PHASE BEHAVIOR AND MORPHOLOGY OF MICROEMULSIONS IN A POLYMER-SURFACTANT SYSTEM

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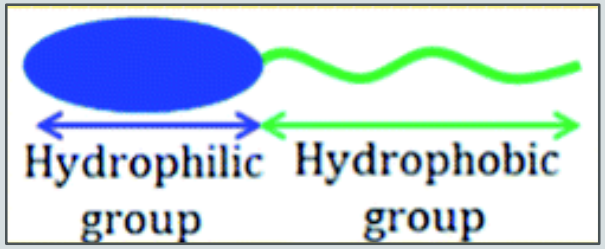
OVERVIEW

- Microemulsions and phase morphologies
- The Pluronic system
- Using SANS to determine structural phases
- Rheological properties related to structural phases

MICROEMULSIONS

- Ternary system of oil, water, and surfactant
- Self assembly
- Size domain: ~1-100 nm
- Prominent roles in pharmaceutical and industrial applications
- Understanding nanostructures is critical for understanding bulk material properties



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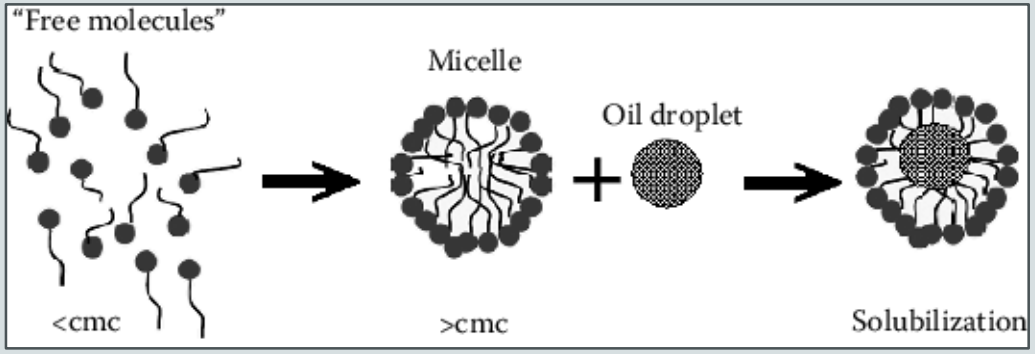
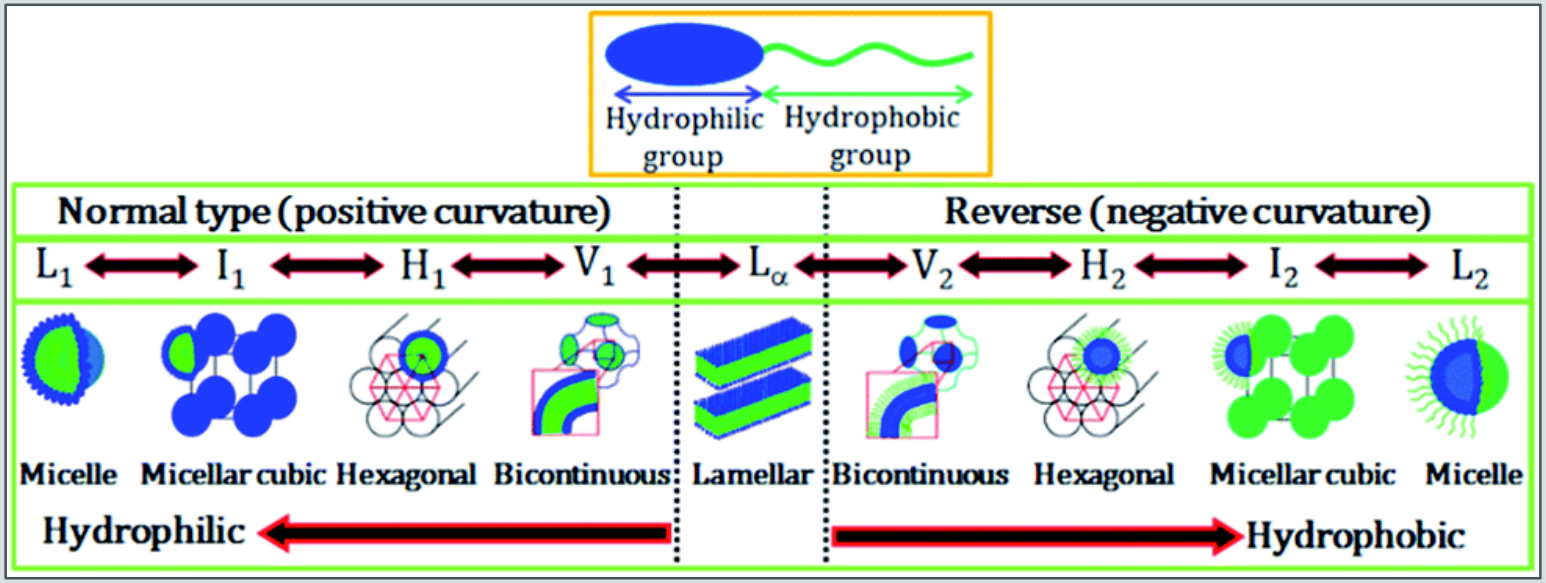


https://sites.ualberta.ca/~csps/JPPS8(2)/C.Rangel-Yagui/solubilization.htm

LYOTROPIC LIQUID CRYSTALLINE MESOPHASES

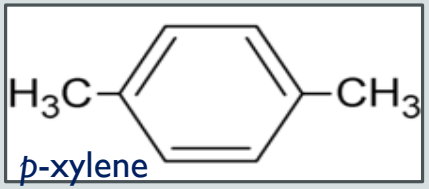
- Oil-in-water or water-in-oil (reverse microemulsion)
- Intermediate phases depending on surface curvature
- Preferred surface curvature is given by volume ratio between hydrophobic and hydrophilic domains

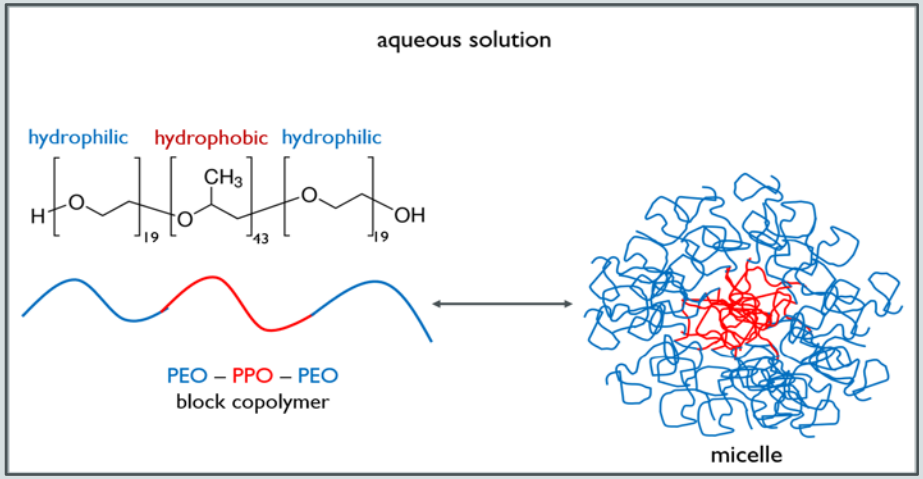


https://www.semanticscholar.org/paper/Lyotropic-liquid-crystal-systems-in-drug-delivery%3A-Kim-Jahn/020c104ac5d99038e0493d684489fa737ad2bede

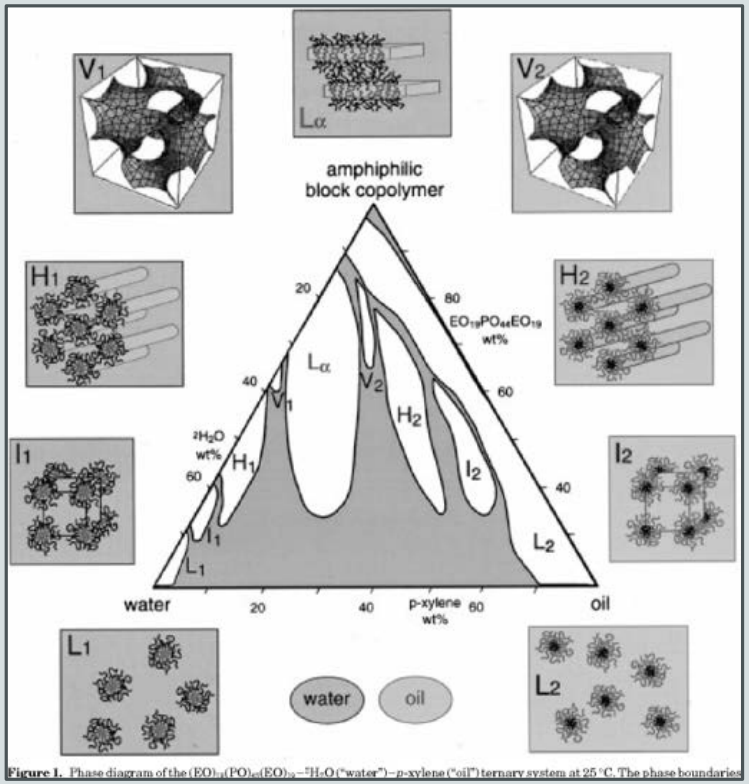
PLURONICS AS POLYMERIC SURFACTANTS

- System of interest: Pluronic P84 – p-xylene – water
- 60 wt% and 70 wt% pluronic microemulsions
- Exhibits many phases
- Phase boundaries may be identified by turbidity in response to temperature





https://www.acsu.buffalo.edu/~m27/projects.html



http://iopscience.iop.org/article/10.1088/0957-

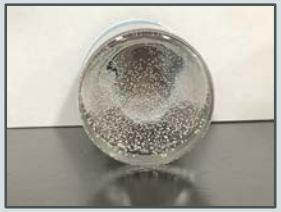
DETERMINATION OF PHASE BOUNDARIES

60 wt% P84 at 35°C

surfactant-oil-water

Increasing oil to water ratio

60-0-40



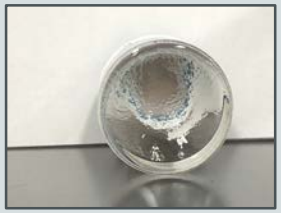
60-2-38

60-5-35

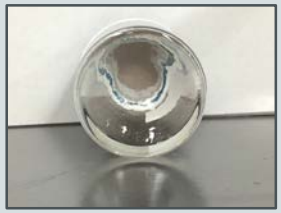
60-14-26

60-19-21

60-23-17

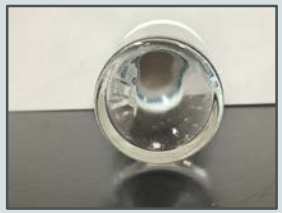


60-27-13



60-29-11

60-31-9

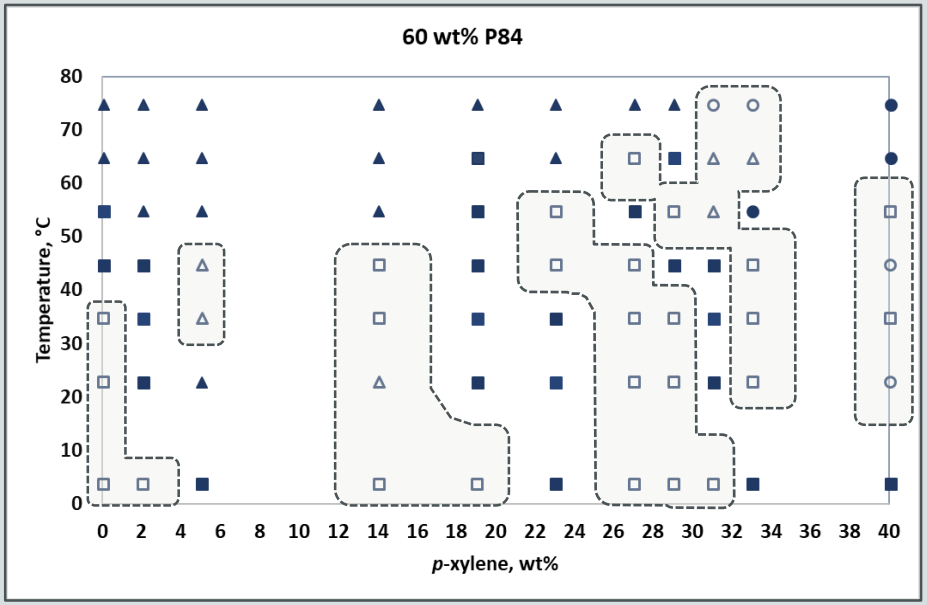


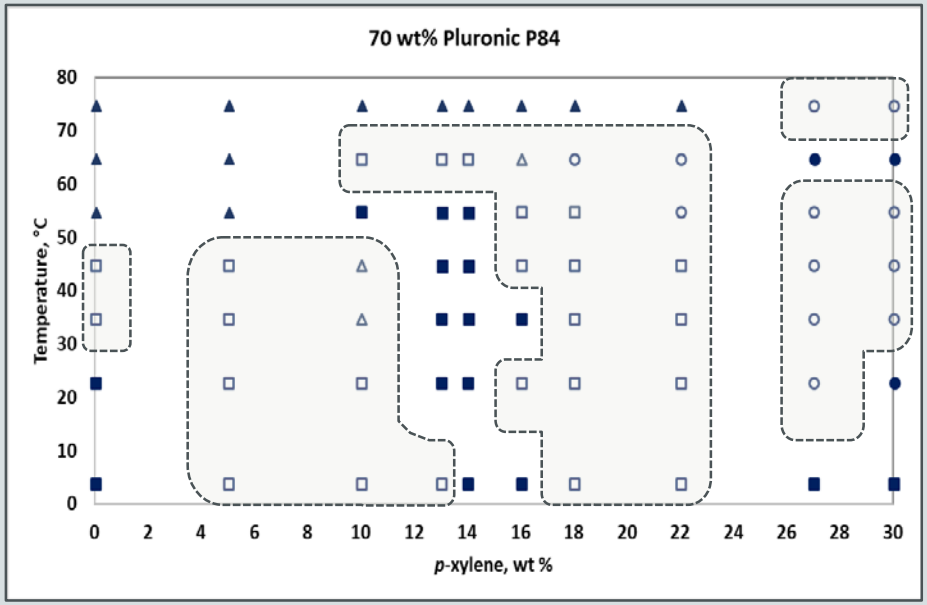
60-33-7

60-40-0

Increasing oil to water ratio

PHASE BOUNDARY TEMPERATURE DEPENDENCE



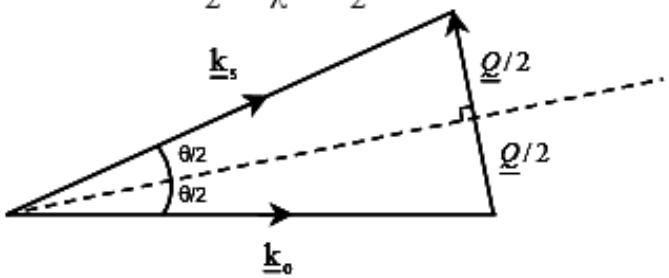


SMALL ANGLE NEUTRON SCATTERING (SANS)

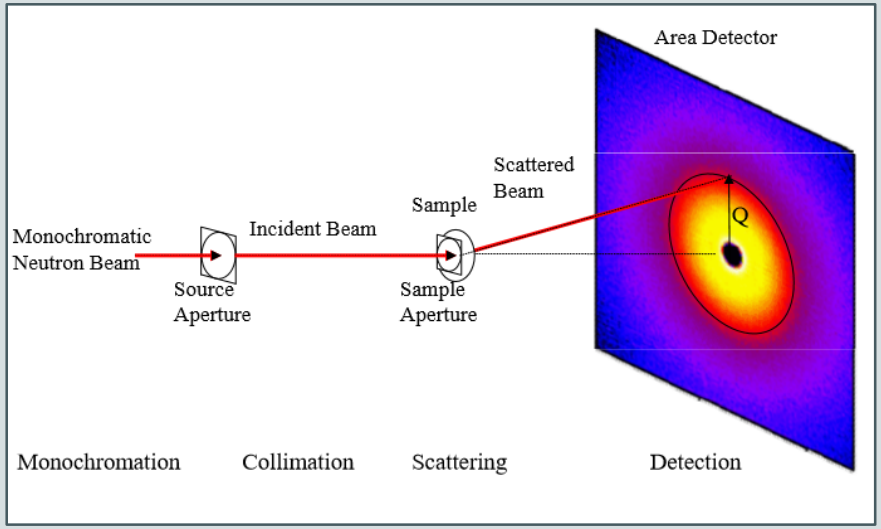
- Beam of neutrons scatters off sample at an angle and onto detector
- Scattered distance (Q) is measured in reciprocal space
- Q reveals structures and dimensions within sample

For elastic scattering,

$$|\underline{Q}| = Q = 2|k_o|\sin\frac{\theta}{2} = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}$$

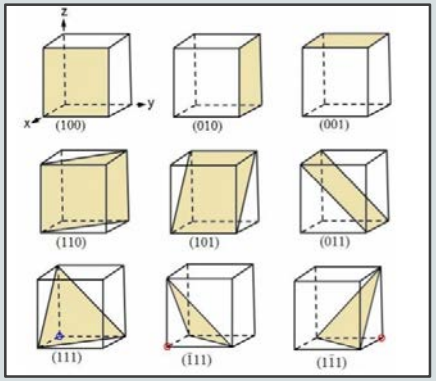


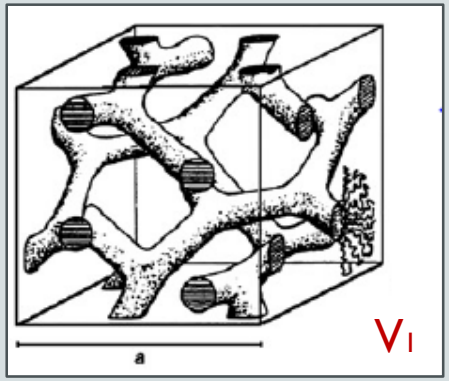
https://www.ncnr.nist.gov/summerschool/ss10/pdf/SANS_NR_Intro.pdf

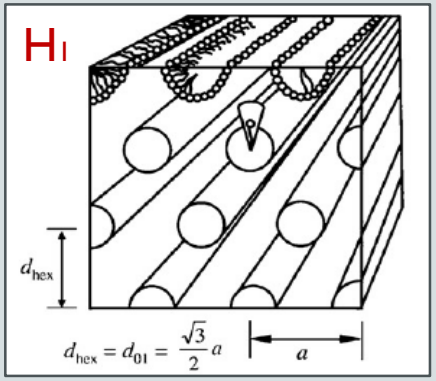


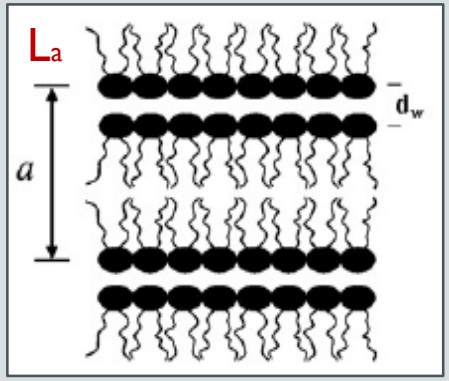
https://www.ncnr.nist.gov/programs/sans/pdf/part_ii_sans_nuts_and_bolts.pdf

CRYSTALLOGRAPHY





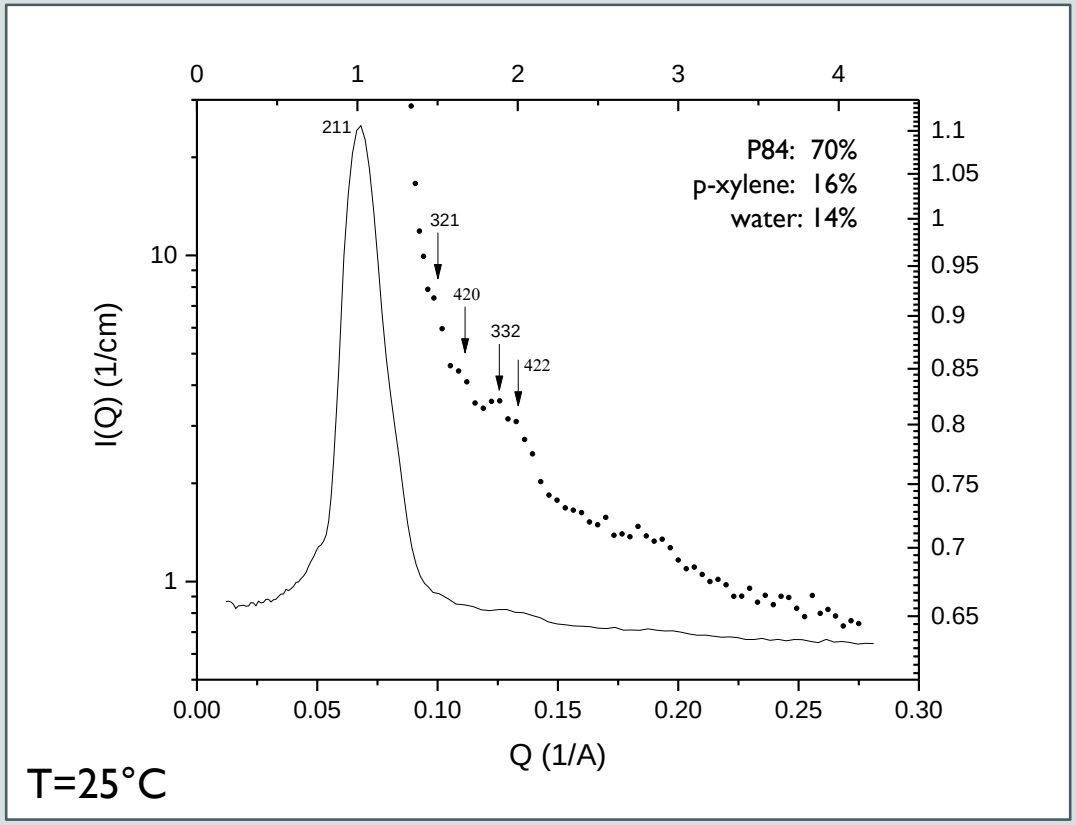


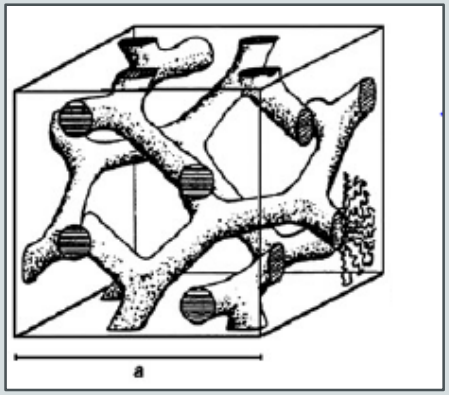


https://www.researchgate.net/profile/David_Mannock/publication/6309243/figure/fig2/AS:281244538556419@1444065331801/A-schematic-drawing-of-various-lipid-water-mesophases-and-states-of-aggregation-adopted.png

- Mesophases can be liquid crystalline in structure
- Periodicity of liquid crystal results in Bragg reflections from different sets of crystallographic planes
- Reflections probed by SANS serve as structure IDs for mesophases

REVERSE BICONTINUOUS CUBIC MESOPHASE

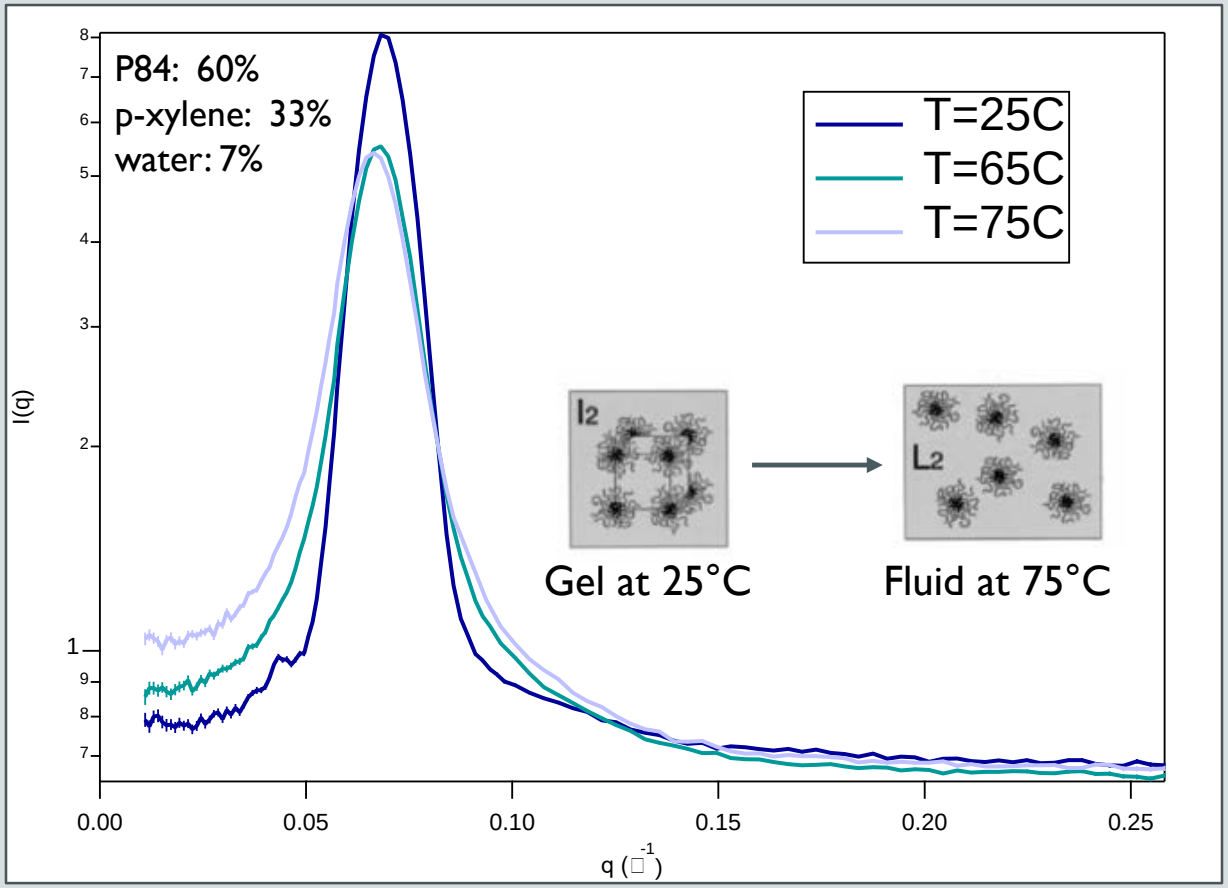




- The relative peak positions identify the phase
- The q values of peaks are a function of the plane indices (hkl) and the unit cell dimension (a)

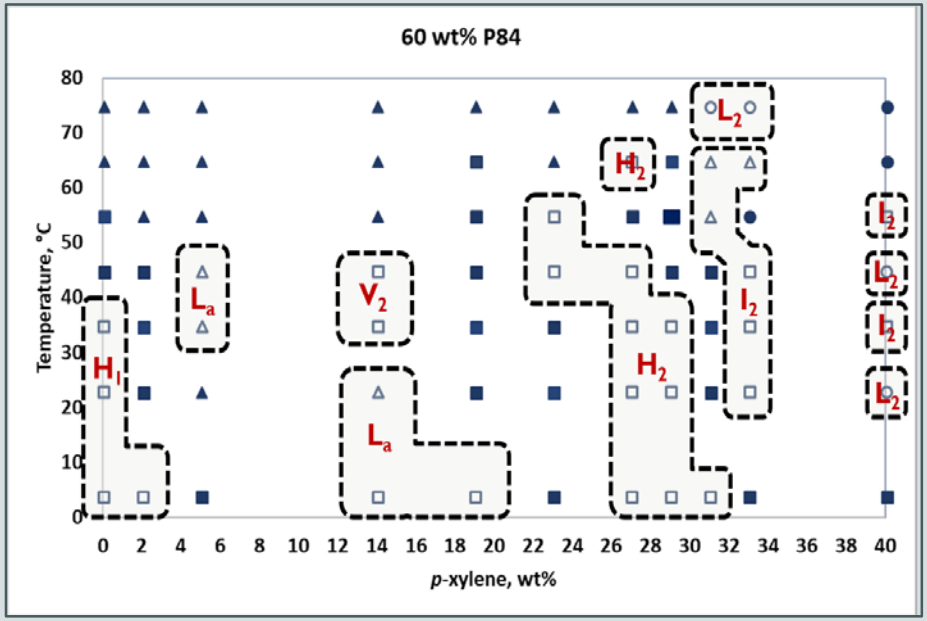
$$\{hkl\} \rightarrow q = \frac{2\pi\sqrt{h^2 + k^2 + l^2}}{a}$$

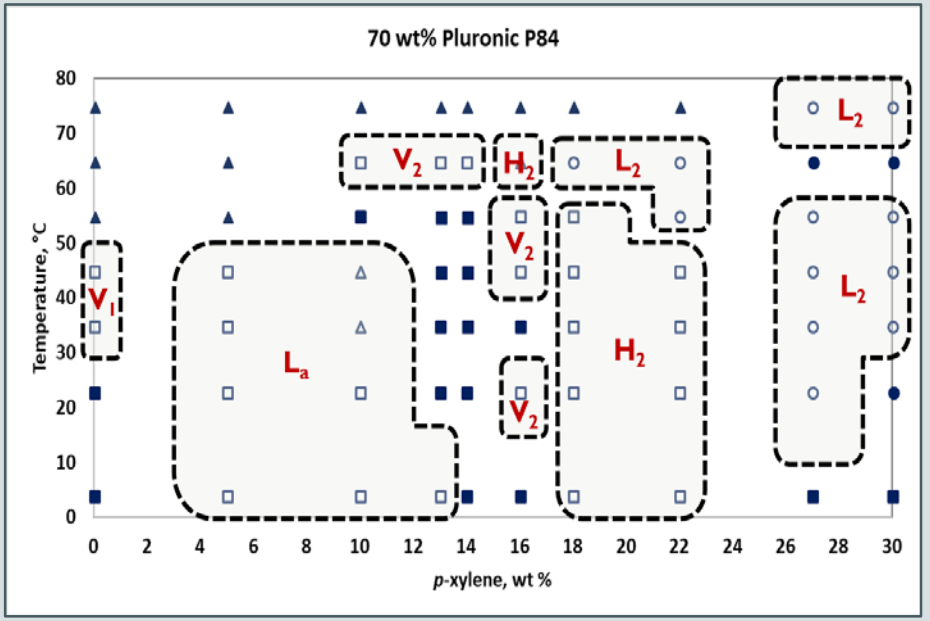
IDENTIFYING PHASE TRANSITIONS USING SANS



- Reverse micellar cubic at 25°C
- Phase transition around 65°C
- Reverse micellar solution at 75°C

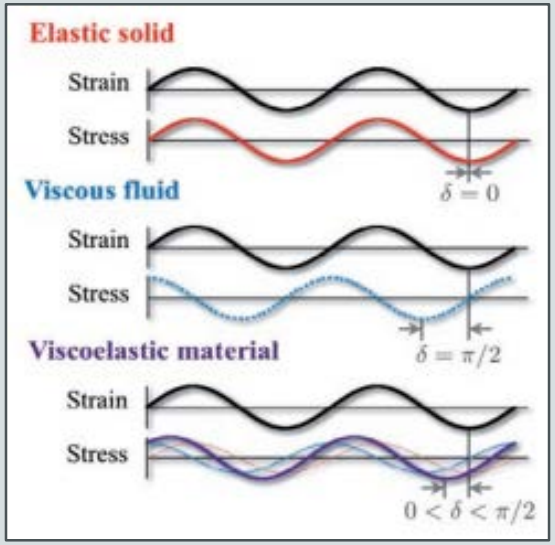
PHASE BOUNDARY TEMPERATURE DEPENDENCE

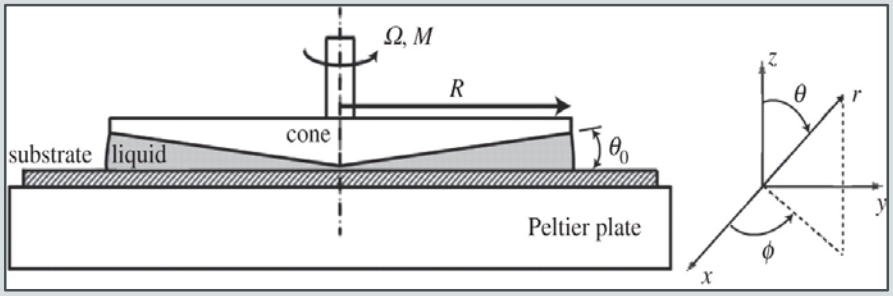




RHEOLOGY

- Small-Amplitude Oscillatory Shear
- Elastic modulus *G'*
- Viscous modulus *G"*
- Moduli expected to change upon phase transition



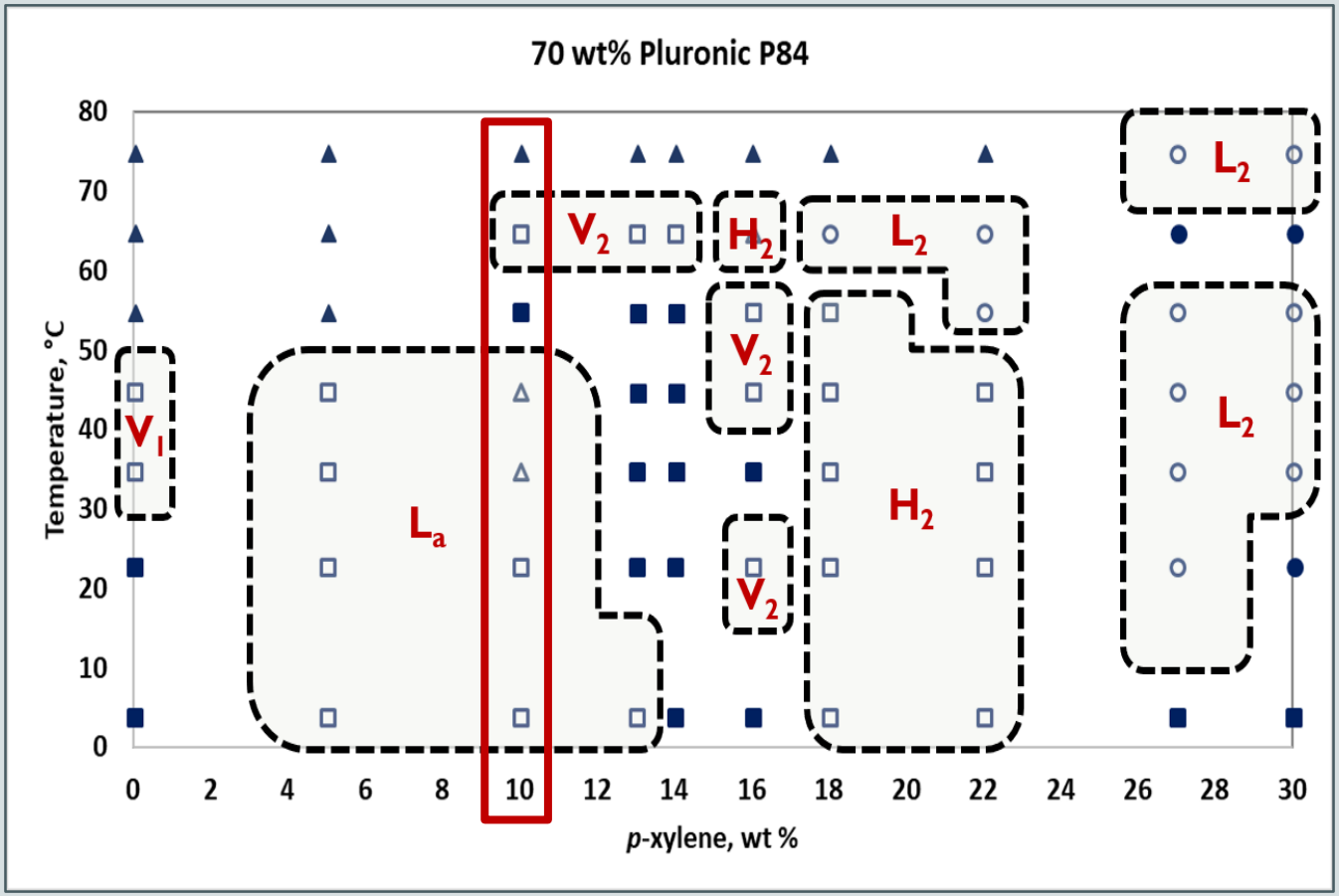


http://plate.goodwheel.site/parallel-plate-geometry-rheometer/

$$G' = (\sigma_o / \gamma_o) \cos \delta$$

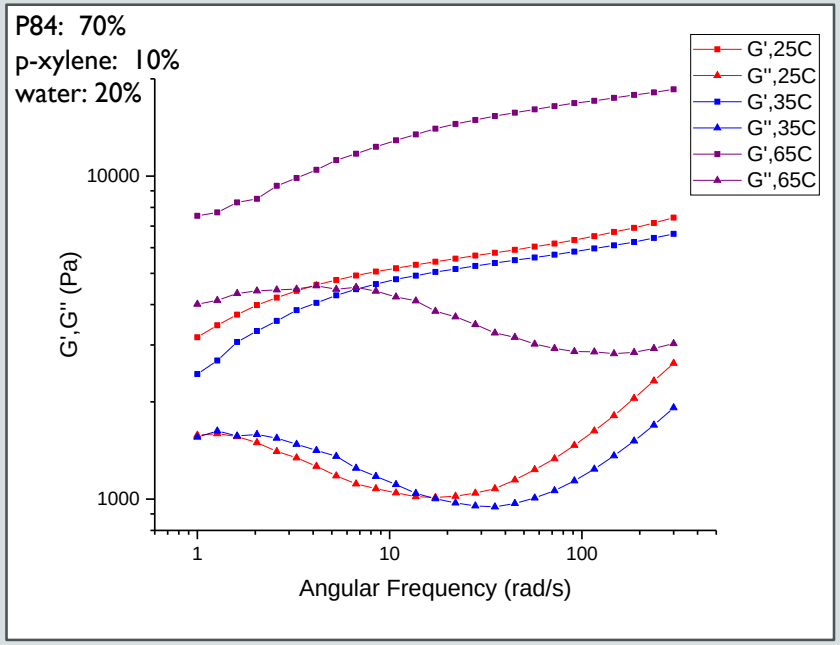
$$G'' = (\sigma_o / \gamma_o) \sin \delta$$

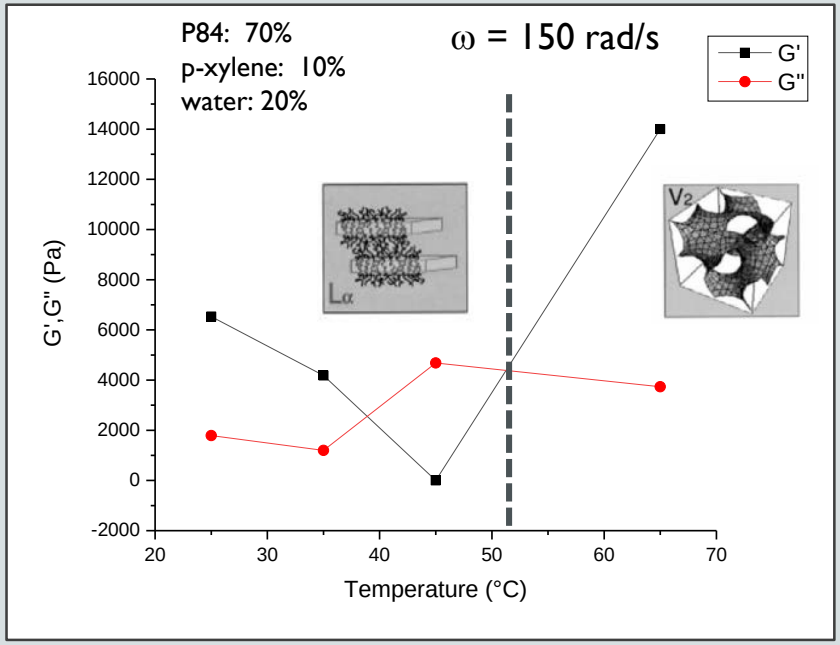
PHASE BOUNDARY TEMPERATURE DEPENDENCE



RHEOLOGY RESULTS

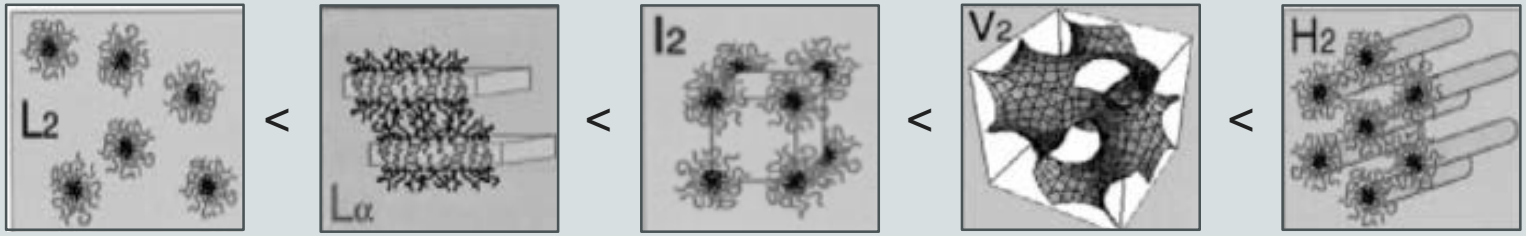
- Example of transition: 70 % P84, 10 % oil, 20 % water
  - Transition at ca. 50 °C
  - From lamellar gel to bicontinuous gel
  - Bicontinuous gel has higher connectivity and is therefore stronger





RHEOLOGY RESULTS

- The storage modulus generally increases with connectivity:



0D	1D	2D	3D	3D
Liquid	Gel	Gel	Gel	Gel

- Bulk rheological properties can be explained by mesophase nanostructures

CONCLUSION

- Temperature dependent phase behavior determined from SANS
- Connectivity of mesophase directly relates to rheological properties
- Future study: Relate connectivity and rheology to electrical conductivity

ACKNOWLEDGEMENTS

- Mentors: Grethe Jensen and John Riley
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