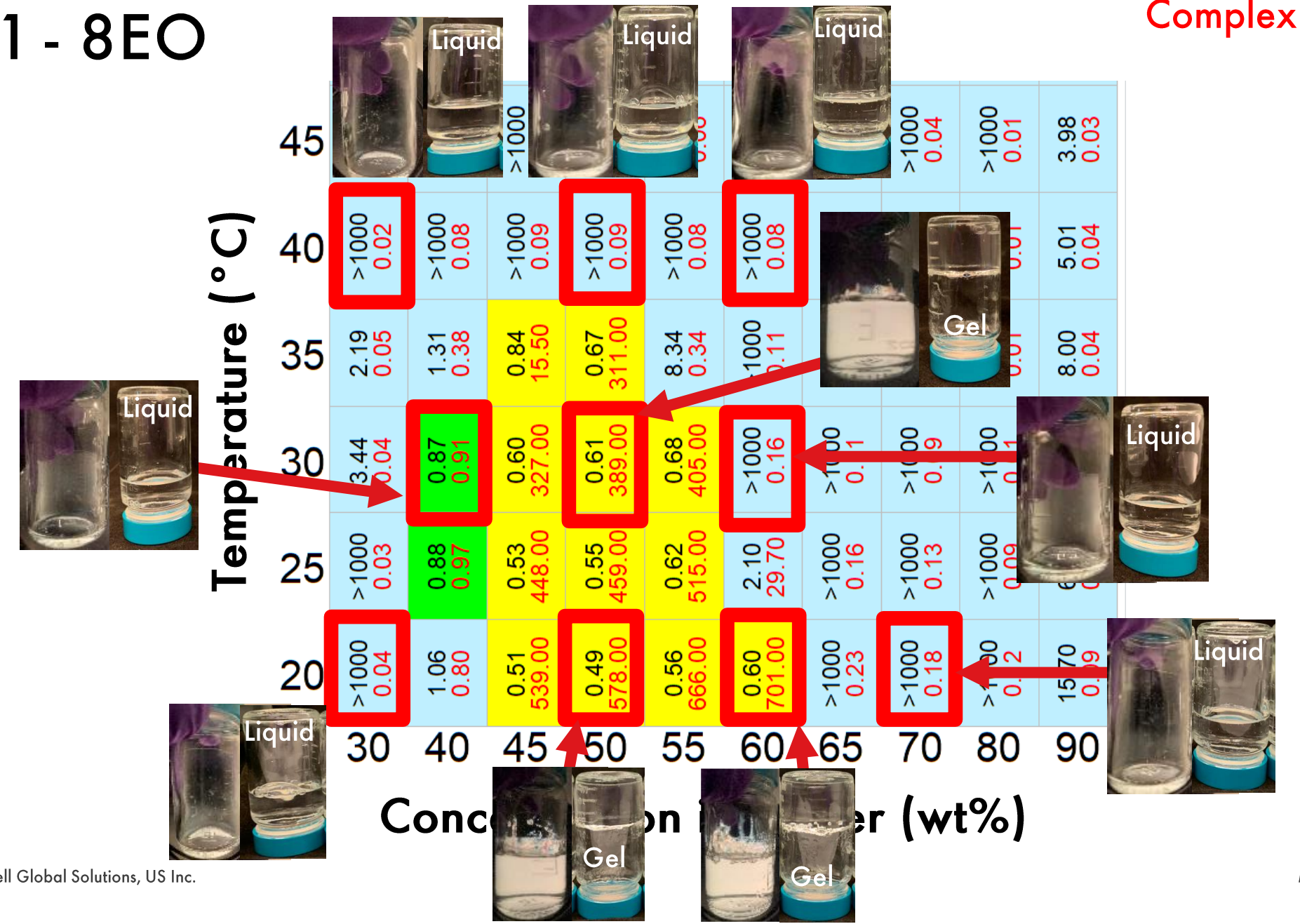
- Measurements were combined to generate a gel map using earlier classification ranges via conditionals

Gel Map Comparison to Visual-Based Observation

Tan Delta

Complex Viscosity (Pa · s)

C9-11 - 8EO



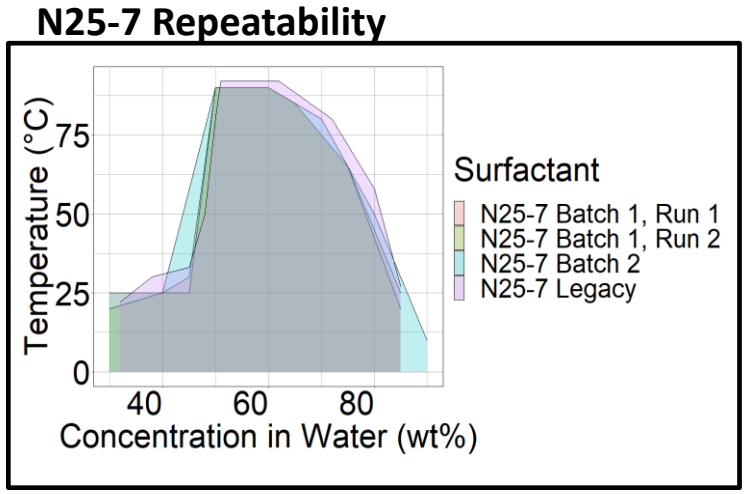
Solution Time Data to Date

- 25°C (full slice)

30% 40% 50% 60% 70% 80% 90%

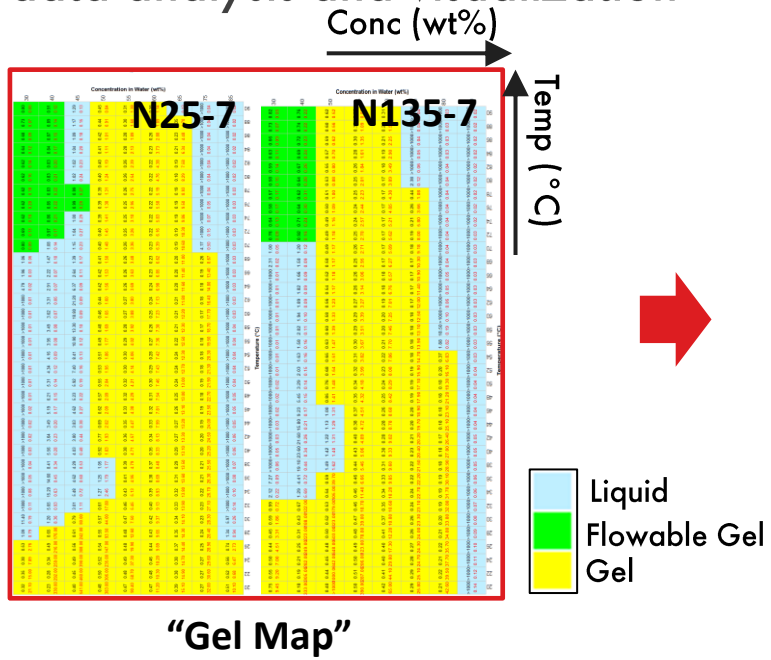
New Gel Curve Methodology Background

- Motivation
  - Effort to both reduce subjective nature and effort of existing methodology
    - Objective-based and faster turnaround (from days to hours)
  - Embrace digitization
    - Rheological properties used entirely for gel characterization
    - R statistical programming language for data analysis and visualization

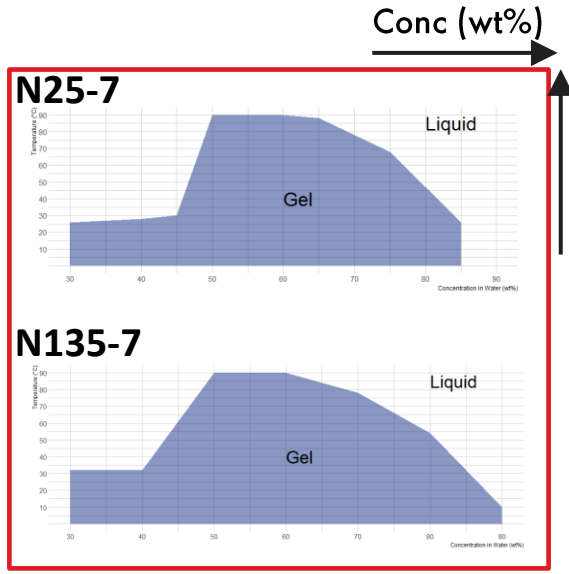


Rheometer

Data Analysis



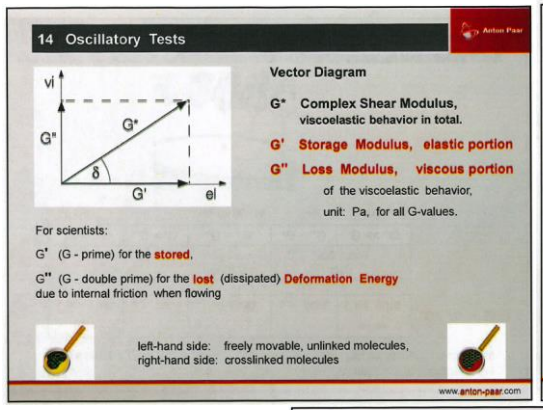
"Gel Map"

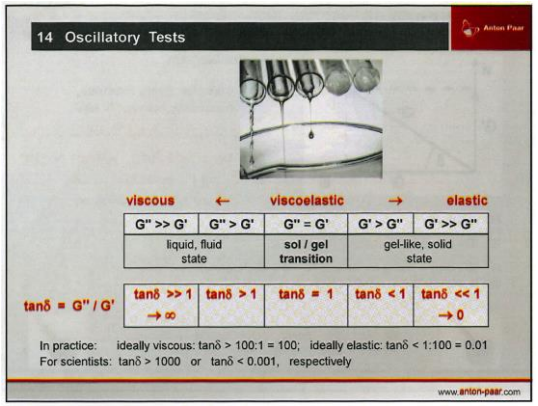


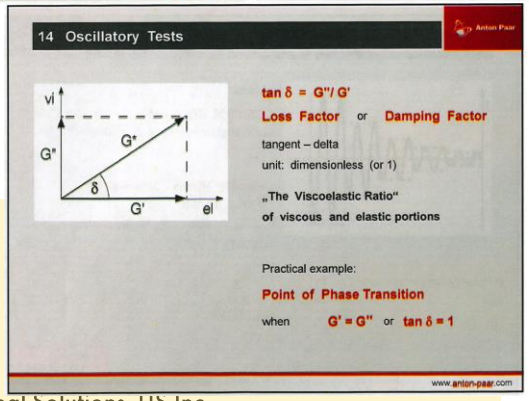
Gel Curve

Guidance for Gel Identification via Oscillatory Testing

- Methodology follows published information from Anton-Paar
  - **Book:** Mezger, T.G., Applied Rheology: With Joe Flow on Rheology Road. 2015: Anton Paar GmbH. PP. 98-100
  - **Various slide packs (training, seminars, etc.)** – Refer to image below left
  - Online: Basics of rheology :: Anton Paar Wiki (anton-paar.com) – Refer to image below right







Loss factor or damping factor: tan δ = G"/ G'

(tangent delta), unit: dimensionless or 1. This factor describes the ratio of the two portions of the viscoelastic behavior. The following applies (see also the vector diagram in Figure 9.10):

1. For ideally elastic behavior δ = 0°. There is no viscous portion. Therefore, G" = 0 and with that tan δ = G"/ G' = 0.
2. For ideally viscous behavior δ = 90°. There is no elastic portion. Therefore, G' = 0 and thus the value of tan δ = G"/ G' approaches infinity because of the attempt to divide by zero.

In some diagrams, the loss factor tan δ is plotted in addition to the curves of G' and G", in particular if there is a phase transition in the sample. This is also called the sol/gel transition point or simply the gel point. It means that the character of the sample has changed during the measurement from the liquid or sol state to the solid or gel state and vice versa. Usually, for practical applications, a liquid is called ideally viscous if tan δ > 100:1 = 100, while a solid material is called ideally elastic if tan δ < 1:100 = 0.01

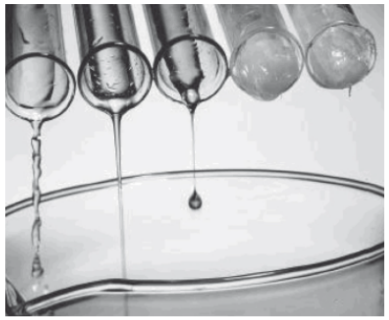


Figure 9.13: Demonstration of various kinds of behavior of water samples with increasing amounts of thickener, from the left: ideally viscous, viscoelastic liquid, sol/gel transition, viscoelastic solid or gel-like, and ideally elastic.

Amplitude sweeps generally aim at describing the deformation behavior of samples in the non-destructive deformation range and at determining the upper limit of this range (Figure 9.14). Often, it is also interesting to characterize behavior that occurs if this upper limit is exceeded with increasing deformation, when the inner structure gets softer, starts to flow, or breaks down in a brittle way.

Frequency sweeps generally serve the purpose of describing the time-dependent behavior of a sample in the non-destructive deformation range. High frequencies are used to simulate fast motion on short timescales, whereas low frequencies simulate slow motion on long timescales or at rest. In frequency sweeps (Figure 9.15), the oscillation frequency is increased or decreased step-wise from one measuring point to the next while keeping the amplitude constant.

Conditionals for Gel Identification

- Liquid:
  - Loss Factor >= 1

- Flowable Gel:
  - Loss Factor < 1 and Loss Factor >= 0.5 and Complex Viscosity <= 0.5 Pa · s (500 cP)
  - Loss Factor < 1 and Loss Factor >= 0.8 and Complex Viscosity <= 2 Pa · s (2000 cP)
  - Loss Factor < 1 and Loss Factor >= 0.2 and Complex Viscosity <= 0.1 Pa · s (100 cP)

- Gel:
  - Everything not categorized as Liquid or Flowable Gel

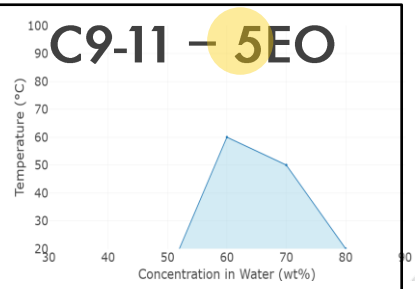
New method: Alcohol ethoxylates Structure-Property Relationship

Average Carbon Number →

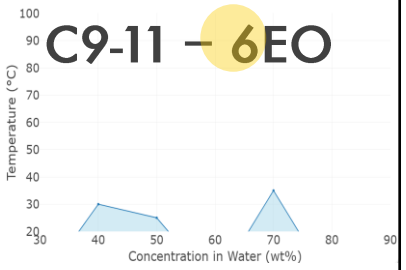
EO Number ↓

10.2

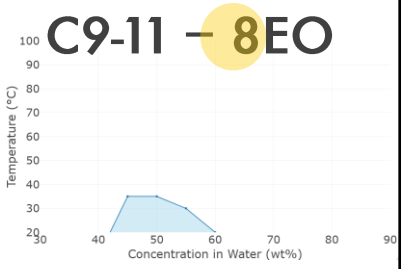
C9-11 – 5EO



C9-11 – 6EO

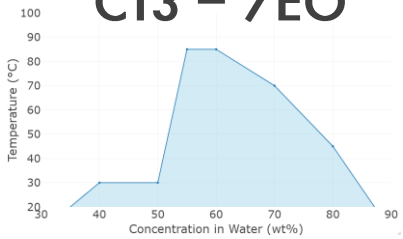


C9-11 – 8EO



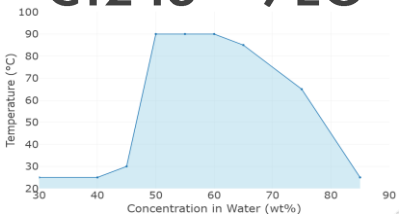
13.0

C13 – 7EO

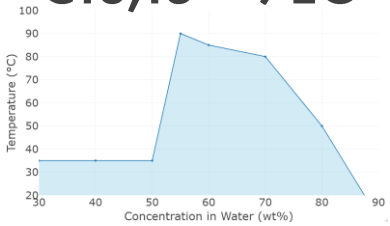


13.6

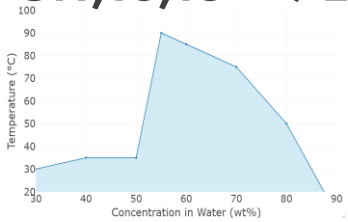
C12-15 – 7EO



C13,15 – 7EO



C11,13,15 – 7EO



14.5

C14,15 – 7EO