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# Inhibition of Scale Formation Using Antiscalant Additives

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



# Presentation Outline

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1. Intro
  - a. Background
  - b. Highlights from Spring 2019 IAB Meeting
2. Materials and Methods
3. Data
  - a. Screening Functional Groups
    - a. Effect on Induction Time
    - b. Interfacial Calculations
    - c. Effect on Morphology
  - b. Screening Molecular Weight
    - a. Effect on Induction Time
    - b. Interfacial Calculations
4. Summary and Timeline



# Background

**Overall Objective:** Understand the mechanisms that govern the effect of the Phosflow<sup>®</sup> (PF) on inhibition of scale formation in phosphoric acid production.

Heat Exchanger Fouling in Phosphoric Acid Evaporators, Behbahani et al. 2003



Limited commercial solutions.

Property	Effect of an antiscalant
Amount	Reduction in the amount of scale formed
Adhesion Strength	Weakening adhesion to surfaces or to other crystals can improve flow induced sloughing
Kinetics	Faster kinetics leading to more, smaller crystals, and slower kinetics to fewer, but larger crystals
Morphology	Structures of successive deposition may impact sloughing

Scale species found in phosphoric acid production:

➤ Calcium Sulfates

- Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ )
- Bassanite ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ )
- Anhydrite ( $\text{CaSO}_4$ )

➤ Fluorosilicates

- $\text{Na}_2\text{SiF}_6$
- $\text{K}_2\text{SiF}_6$
- $\text{NaKSiF}_6$



# Highlights from Spring 2019 IAB Meeting<sup>Intro</sup>

## Key Findings

- Orientation can alter the mechanism of scale growth and has a larger impact on secondary scale.
- PF altered scale is both porous and is more easily removed, favoring the nucleation of new crystals over deposition. (morphology, adhesion strength, and kinetics)

## Goals for this Period (Feb 2019-Aug 2019)

- Screening of additives for further study
- NSF INTERN

## Feedback from Industry Members

### How does PF compare to other commercial scale inhibitors?

There is some limited evidence/ patents for interactions between carboxylate functional groups and fluorosilicate scale but there is almost nothing documented to inhibit  $\text{CaSO}_4$  aside from PF.

### Why was the morphology of $\text{CaSO}_4$ different on the graphite surface?

Recent shorter experiments have shown that the initial crystals stack or nucleate on the surface before growing into the flower-like clusters through Ostwald's ripening.



# Presentation Outline

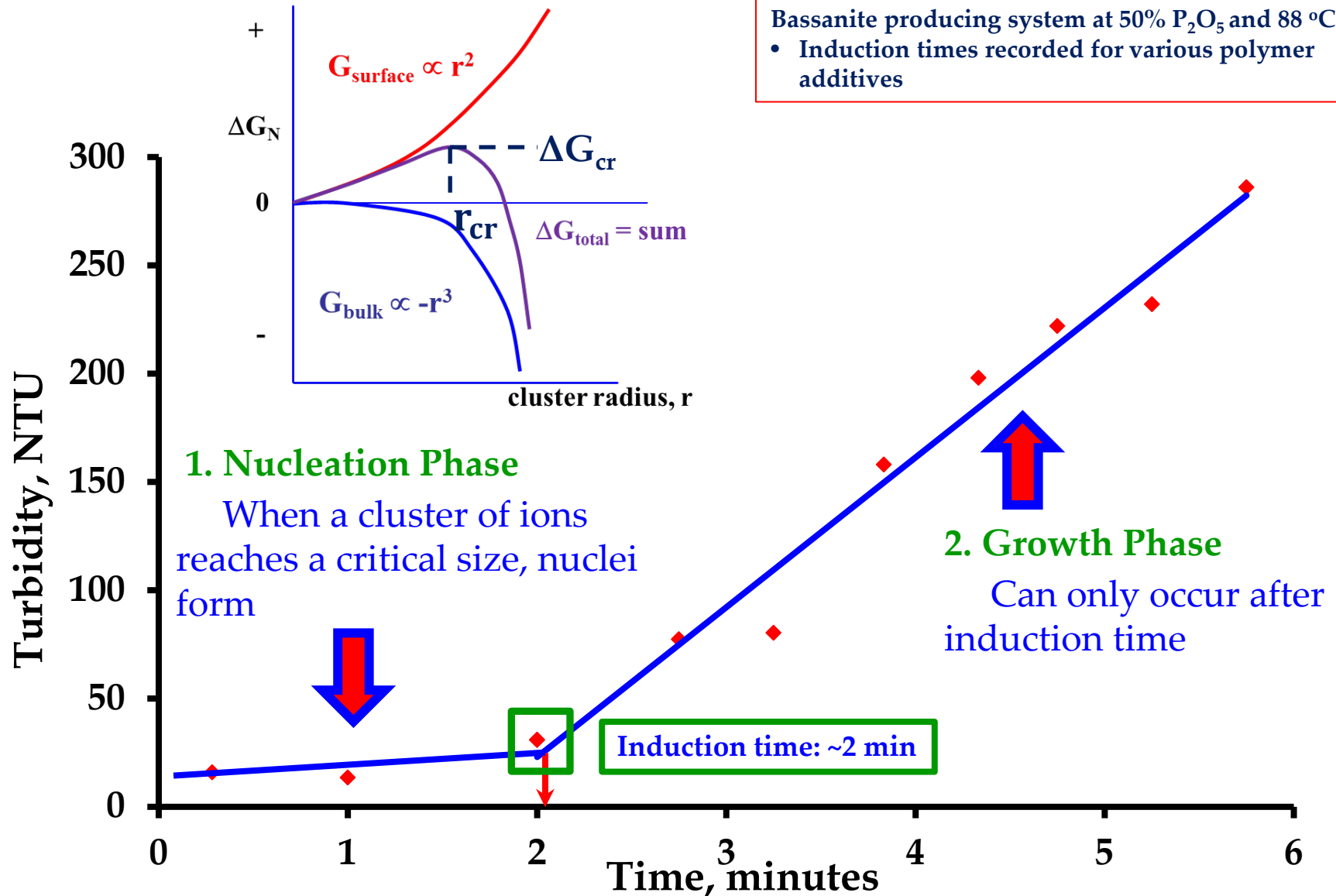
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# Calculation of Induction Times

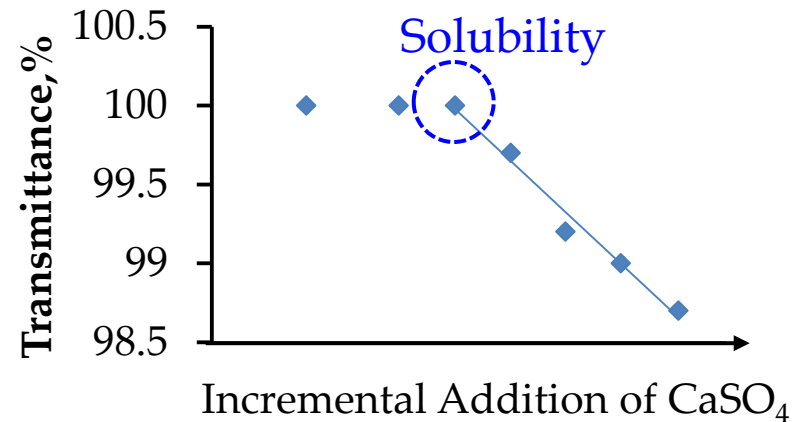
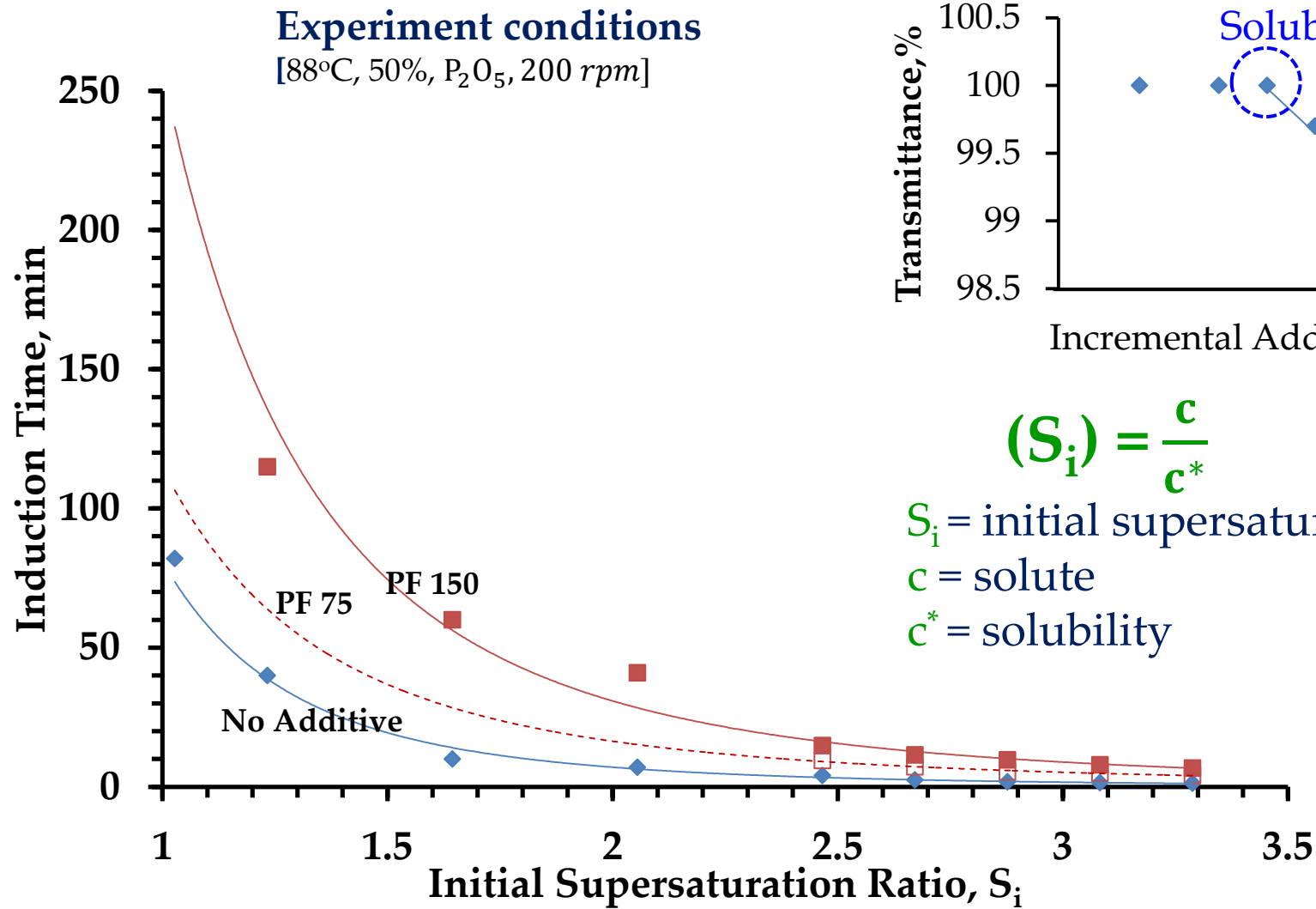
Bassanite producing system at 50%  $P_2O_5$  and 88 °C  
• Induction times recorded for various polymer additives







# Induction Time as a Function of Supersaturation



$$(S_i) = \frac{c}{c^*}$$

$S_i$  = initial supersaturation ratio

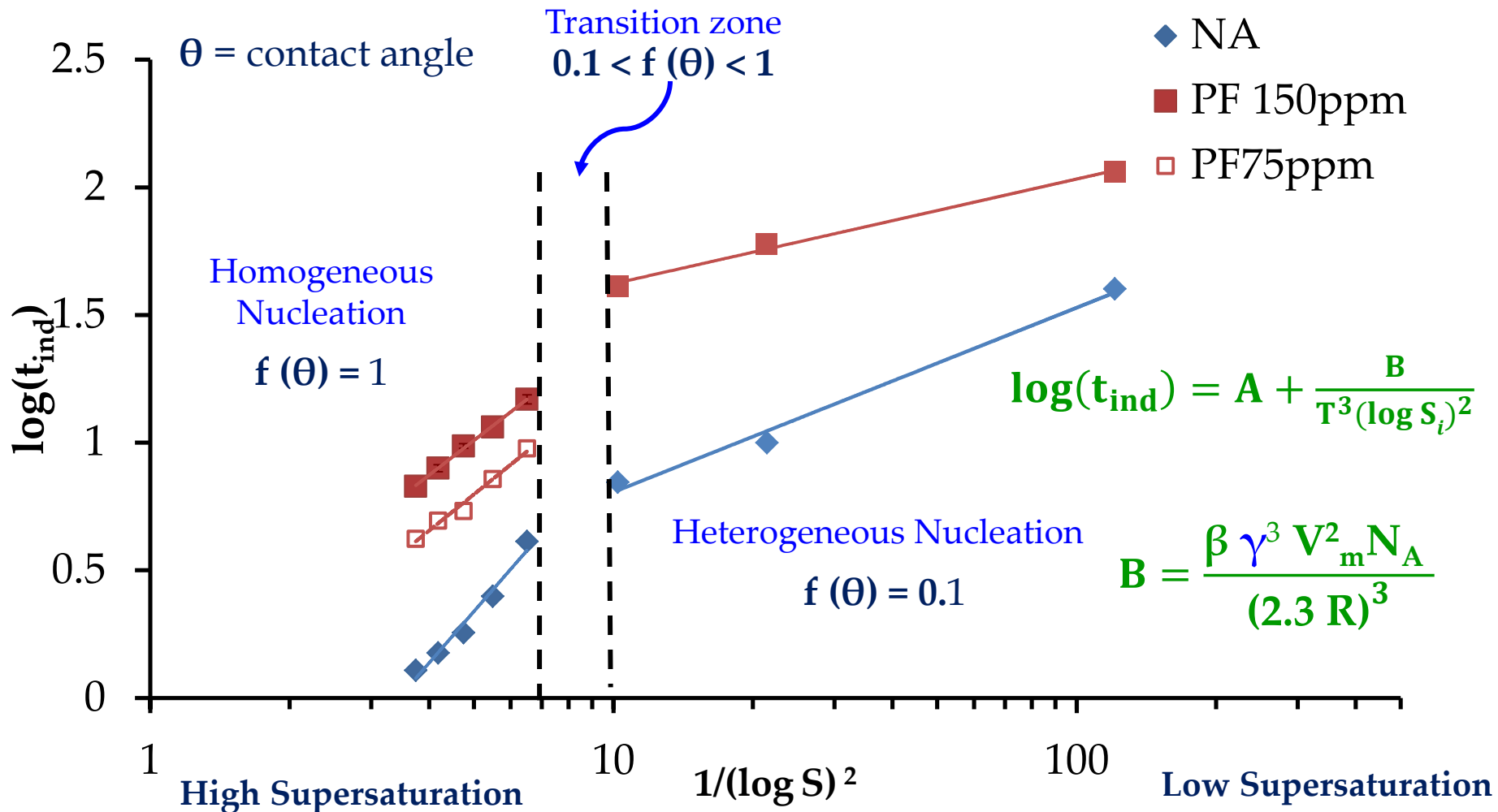
$c$  = solute

$c^*$  = solubility

PF increases induction times across all supersaturation ratios.



# Homogeneous vs Heterogeneous Materials & Methods



Three distinct regions can be seen in which the homogeneous region can be used for further calculation because it simplifies interactions.



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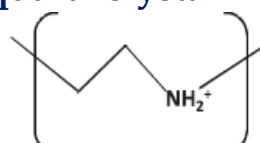
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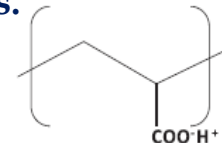
# Selection of Polymers

Based on literature, charge and topography play a role in the inhibition of  $\text{CaSO}_4$  on polymer coated quartz crystal microbalances.

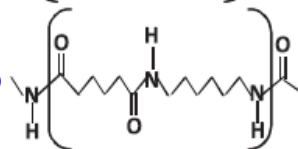
PEI



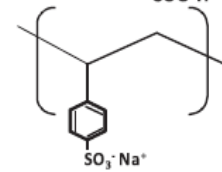
PAA



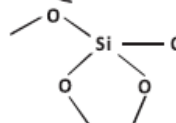
PA6,6



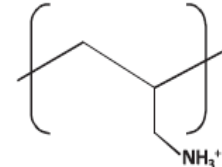
PSS



$\text{SiO}_2$



PAH



- Polyacrylic Acid (PAA) – typically used  $\text{CaSO}_4$  antiscalant negative or neutral under system conditions
- Polydiallyldimethylammonium chloride (PDADMAC) – positively charged under the system conditions
- Polyethylenimine (PEI) – positively charged under the system conditions containing primary amines

PAA

PAH

PA 6,6

PSS

PEI

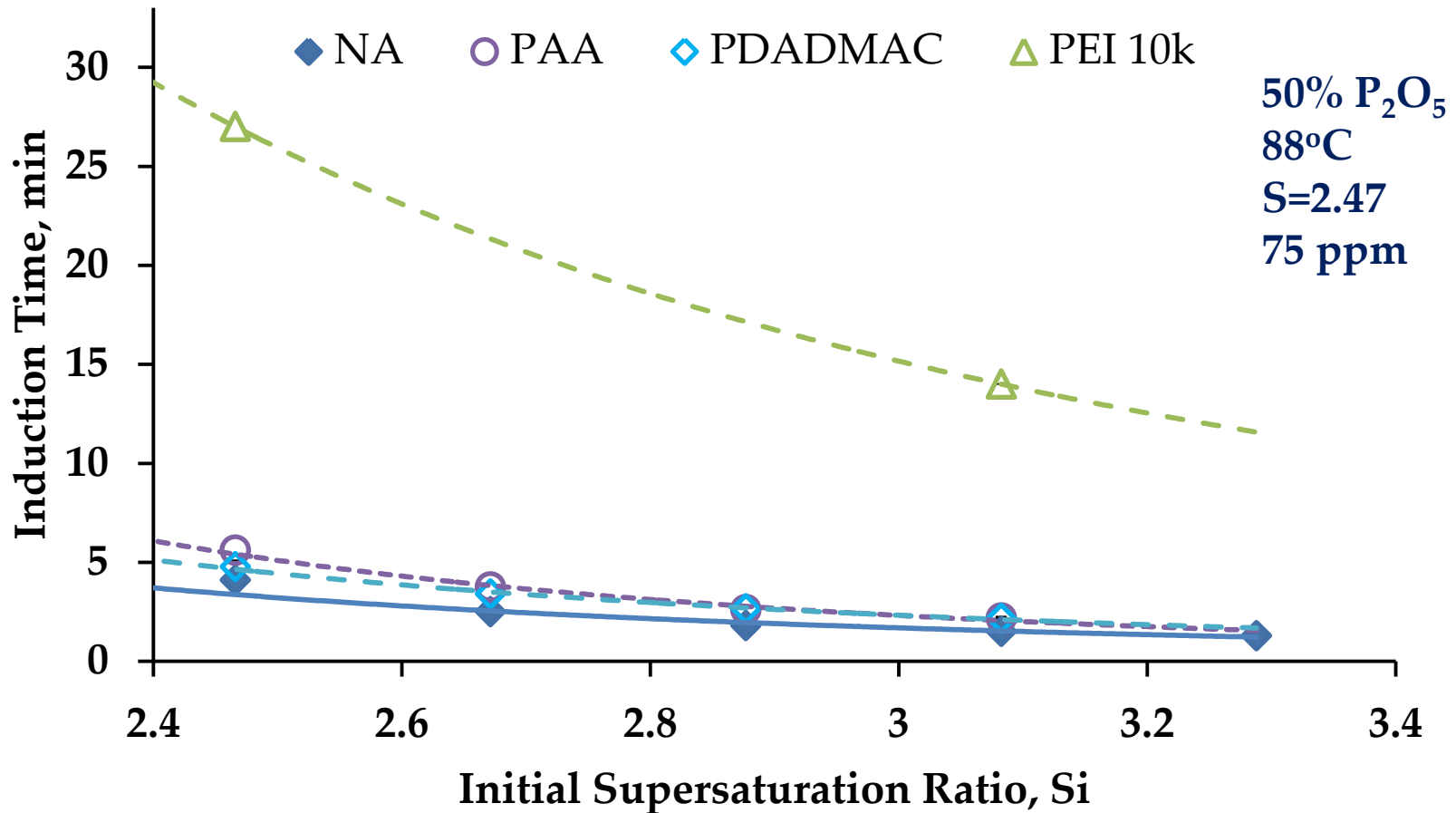
$\text{SiO}_2$

Control



# Screening of Additives

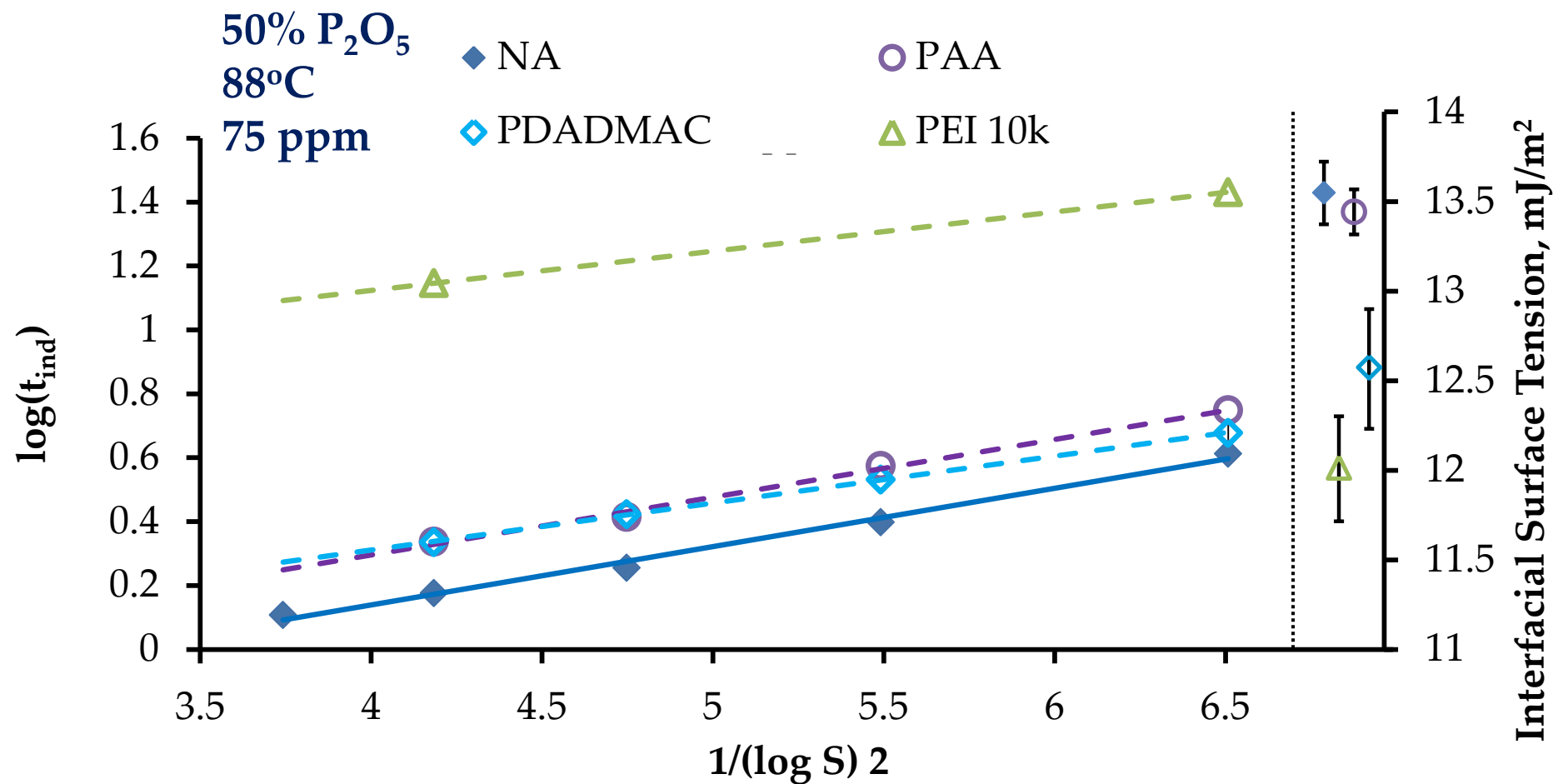
Data



PEI is the most effective additive at delaying the induction time of calcium sulfate hemihydrate.



# Interfacial Surface Tension Calculations



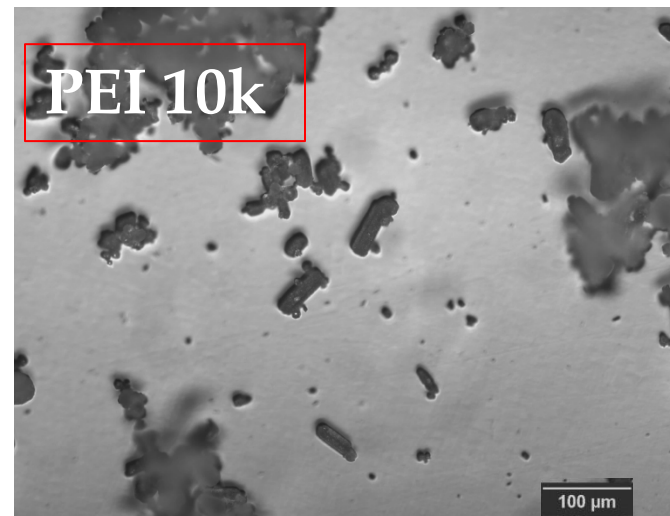
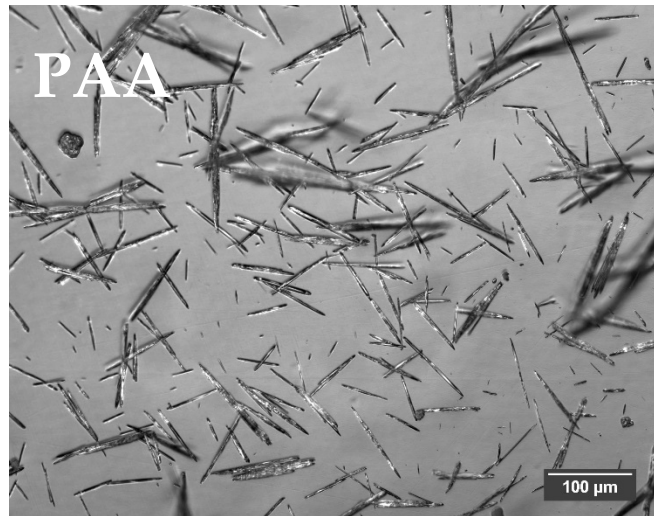
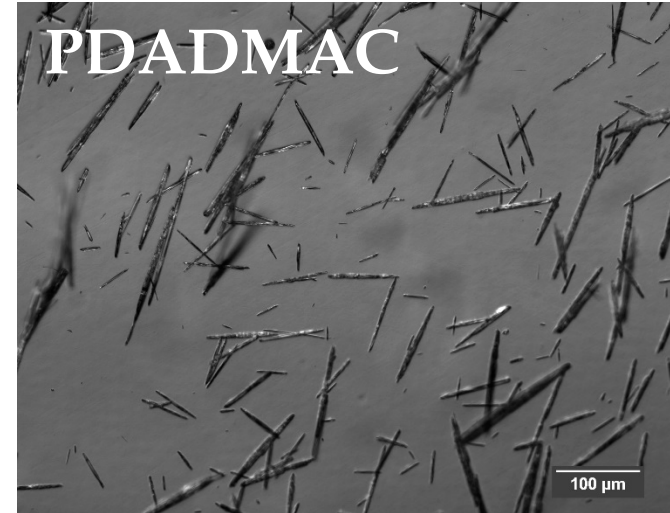
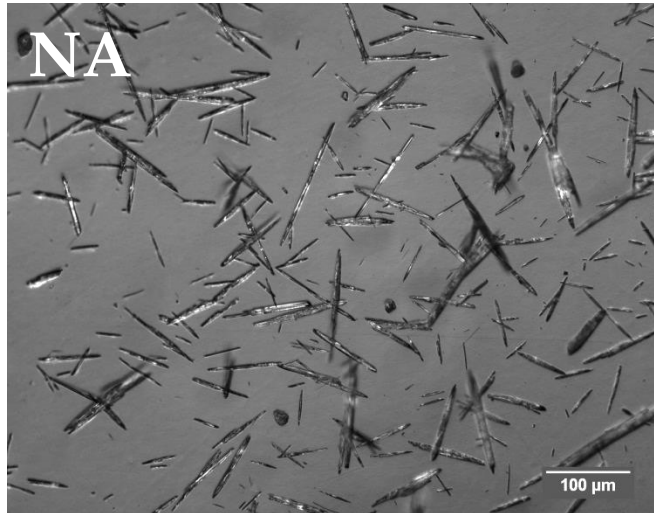
Positively charged additives appear to decrease the surface energy of the crystals while PAA shows almost no effect. PEI has been reported in literature to increase the solubility of  $CaSO_4$ .





# Effect on Bassanite Morphology

Data



Based on the above results, PEI was selected for further studies.



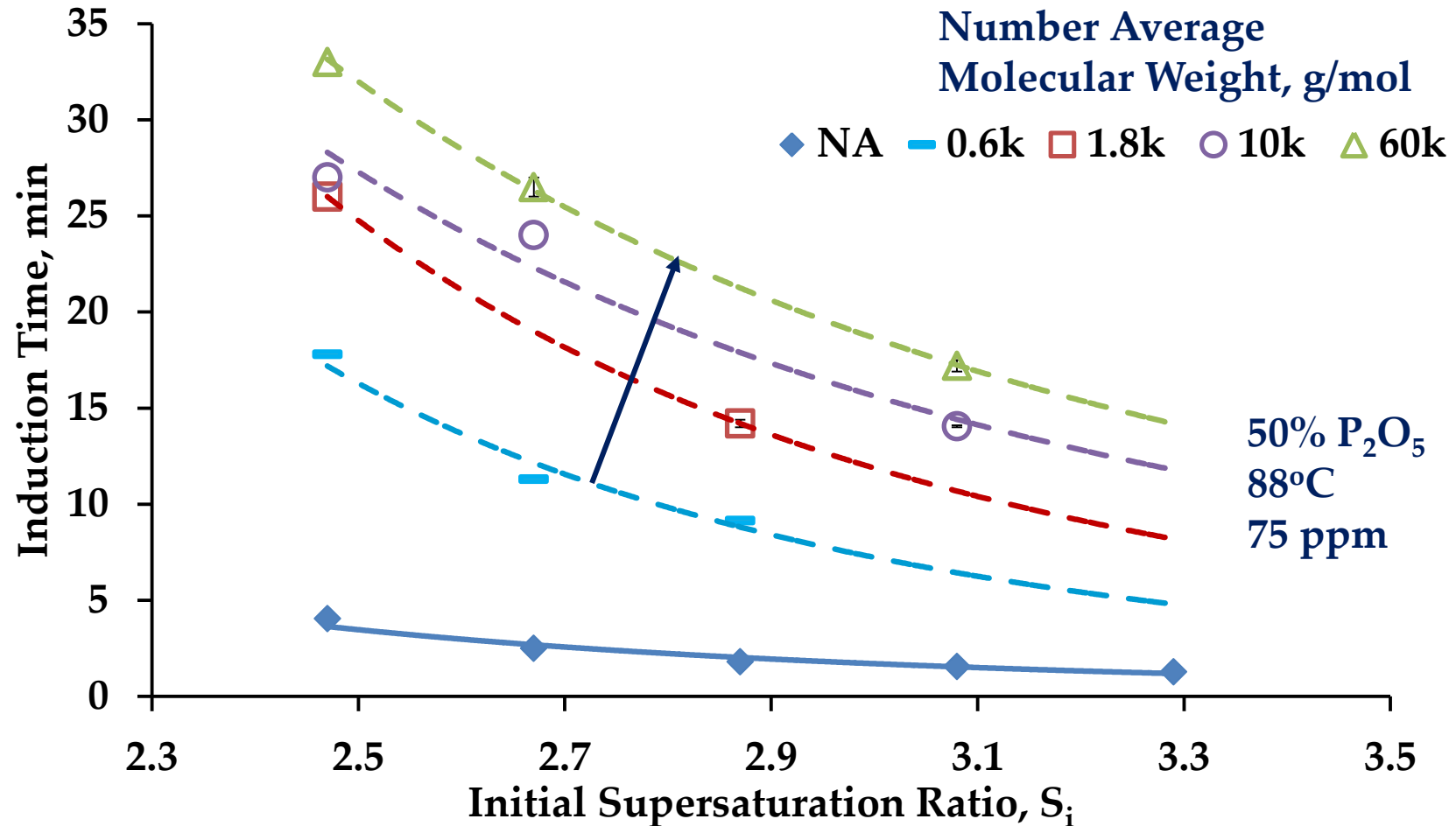
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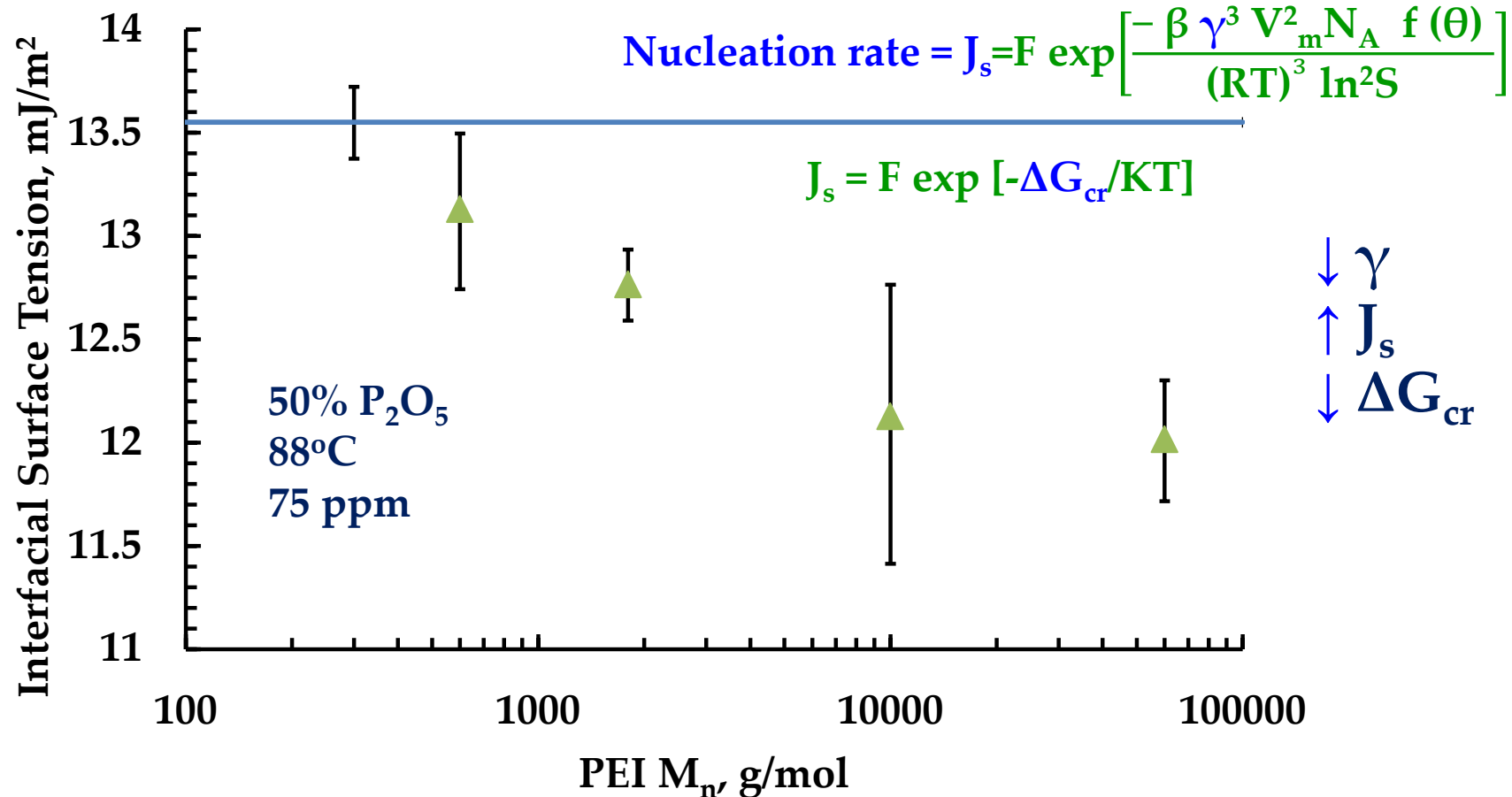
# Effect on Induction Time



The induction time for calcium sulfate hemihydrate increases with the molecular weight of PEI.



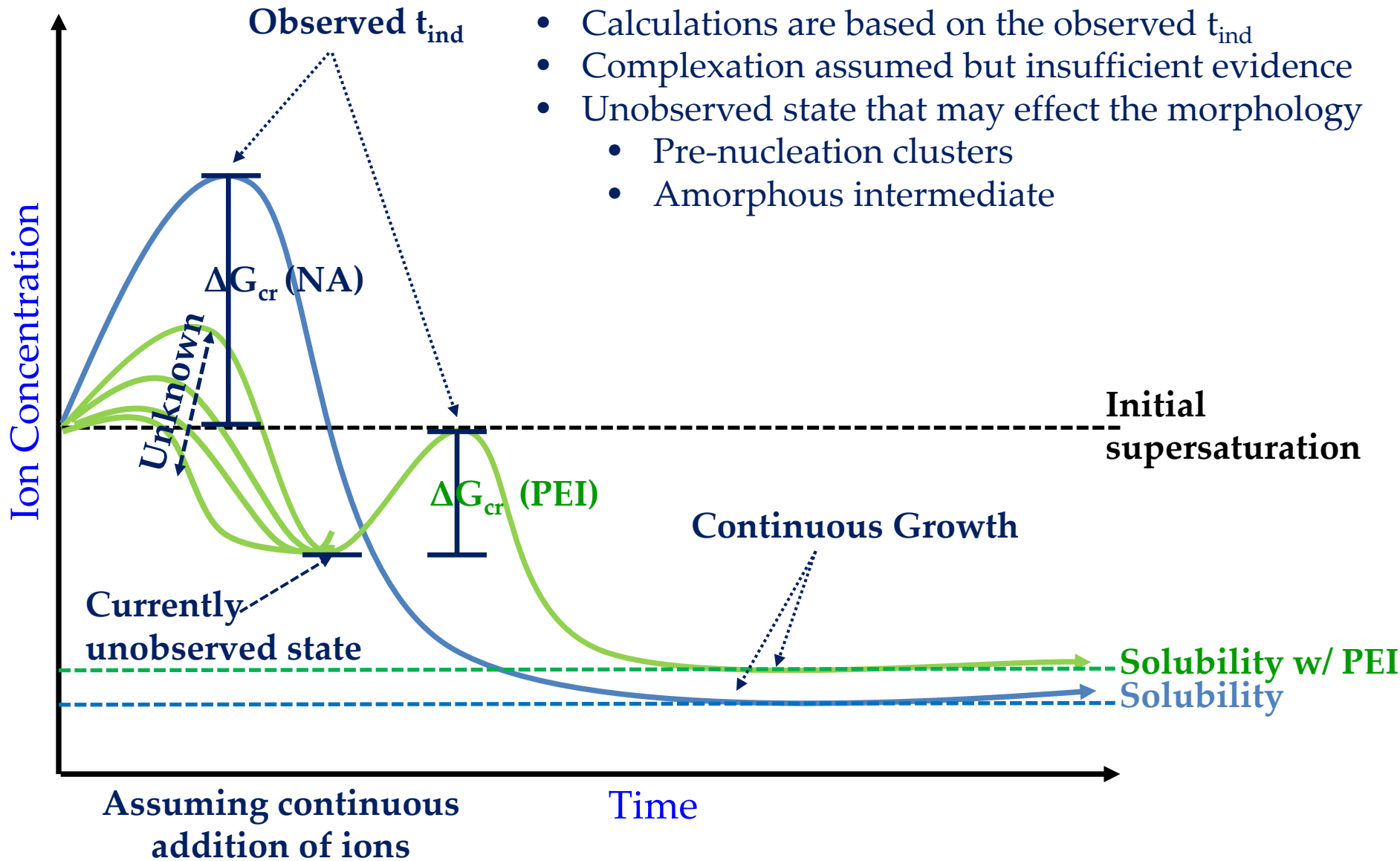
# Effect of Molecular Weight



- There appears to be a plateau M<sub>n</sub>>10k g/mol, future tests will be conducted at 60k g/mol
- The reduction in the interfacial surface tension results in:
  - Increased nucleation rate
  - Reduced Gibbs free energy barrier
  - Competition between nuclei for ions: Ca<sup>2+</sup> & SO<sub>4</sub><sup>2-</sup> (to be confirmed)



# Possible Mechanism





## Key Findings

### ➤ PEI

- Inhibits the precipitation of  $\text{CaSO}_4$  hemihydrate
- Increases induction times
- Alters the morphology of  $\text{CaSO}_4$  hemihydrate
- Reduces interfacial surface tension

### ➤ The efficacy of PEI

- Dependent on MW
  - Reaches a plateau at  $M_n > 10\text{k g/mol}$
- Not explained by interfacial surface tension changes
  - Exemplified by PDADMAC data
- May be related to its branched structure



# Future Work

## Specific Tasks for Next Reporting Period (Aug 2019-Feb 2020)

- Concentration sweep of  $M_n$  60k g/mol PEI to obtain
  - Induction time (Turbidity)
  - Solubility (UV-Vis)
- A DOE to optimize PEI's interaction with  $\text{CaSO}_4$  hemihydrate

## Long Term Plans

- Monitor solubility changes with another method to confirm complexation
- Observe foreign surface interactions (T.O.C.)
- Deposition experiments with coupons as done previously with PF



# Thank you

TASK NAME	Q1'17	Q2'17	Q3'17	Q4'17	Q1'17	Q2'17	Q3'18	Q4'18	Q1'19	Q2'19	Q3'19	Q4'19
Induction time studies												
-Calcium sulfate												
-Fluorosilicates												
-Mixed scale studies												
Set up inline analysis												
Characterize												
Adsorption studies												
Mechanism studies												
Objectives/Aim		1										

Completed, Planned, Delayed

Project specific

- Number of papers in progress = 2
- Technical presentations = 8

## Acknowledgment

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## Disclaimer

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# Classical Nucleation Theory

## Supersaturation Ratio:

$$(S_i) = \frac{c}{c^*}$$

## Relation between induction time and supersaturation:

$$\log(t_{\text{ind}}) = A + \frac{B}{T^3(\log S)^2}$$

Where  $B = \frac{\beta \gamma^3 V_m^2 N_A f(\theta)}{(2.3 R)^3}$

## Nucleation rate:

$$J_s = F \exp \left[ \frac{-\beta \gamma^3 V_m^2 N_A f(\theta)}{(RT)^3 \ln^2 S} \right]$$

## Free energy change

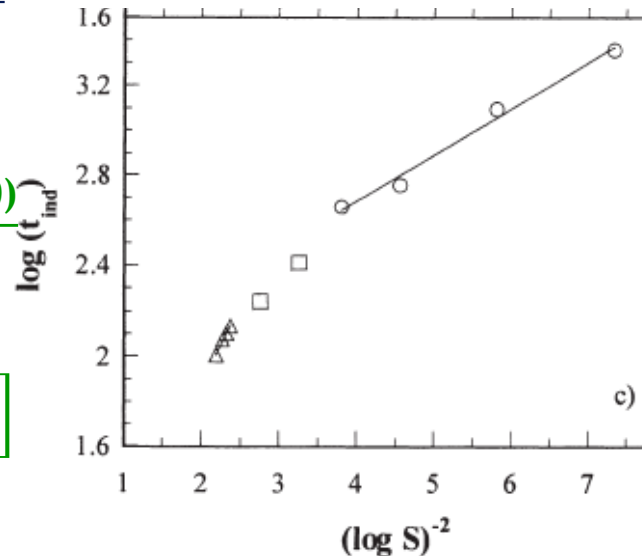
$$J_s = F \exp [-\Delta G_{\text{cr}}/KT]$$

Where  $\Delta G_{\text{cr}} = 4/3 \pi r_{\text{cr}}^2 \gamma$

## Number of molecules in the critical nucleus

$$i = 4N_A \pi r^3 / 3V_m$$

## Example Graph



Δ Homogeneous nucleation

□ Transition zone

○ Heterogeneous nucleation

## Nomenclature

$S_i$  = initial supersaturation ratio

$c$  = solute

$c^*$  = solubility

$T$  = temperature

$t_{\text{ind}}$  = Induction time

$A$  = Intercept based on results

$B$  = Slope based on results

$\beta$  = Geometric factor

$\gamma$  = Surface energy

$V_m$  = Molar volume

$N_A$  = Avogadro's number

$f(\theta)$  = homo/heterogeneous

$R$  = Gas constant

$J_s$  = nucleation rate

$F$  = Pre-exponential factor

$r_{\text{cr}}$  = Critical radius

$\Delta G_{\text{cr}}$  = Gibb's free energy at  $r_{\text{cr}}$

$i$  = Number of molecules in  $r_r$