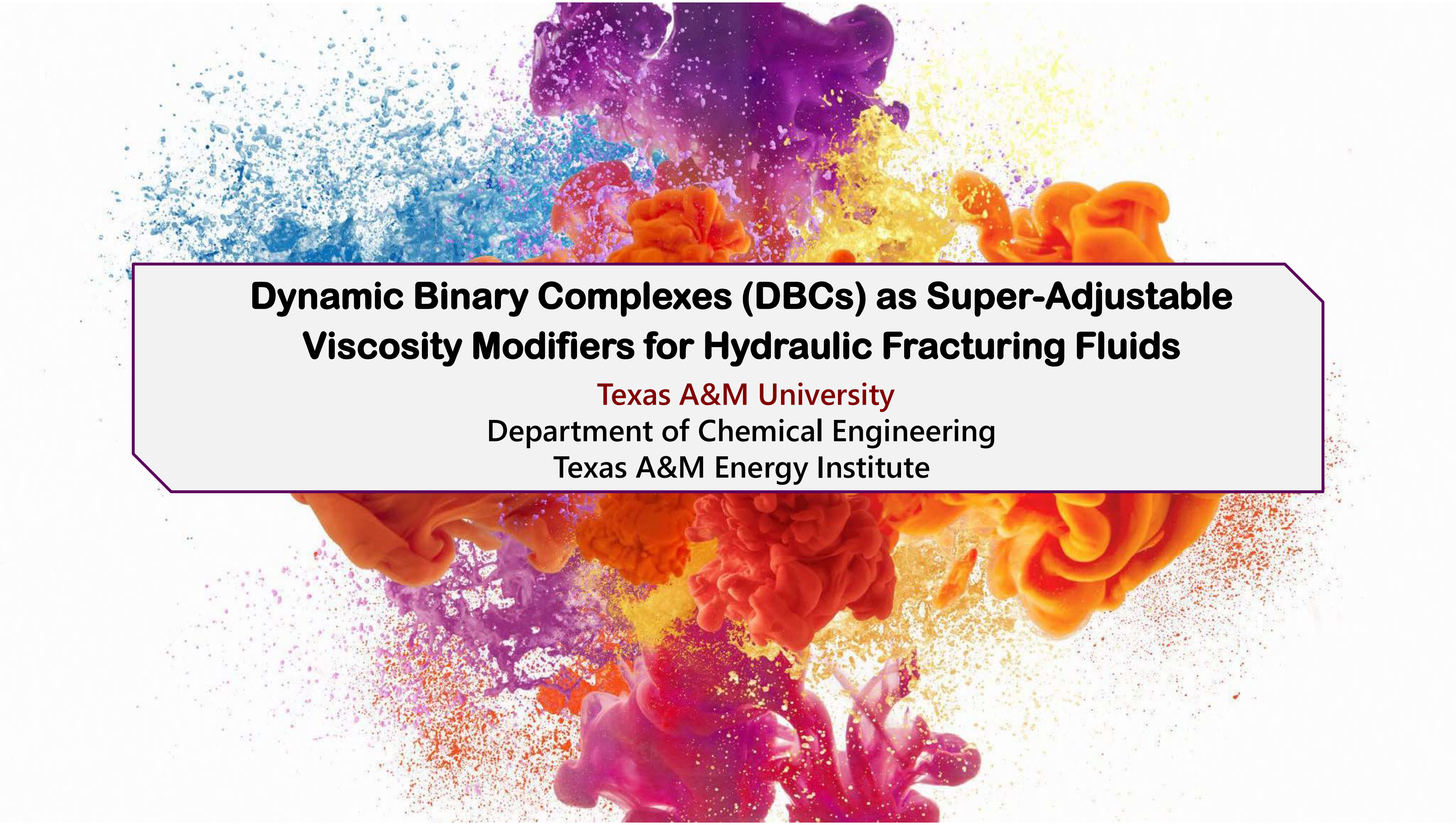


Dynamic Binary Complexes (DBCs) as Super-Adjustable Viscosity Modifiers for Hydraulic Fracturing Fluids

Texas A&M University
Department of Chemical Engineering
Texas A&M Energy Institute

Project Overview

- **Project Participants**

  Texas A&M University (Research and Development)
  - Department of Chemical Engineering
  - Texas AM& Energy Institute

  Incendium Technologies (Commercialization)

- **Project Personnel**

  Mustafa Akbulut, Associate Professor, Texas A&M University
  Joseph Kwon, Associate Professor, Texas A&M University

  Shuhao Liu, Graduate Student
  Silabrata Pahari, Graduate Student
  Yu-Ting Lin, Graduate Student
  Bhargavi Bhat, Graduate Student

  Spencer Doyle, Undergraduate Student
  Landry Ray, Undergraduate Student
  Ankit Anand, Undergraduate Student
  Sek Kai Leong, Project Technician

  Cengiz Yegin, Product Development Engineer, Incendium Technologies

Project Products and Achievements

- **Peer-Reviewed Publications**
  - Dynamic, hollow nanotubular networks with superadjustable pH-responsive and temperature resistant rheological characteristics, *Chemical Engineering Journal (IF:16.74), 2022*
  - Nanostructural and Rheological Transitions of pH-Responsive Supramolecular Systems Involving a Zwitterionic Amphiphile and a Triamine, *Colloids and Surfaces A (IF: 5.52), 2022*
  - SAXS-guided unbiased coarse-grained Monte Carlo simulation for identification of self-assembly nanostructures and dimensions, *Soft Matter (IF: 4.05), 2022*
  - Supramolecular dynamic binary complexes with pH and salt-responsive properties for use in unconventional reservoirs, *PloS one (IF: 3.75), 2021*
  - A slip-spring framework to study relaxation dynamics of entangled wormlike micelles with kinetic Monte Carlo algorithm, *Journal of Colloid and Interface Science (IF: 9.97), 2021*
  - Model predictive control for wormlike micelles (WLMs): Application to a system of CTAB and NaCl, *Energy (IF: 7.15), 2021*
  - pH-responsive viscoelastic supramolecular viscosifiers based on dynamic complexation of zwitterionic octadecylamidopropyl betaine and triamine for hydraulic fracturing applications, *RSC Advances (IF: 4.04), 2021*

Project Products and Achievements

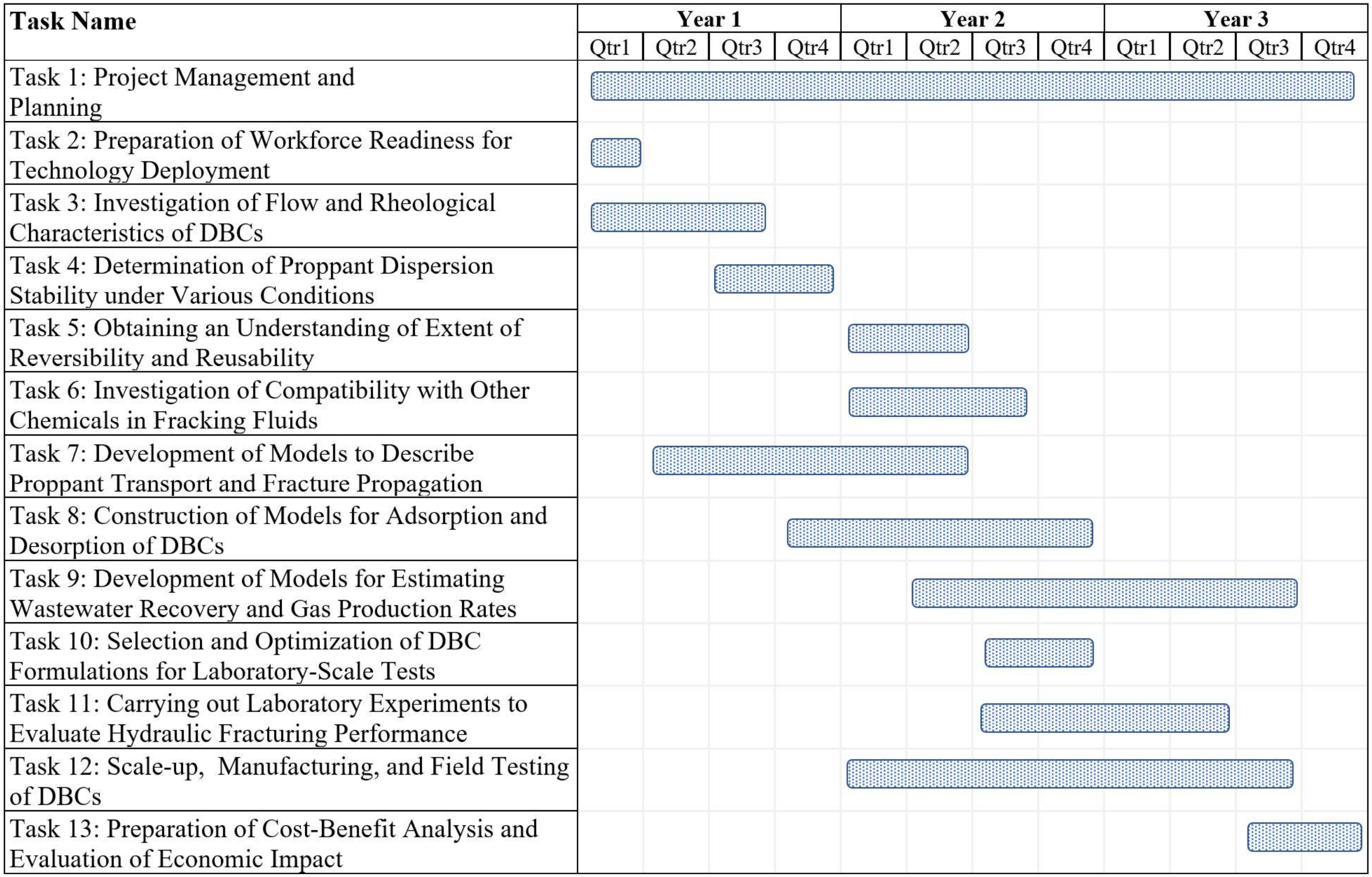
- **Technical and Conference Presentations**
  - 1 Presentation at *International Federation of Automatic Control (2022)*
  - 2 Presentations at the *AIChE Annual Meeting (2021*)
  - 4 Presentations at the *AIChE Annual Meeting (2020)*
  - 1 Presentation at ACS Colloid and Surface Science Symposium (CSSS) (2020)

- **Industrial Accomplishment**
  - Establishment of small pilot scale process for the production of DBCs
  - Demonstrating proof-of-concept at 50 Kg scale

Motivation, Rationale, and Objectives

- **Motivation and Rationale**
  - One of the most important components of a fracking fluid is the viscosity modifying agent(s), which prevents settling and non-homogenous dispersion of proppant and provide a strong driving force on proppant to follow the fluid into cracks, fractures, and fissures.
  - Currently, the lack of effective, reliable viscosifiers is a critical limiting factor causing sub-optimal permeability increases and relatively low productivity index in shale reservoirs even when other steps of hydraulic fracturing are successfully executed.
- **Project Goals/Objectives**
  - This project is aimed at addressing the limitations of existing viscosity modifiers and focuses on the development of dynamic binary complexes to achieve super-adjustable, reversible viscosities and the implementation and wide-spread utilization of these novel viscosifiers in hydraulic fracturing fluids.
  - The project seeks to mature the Technology Readiness Level (TRL) of this concept from TRL 2-3 to TRL 5-6.

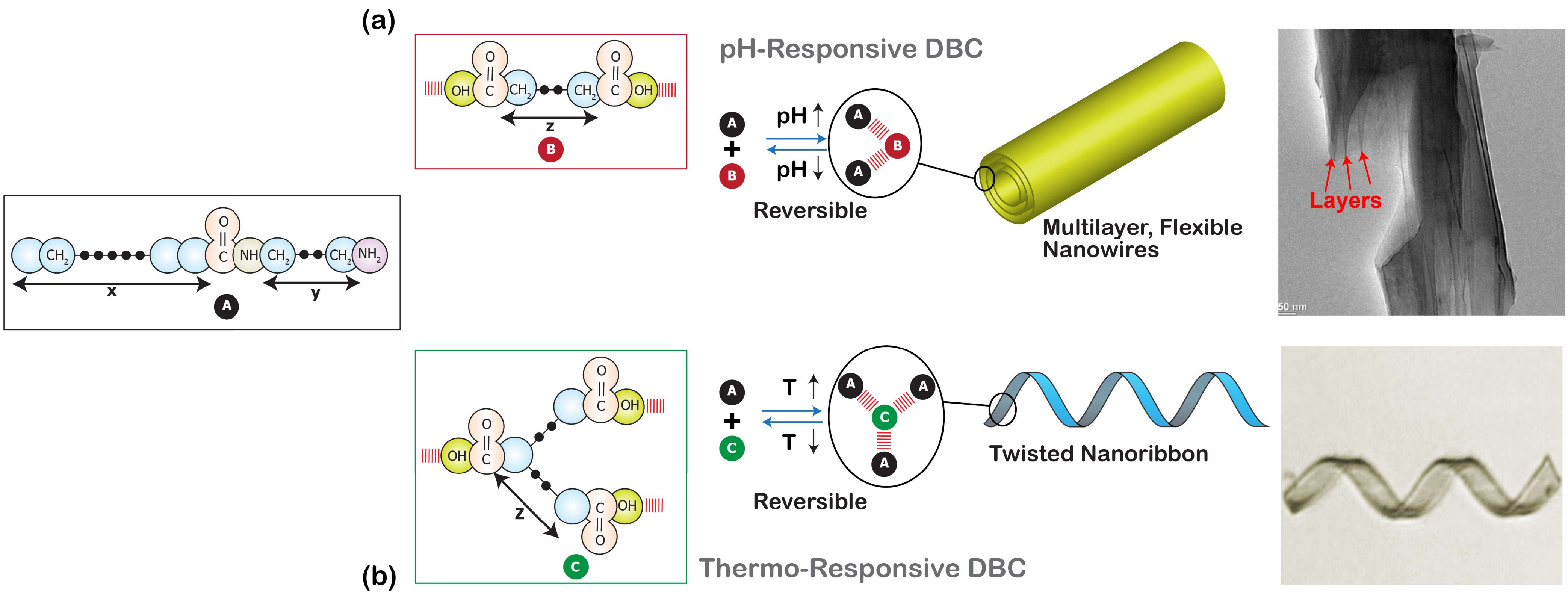
Project Schedule



Current State-of-Art in Hydraulic Fracturing Fluids

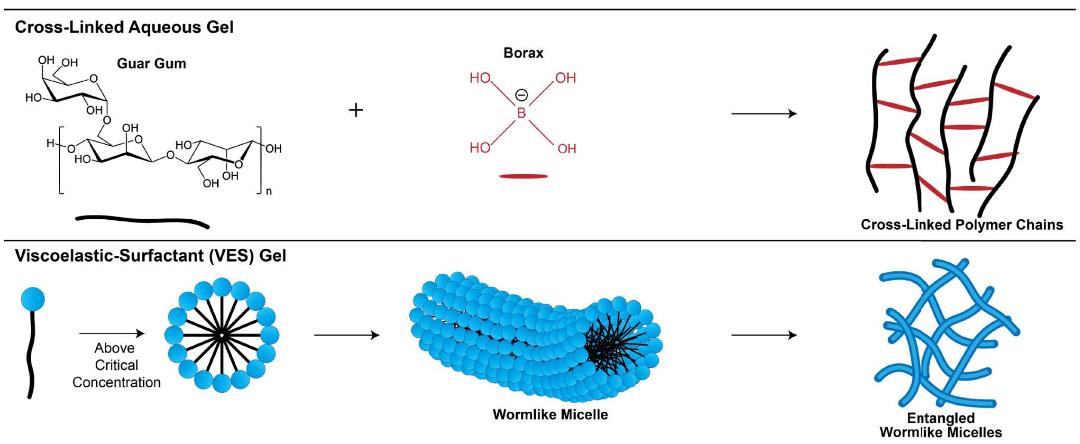
	Viscosity	Advantages	Disadvantages/Limitations
Water frac	2–5 cP	• Inexpensive • Insensitive to salinity	• Requires high pump rates • Poor proppant transport • Narrow fracture width
Linear aqueous gels	10-30 cP	• Environmentally friendly • Support transport of medium-sized proppants	• Not re-usable • Somehow narrow fracture width • Some residue leftover in fractures
Cross-linked aqueous gels	100-1000 cP	• Wide fracture width • Reduced fluid loss • Enhanced proppant transport	• Not re-usable • Corrosive/toxic breakers • Fracture damage by residues
Aqueous viscoelastic surfactant (VES)-based fluids	100-1000 cP	• Wide fracture width • Enhanced proppant transport • No residue leftover in fractures	• High-cost • Poor temperature/salt tolerance • High volume of fluid leak-off
Foam fluids	10-100 cP	• Very low fluid loss • Mediocre proppant transport • Reduced environmental impact	• High-cost of gas • Gas availability • Depressurization damage in fractures
Gelled oil-based fluids	50-1000 cP	• Compatible with all formations • Lower formation damage	• Gelling and clogging problems • Higher cost • More toxic than water-based systems

Smart Viscosity Modifying Systems based on DBCs

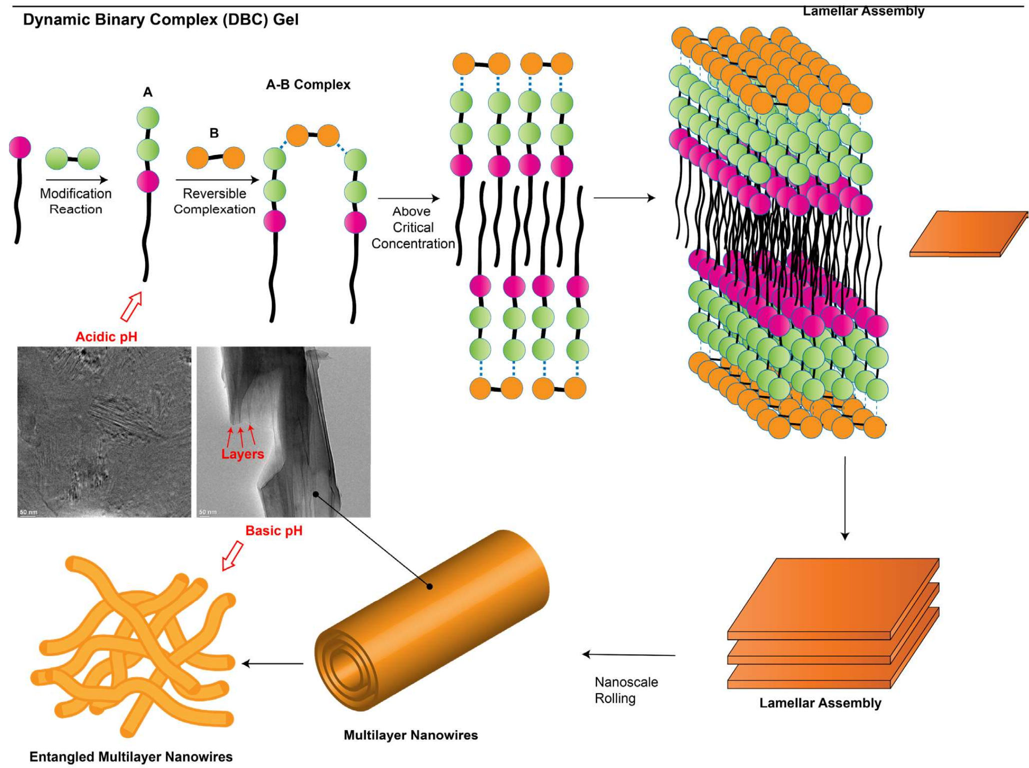


Uniqueness and Novelty

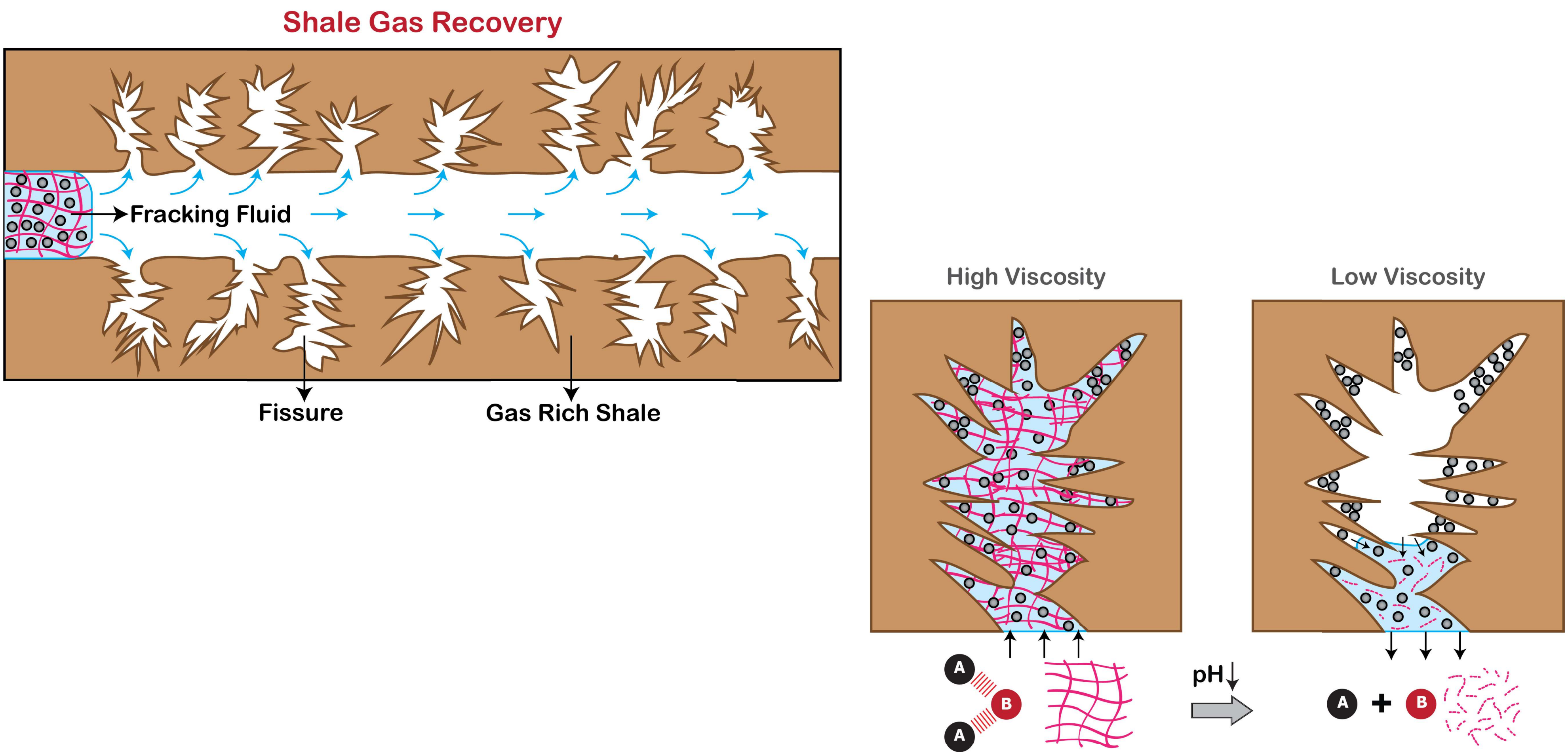
Current Viscosity Modifiers



Proposed, Novel Viscosity Modifiers

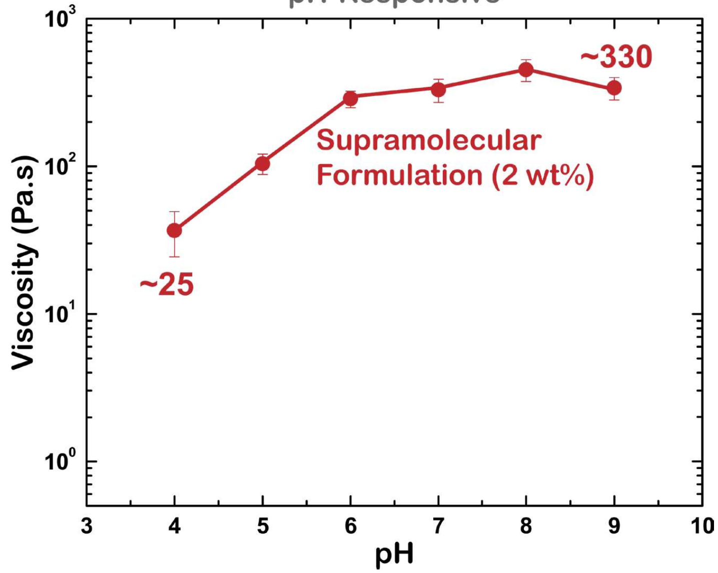


Concept of Utilizing DBCs in Hydraulic Fracturing



Significant Results

pH-Responsive



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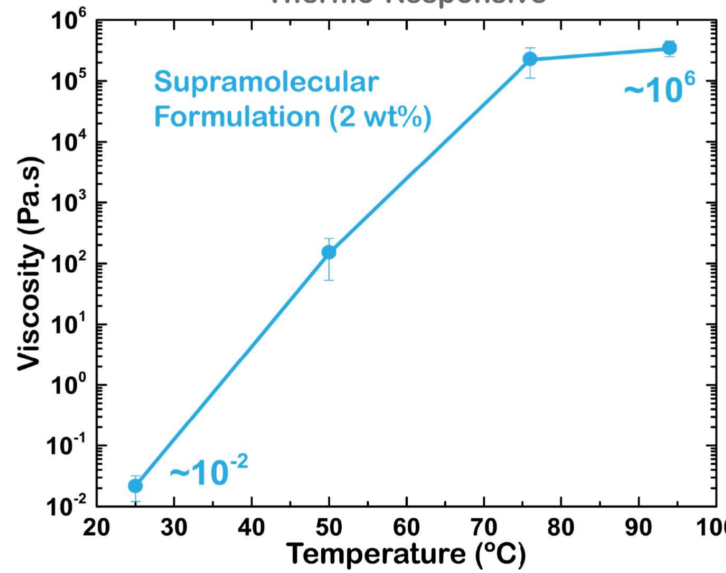
Thermo-Responsive



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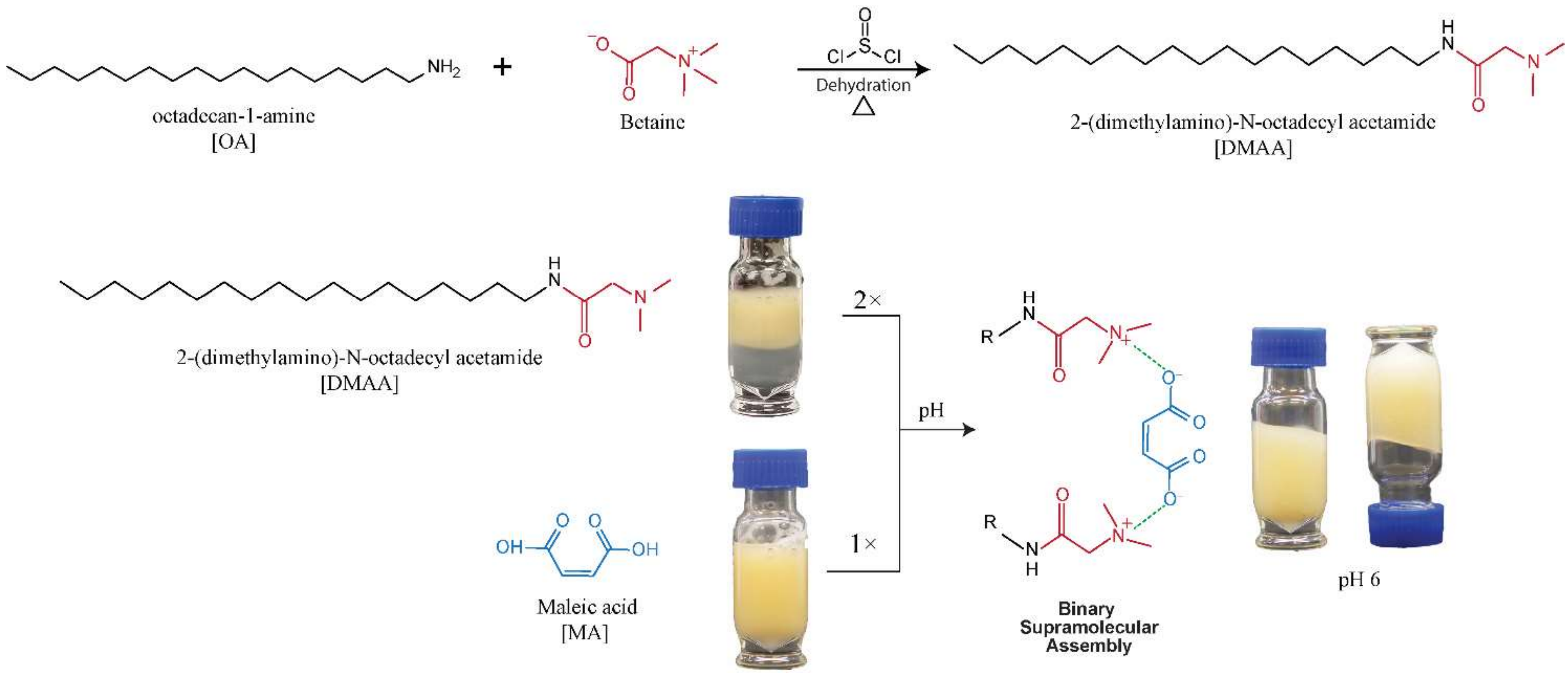
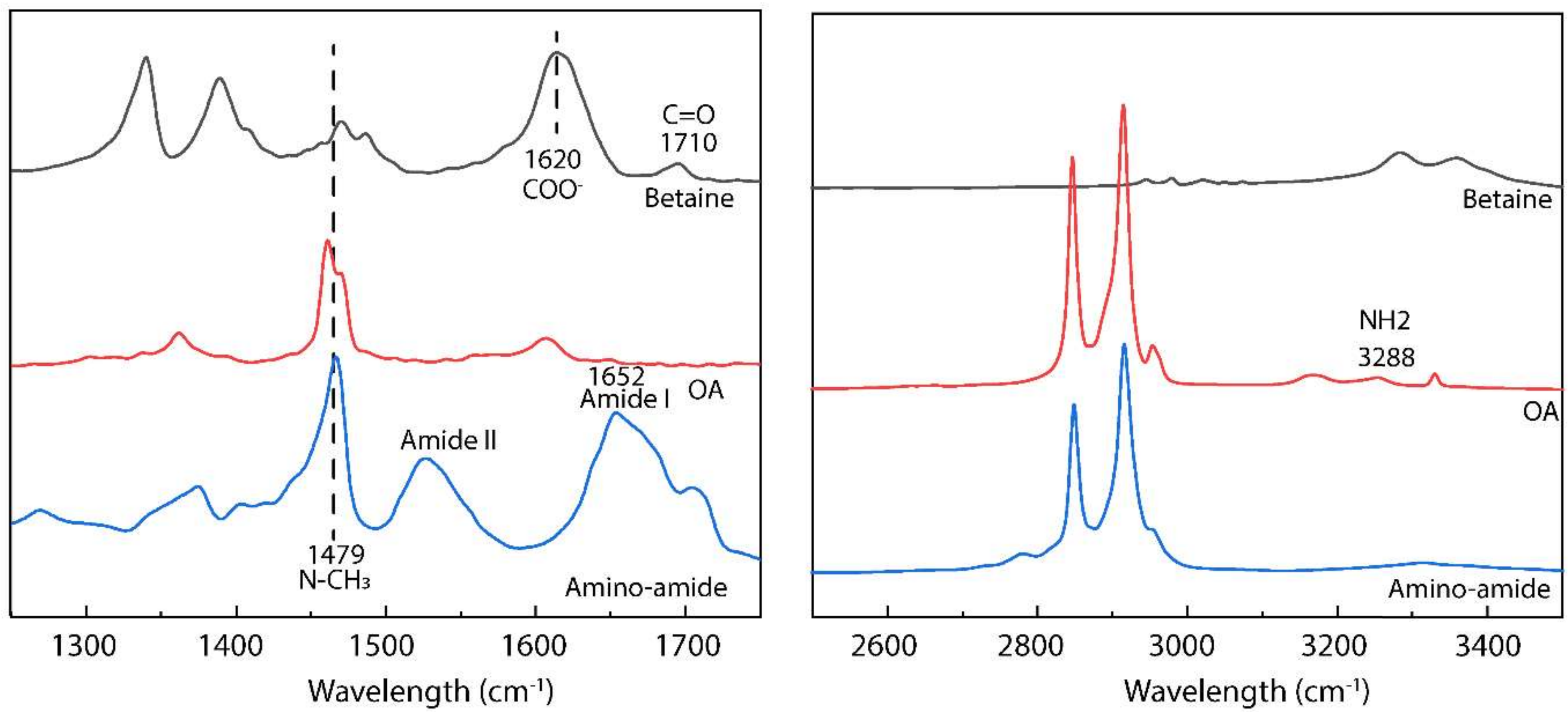
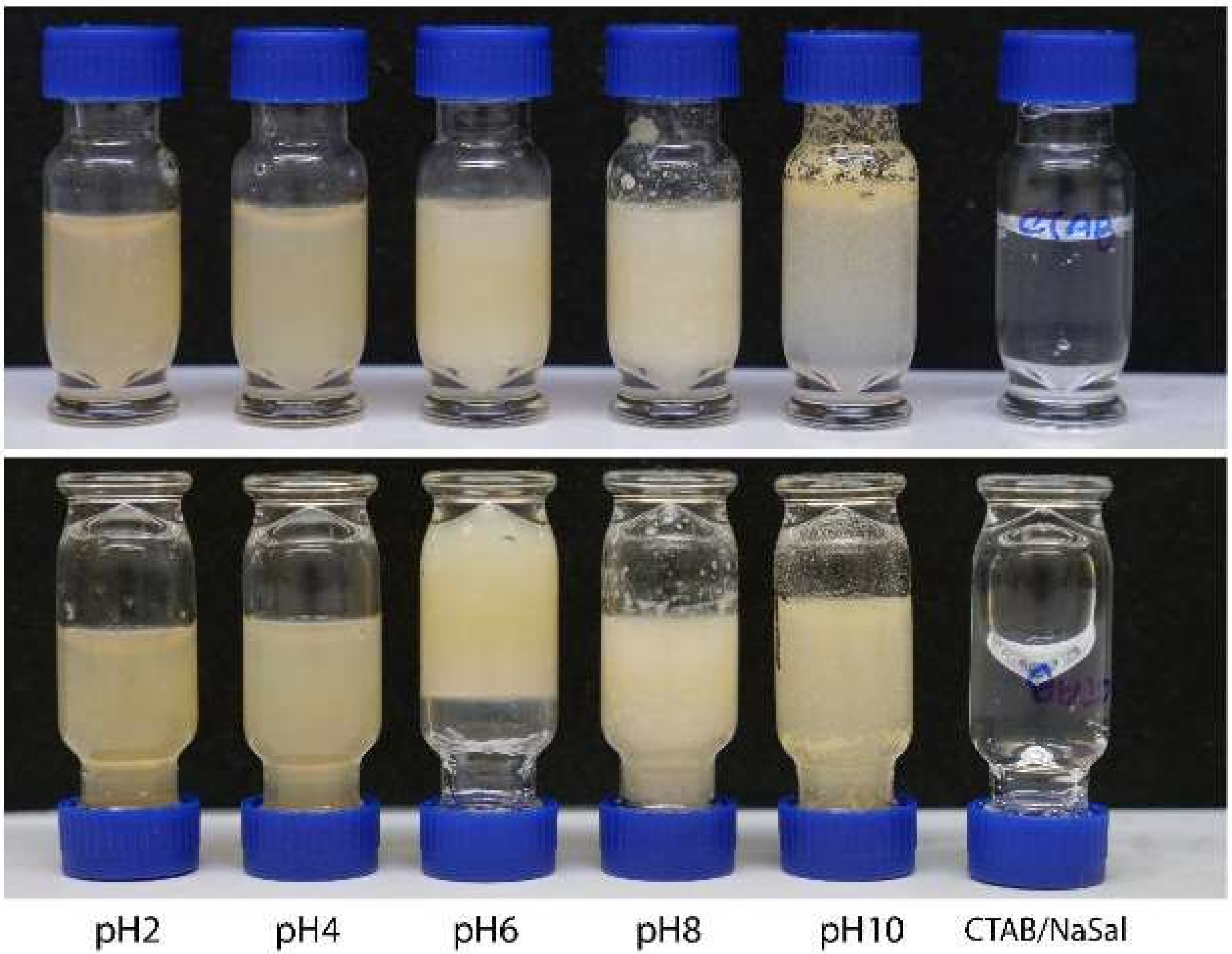
Significant Results: Synthesis Route



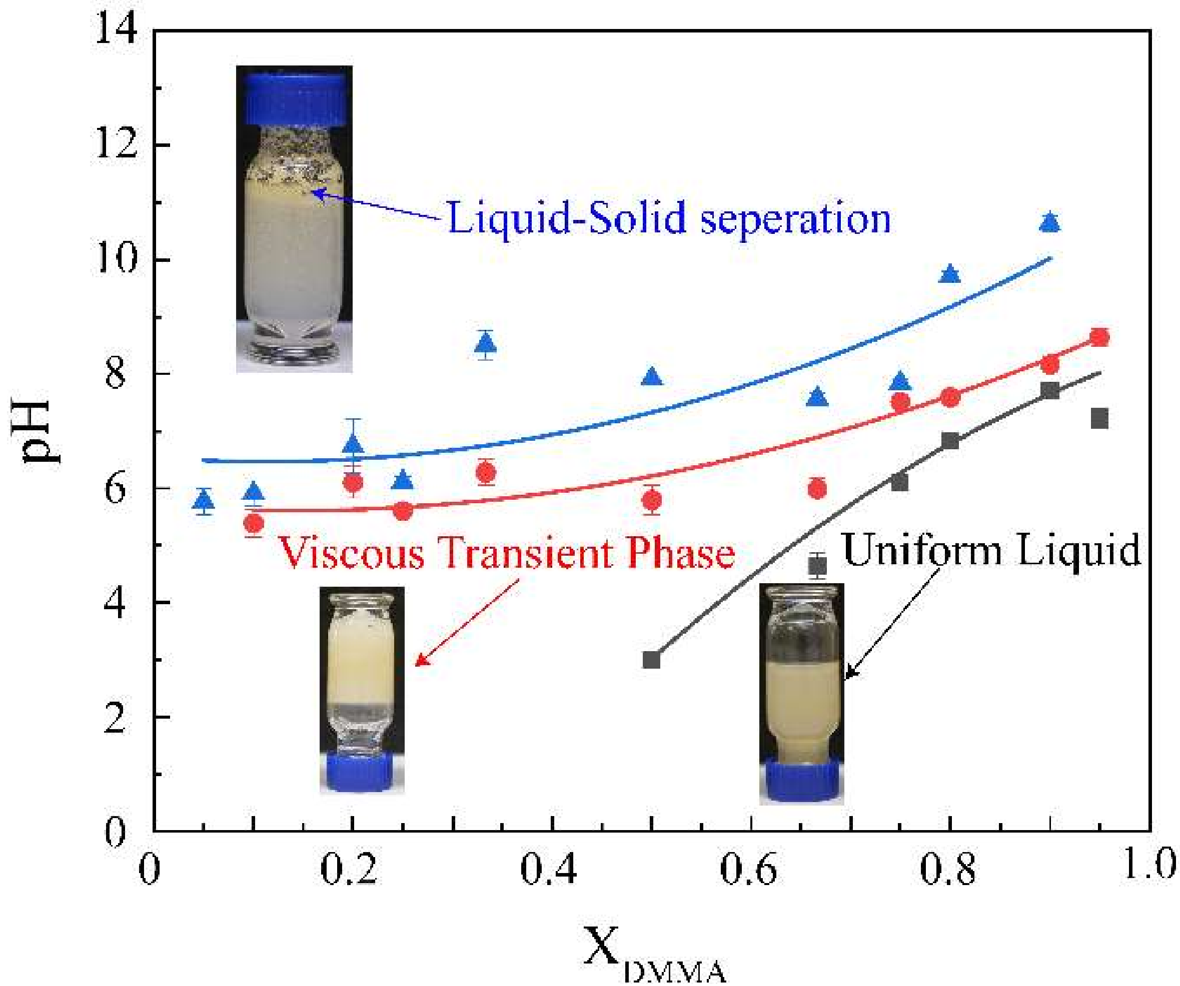
Significant Results: Chemical Analysis



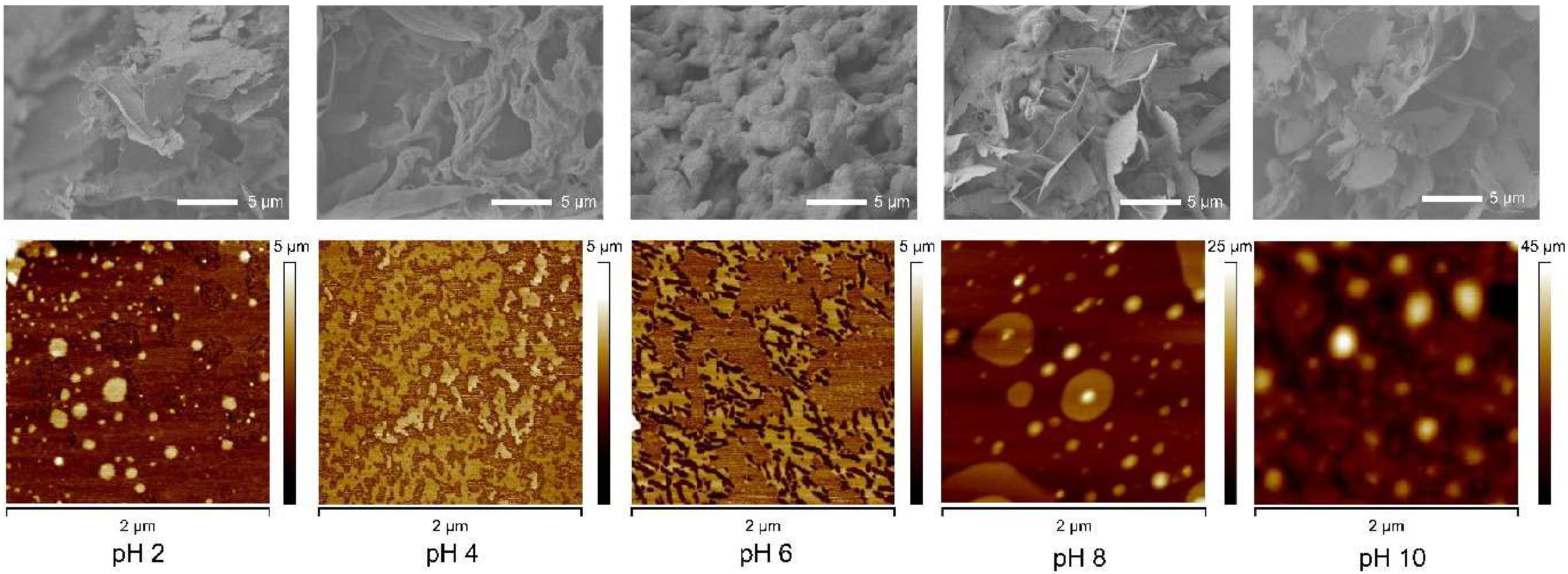
Significant Results: Qualitative Flow Behavior



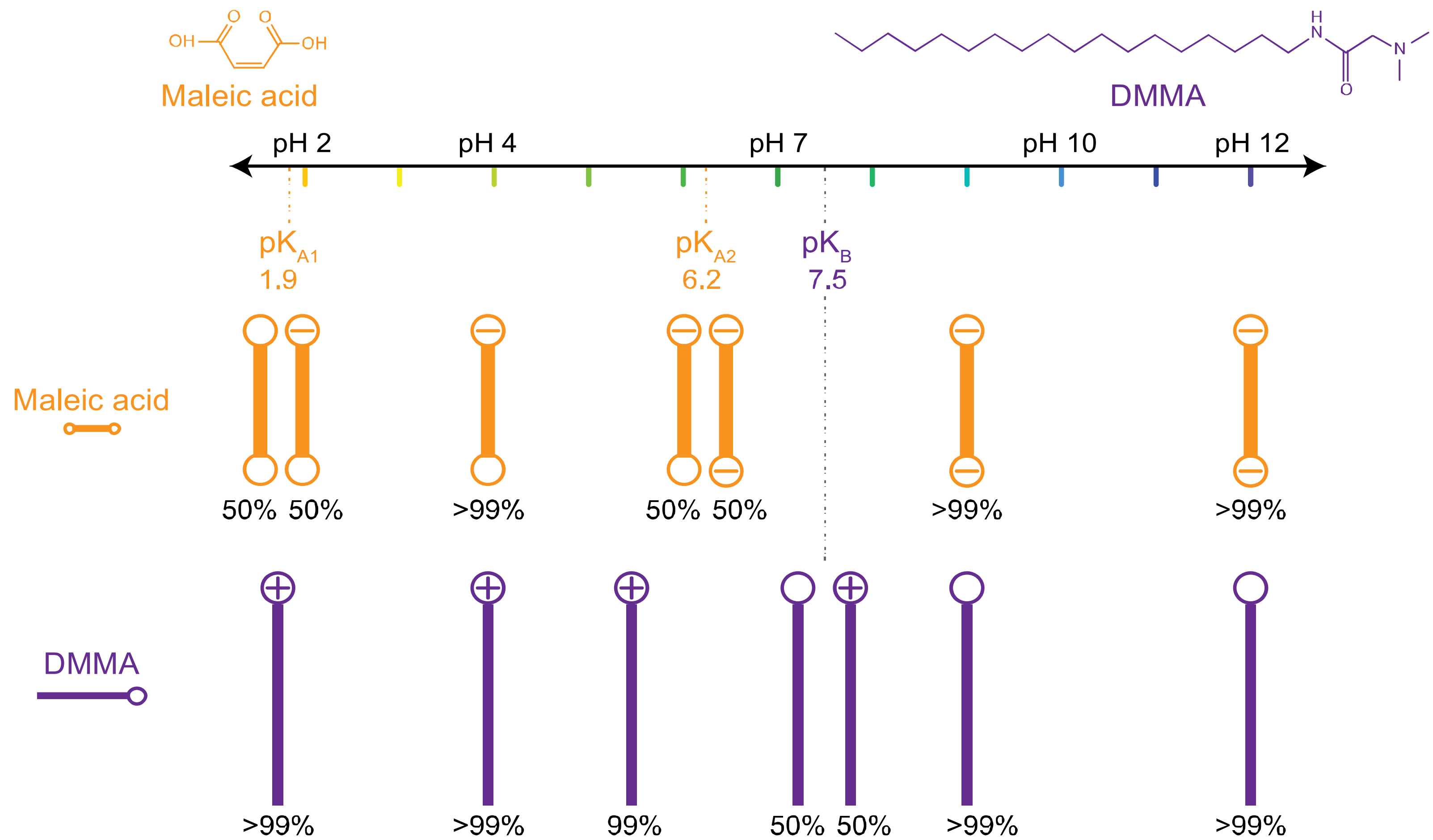
Significant Results: Phase Diagram



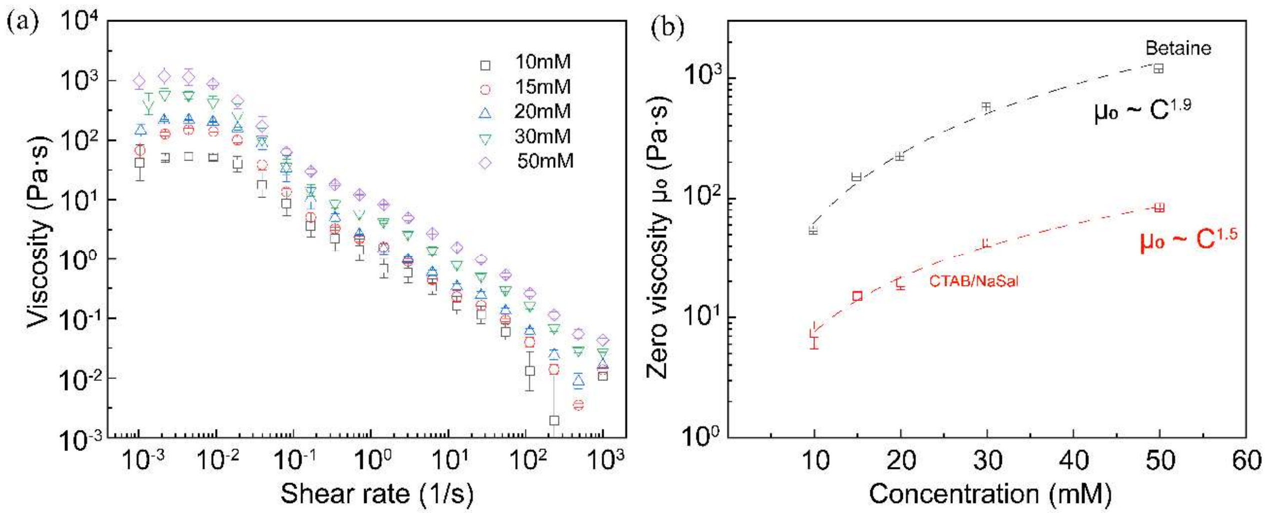
Significant Results: Nanostructural Details

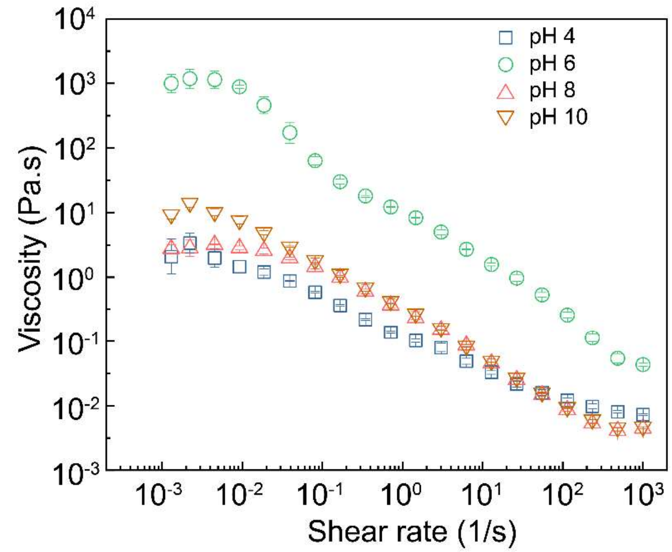


Significant Results: Mechanism of Responsiveness

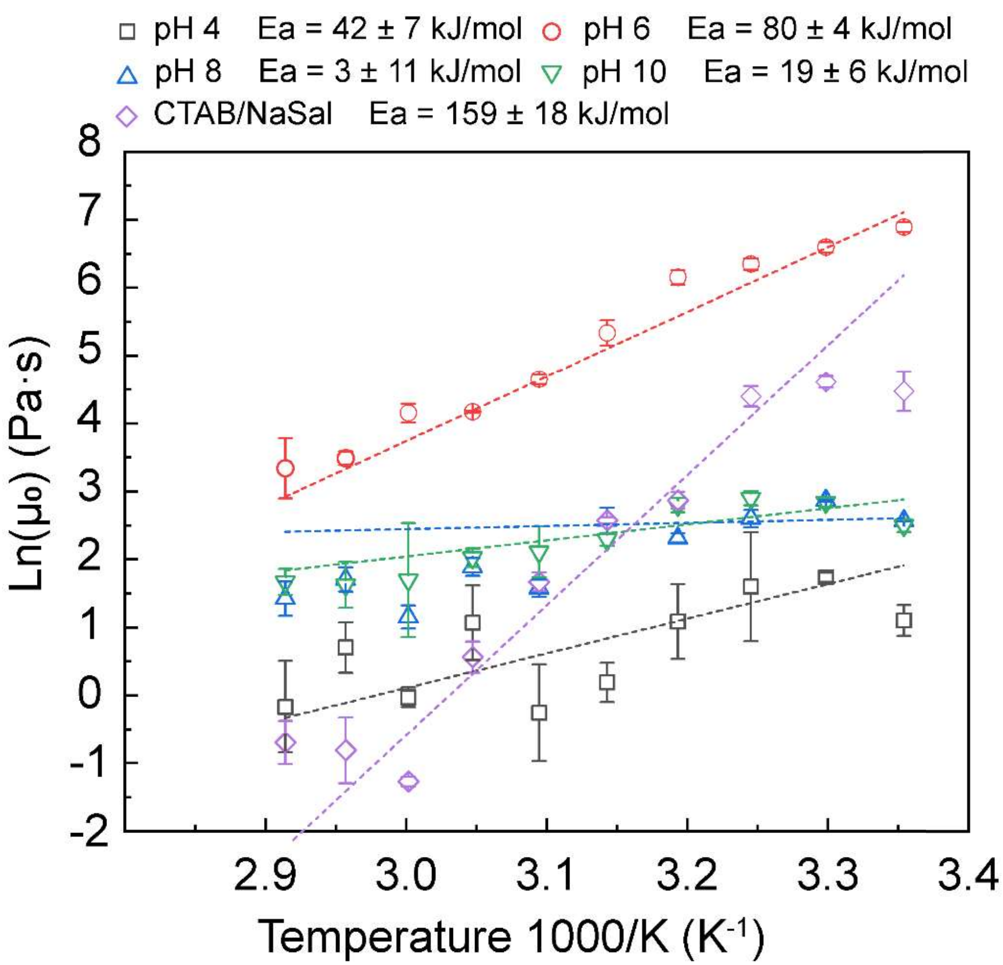


Significant Results: Rheological Characteristics

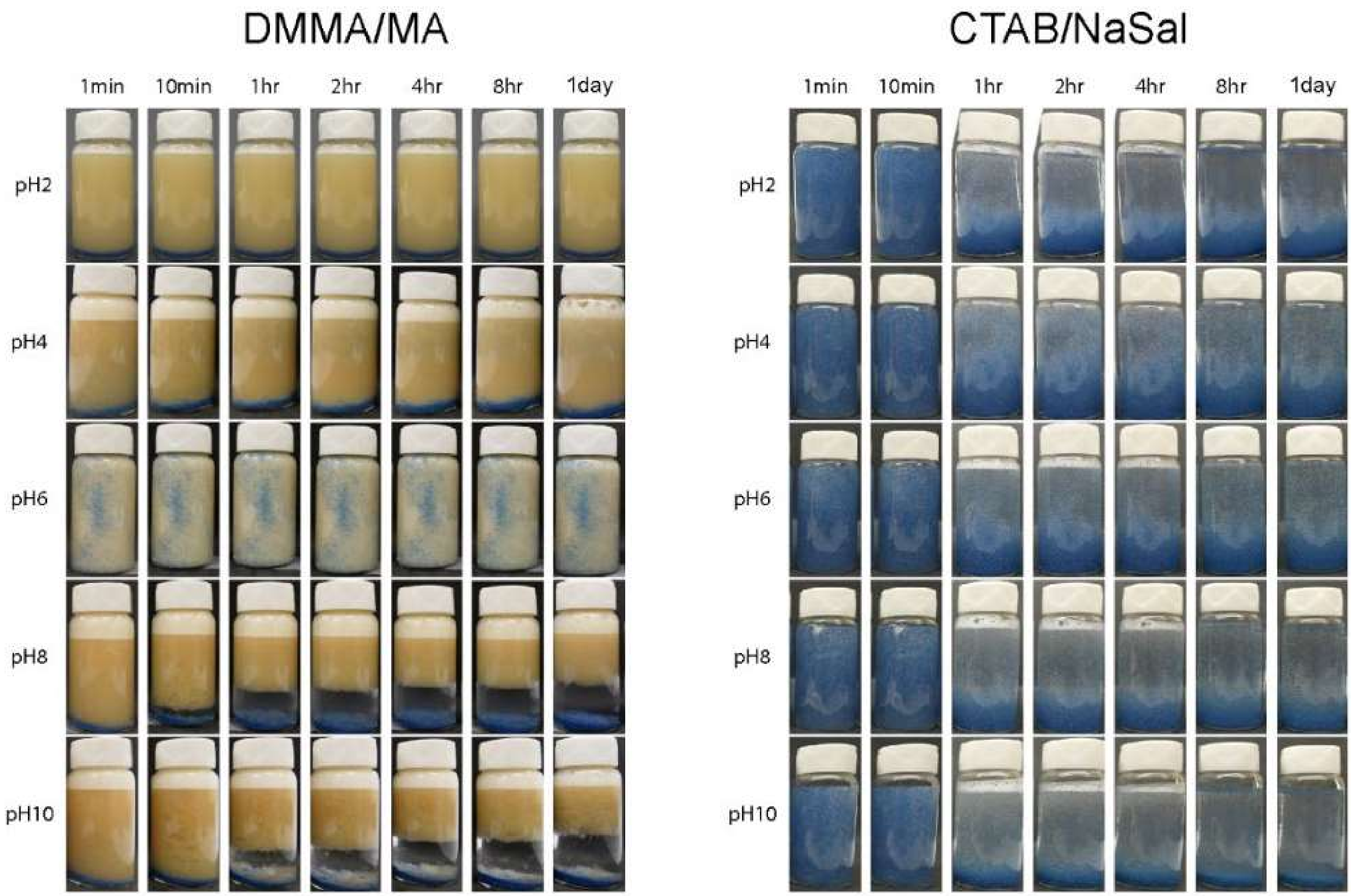




Significant Results: Temperature Sensitivity

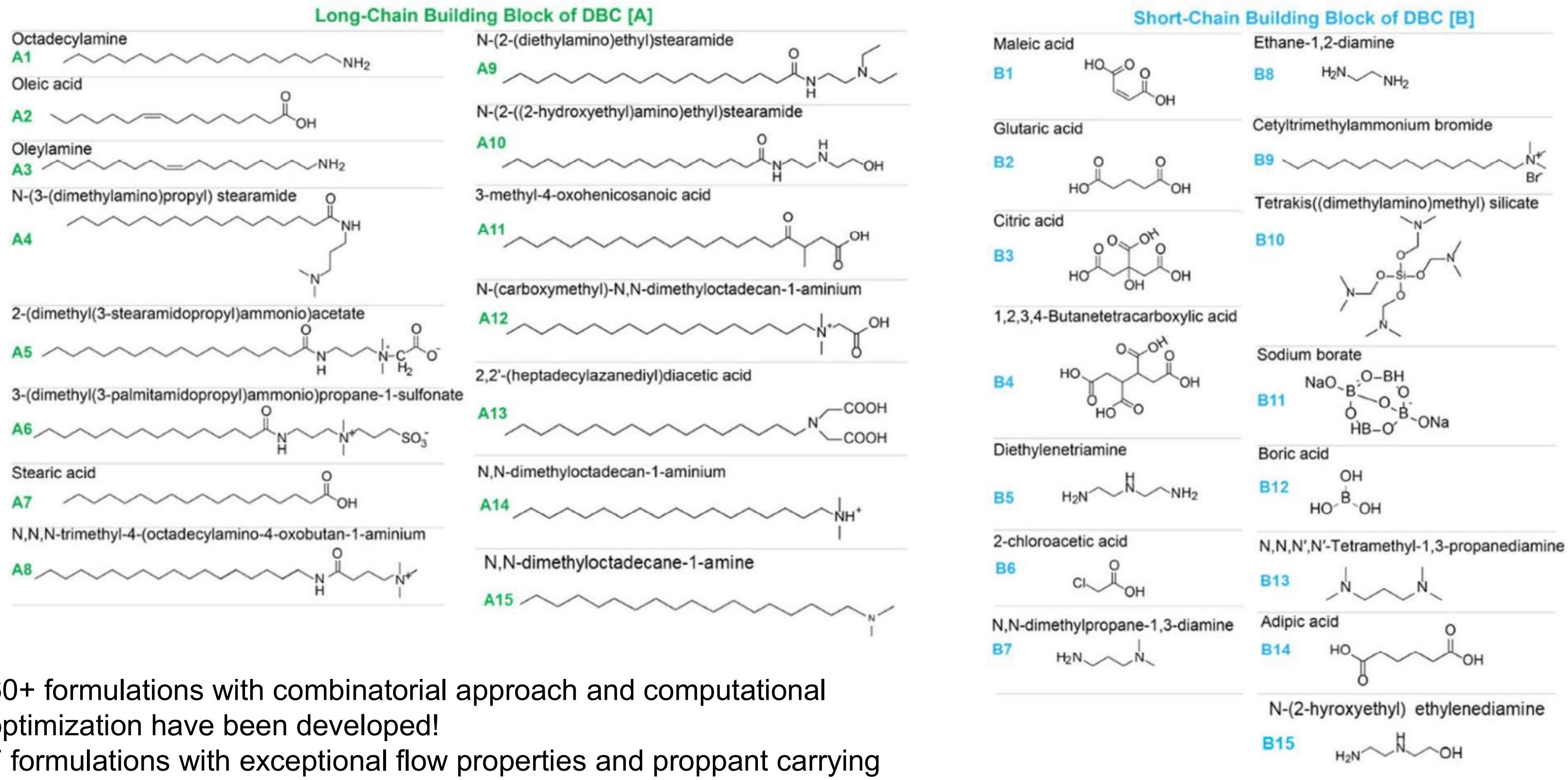


Significant Findings: Proppant Carrying Capabity



Synopsis of Key Findings

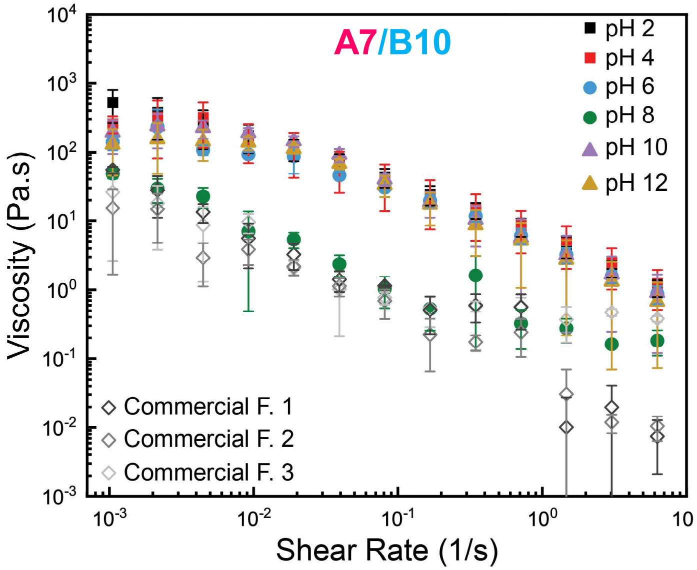
$$nA + mB \leftrightarrows DBC$$

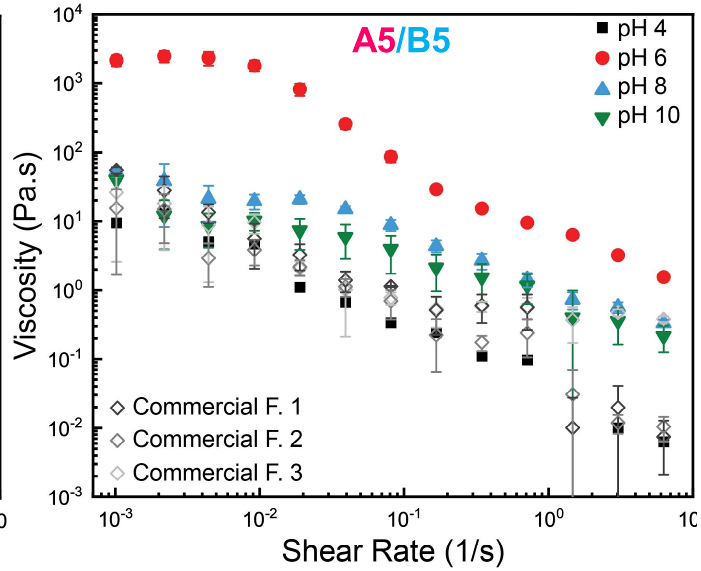


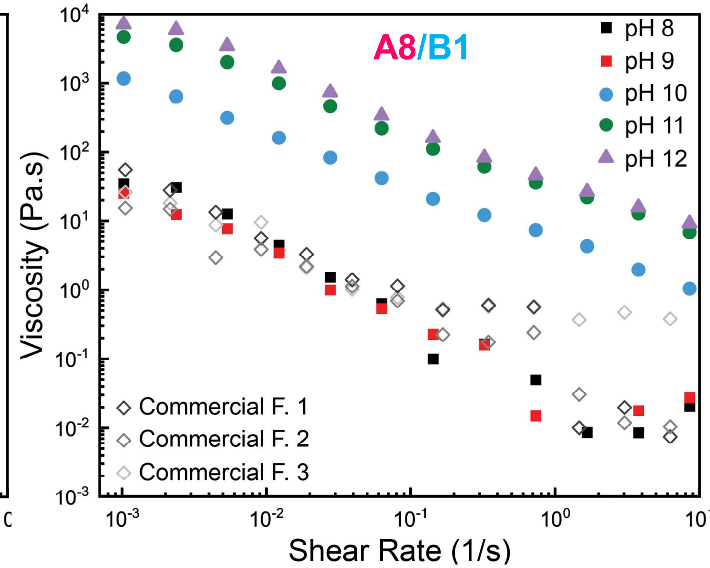
- 60+ formulations with combinatorial approach and computational optimization have been developed!
- 7 formulations with exceptional flow properties and proppant carrying ability have been identified.

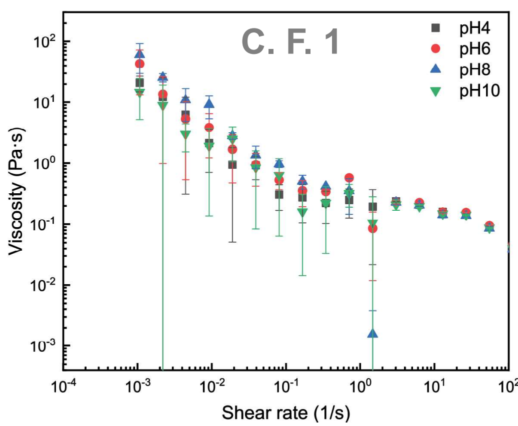
Progress and Current Status of Project

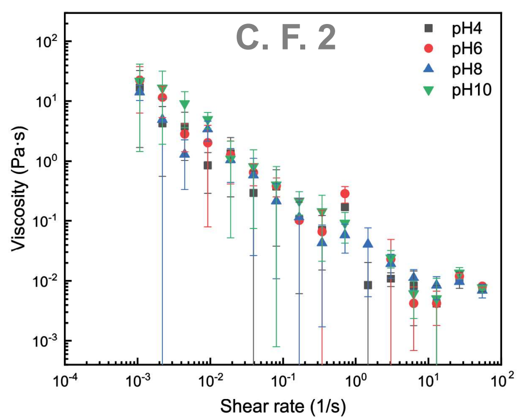
pH-Adjustability of DBC Viscosifiers









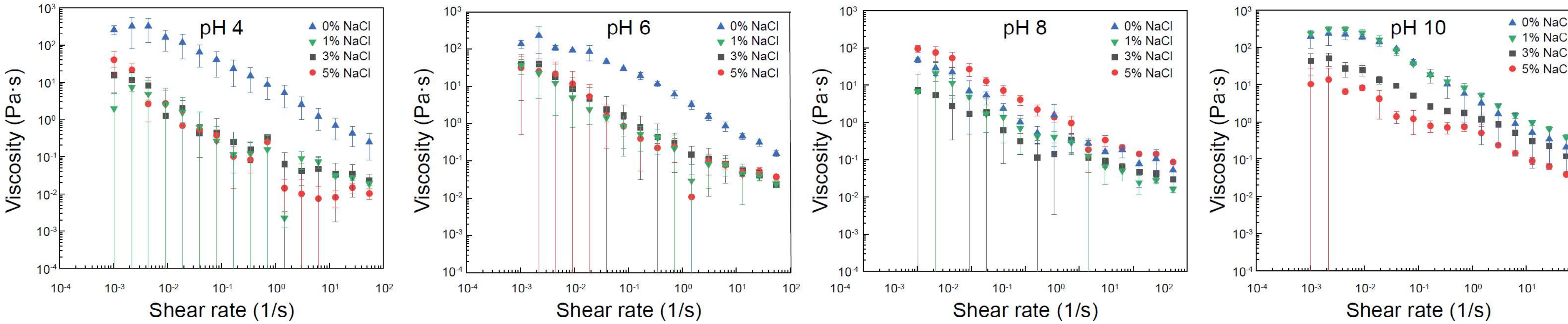


- *pH Adjustability for A7/B10*: 228-fold
- *pH Adjustability for A5/B5*: 1624-fold
- *pH Adjustability for A8/B1*: 284-fold
- *pH Adjustability for CF1*: ~1-3 fold
- *pH Adjustability for CF2*: ~1-3 fold

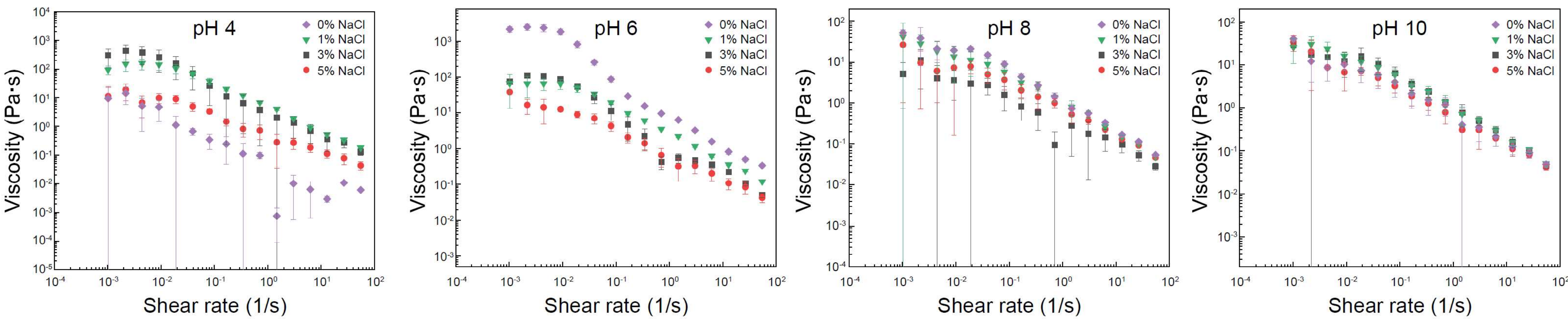
Progress and Current Status of Project

Effect of Salt on Viscosity of DBCs

A7/B10



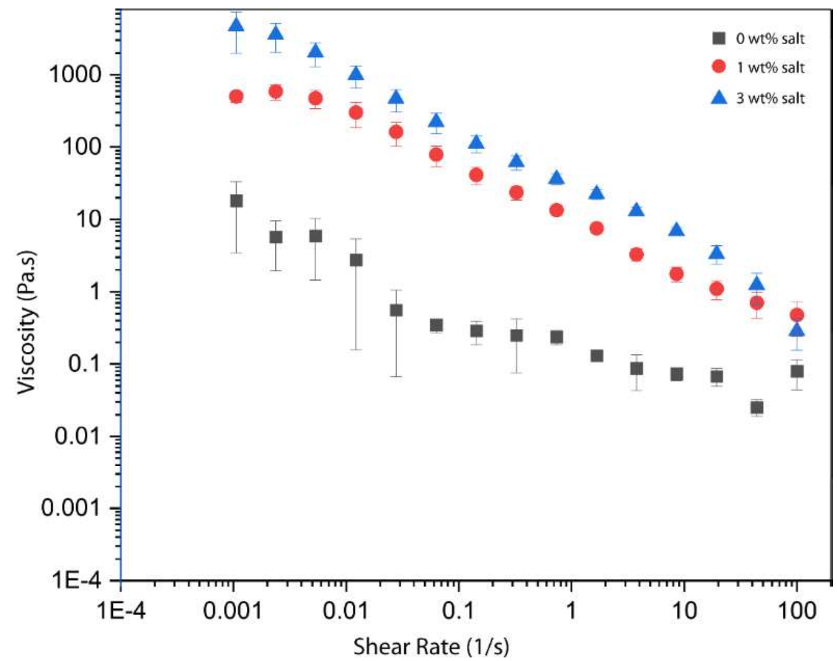
A5/B5



Progress and Current Status of Project

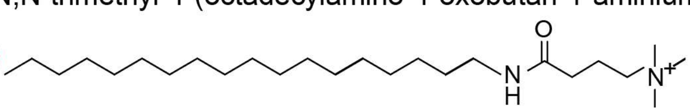
Salt-Induced Viscosification and Gelling of DBC A8/B1 !

DBC A8/B1



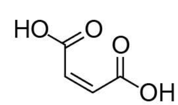
N,N,N-trimethyl-4-(octadecylamino-4-oxobutan-1-aminium

A8

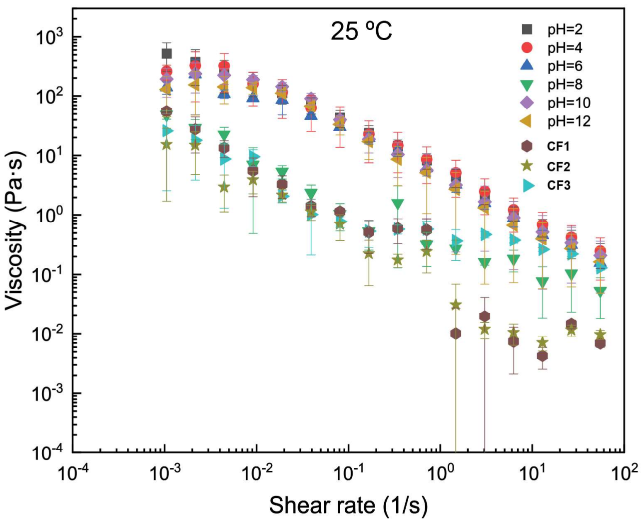


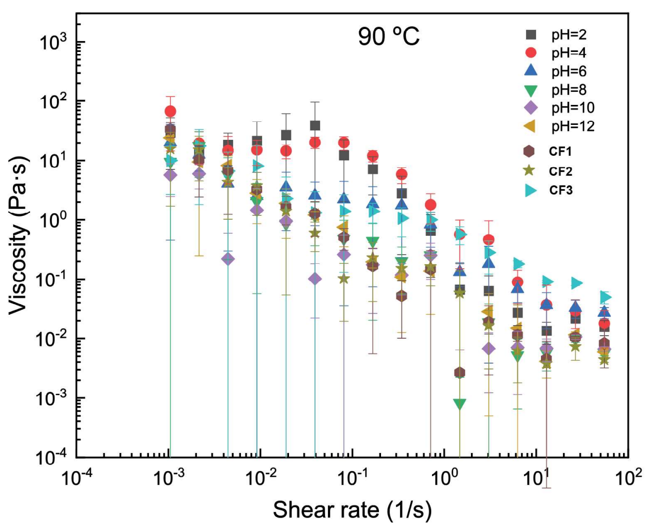
Maleic acid

B1



Progress and Current Status of Project

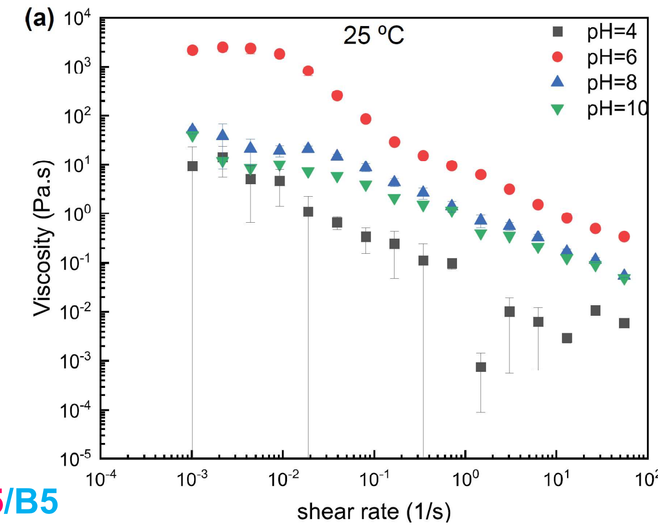


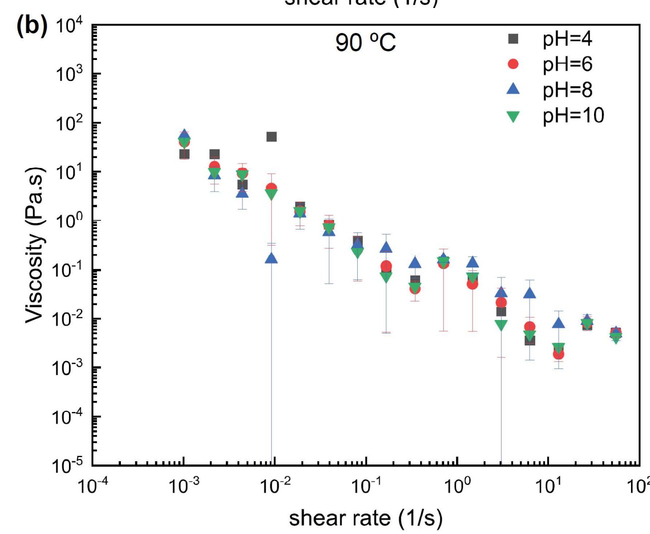


A7/B10

Effect of Temperature on Viscosity of DBCs

A5/B5





Progress and Current Status of Project

Characteristics of "a Dream" Fracking Fluid:

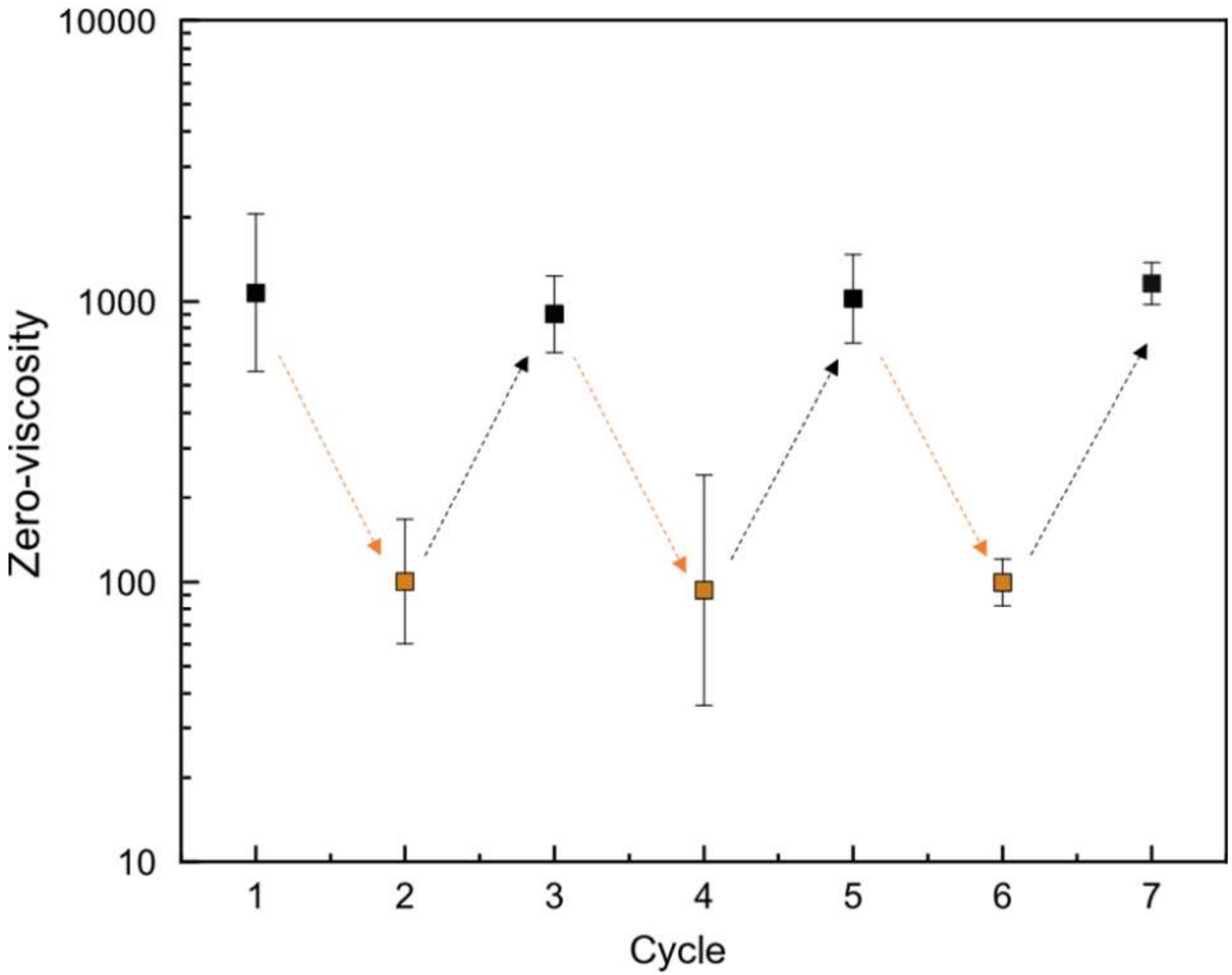
- Superior proppant carrying capacity at elevated temperatures
- Superior proppant carrying capacity at high salinity
- High adjustability to precisely control proppant transport and deposition

DBC A8/B1

Formulation	Proppant Settling Time
CF1 @25 °C	8 min
CF2 @25 °C	< 30 sec
CF3 @25 °C	~ 1 min
DBC A8/B1 @25 °C	~ 3 days
DBC A5/B5 @25 °C	~ 2 days
DBC A7/B10 @25 °C	~ 1 day
CF1 @90 °C	3 min
CF2 @90 °C	< 30 sec
CF3 @90 °C	< 30 sec
DBC A8/B1 @90 °C	**~ 8 hr**
DBC A5/B5 @90 °C	90 sec
DBC A7/B10 @90 °C	~ **15 min**

Progress and Current Status of Project: Reusability

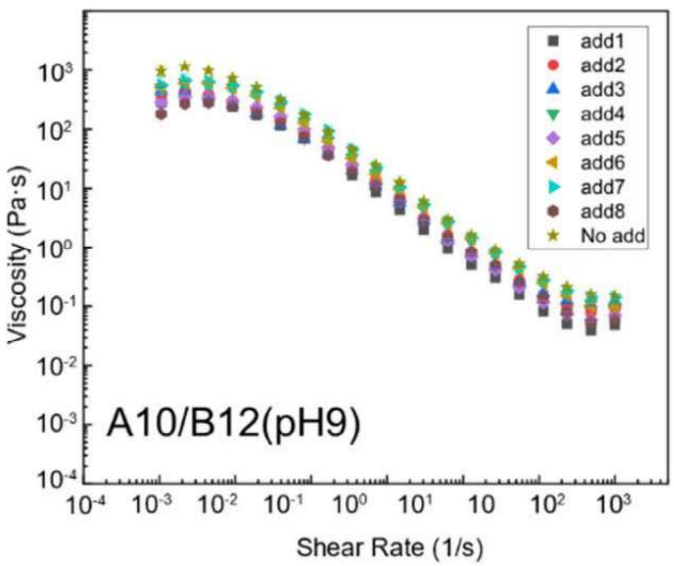
DBC A7/B15

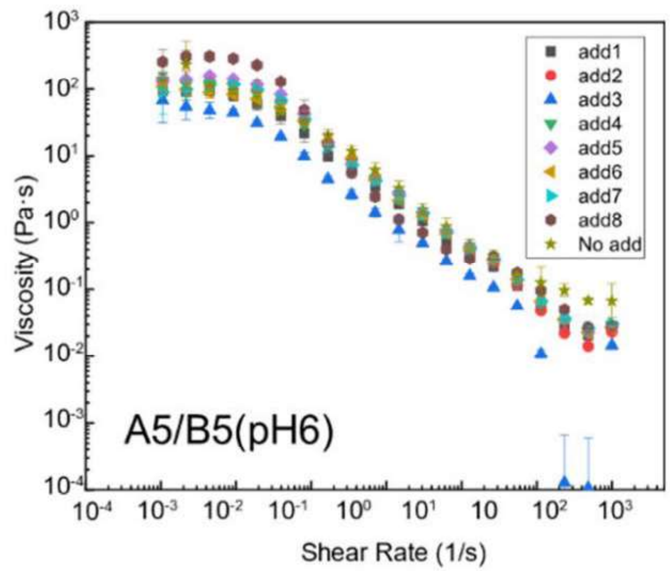


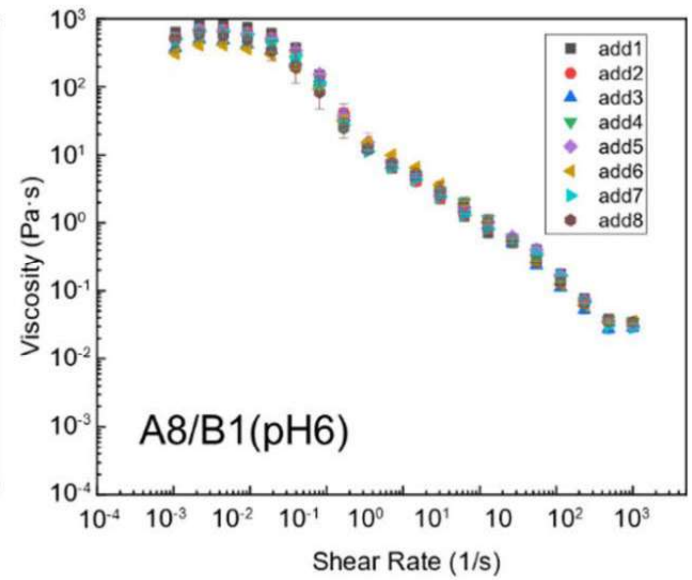
Progress and Current Status of Project: Compatibility

Additive #	Additive ID	Function	Concentration
1	Glutaraldehyde	Biocide	0.0084%
2	Ammonium persulfate	Breaker	0.0045%
3	Choline chloride	Clay stabilizer	0.0091%
4	Isopropanol	Corrosion inhibitor	0.0016%
5	Ethylene glycol	Friction reducer	0.0061%
6	Citric acid	Iron control	0.0017%
7	Isopropanol	Emulsion preventer	0.0035%
8	Sodium acrylate	Scale inhibitor	0.0024%
9	All combined	All combined	0.0373%

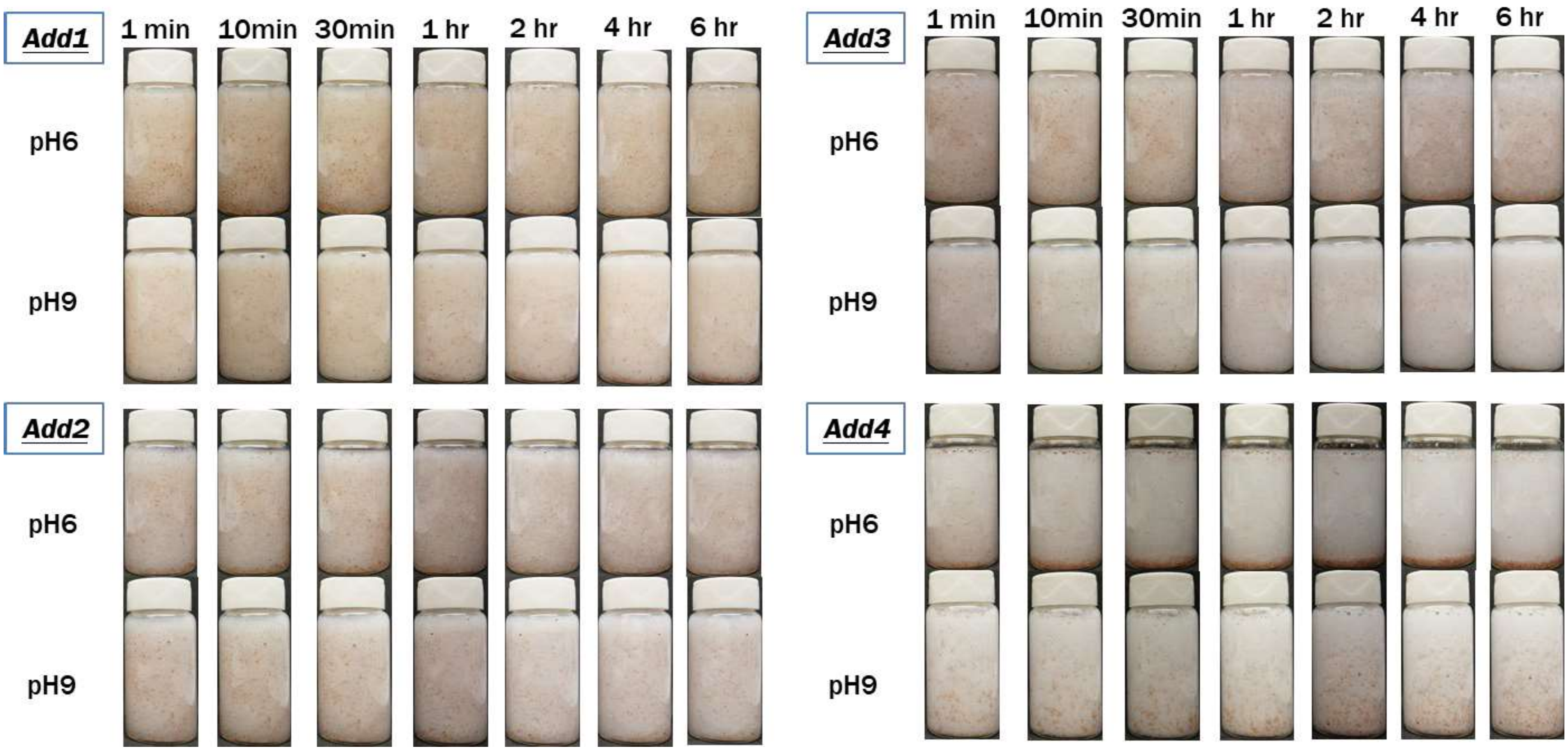
Progress and Current Status of Project: Compatibility





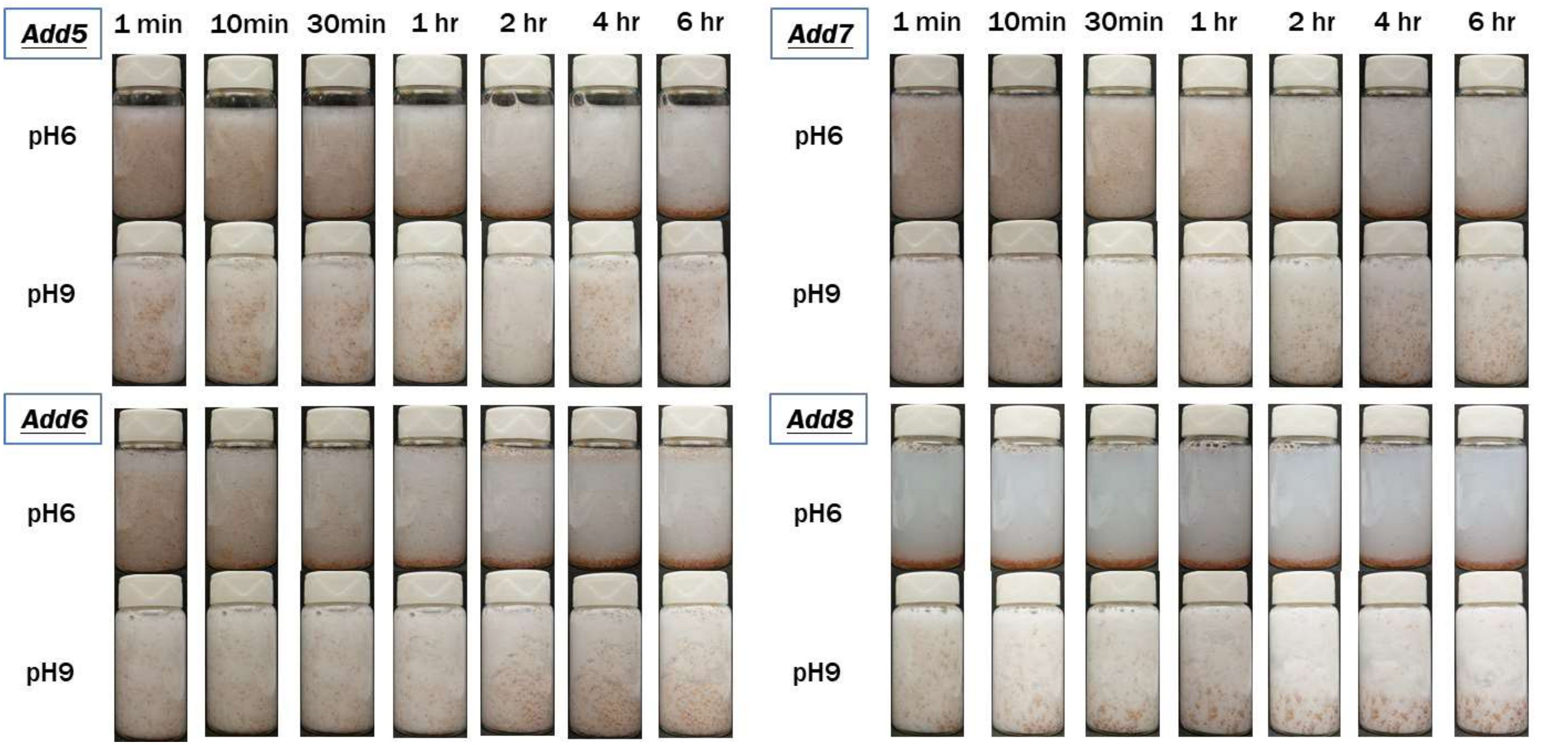


Progress and Current Status of Project: Compatibility



DBC A10/B12

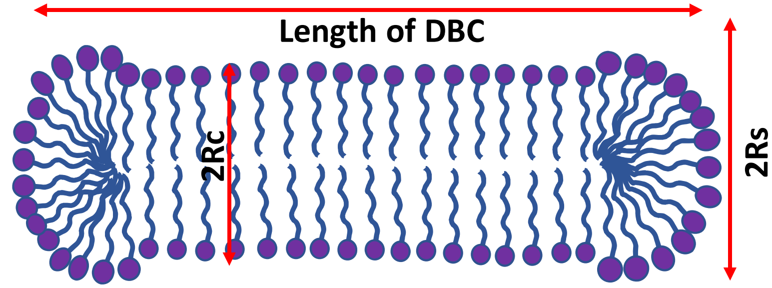
Progress and Current Status of Project: Compatibility



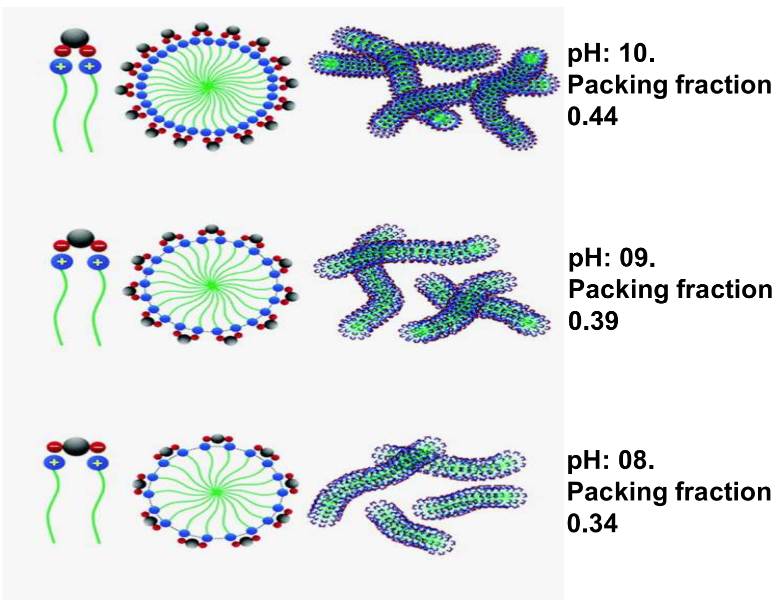
DBC A10/B12

Progress and Current Status of Project

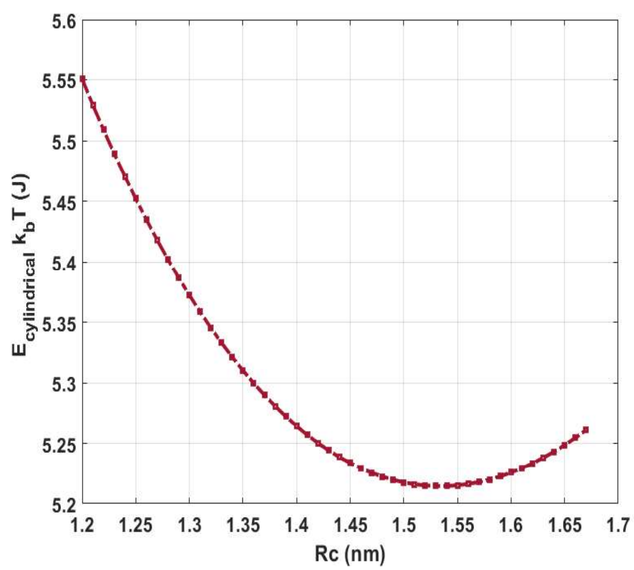
- A thermodynamic model has been developed by considering all the components of the free energy in a cylindrical DBCs.
- The model is able to predict packing fraction of the micelles in response to varying pH.
- Equilibrium dimensions are used to predict the length of DBCs. This length is used as an input for the rheology model discussed in the next slide.



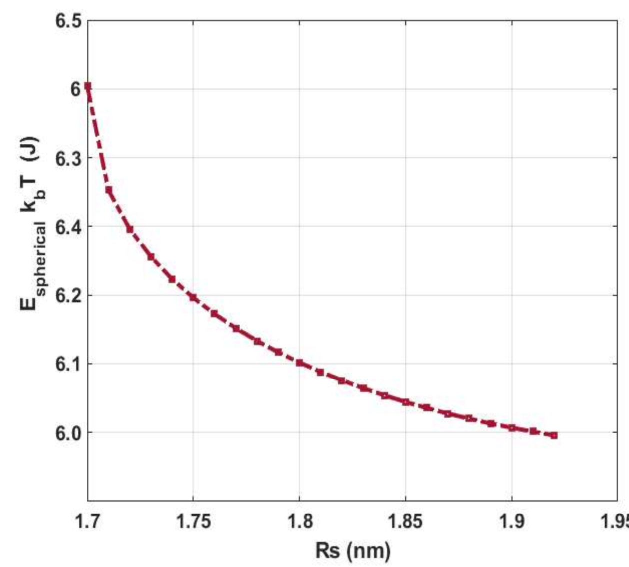
Size considerations of the thermodynamic model.



The altering packing fraction in DBC in response to different pH.



The change of free energy with varying Rc.

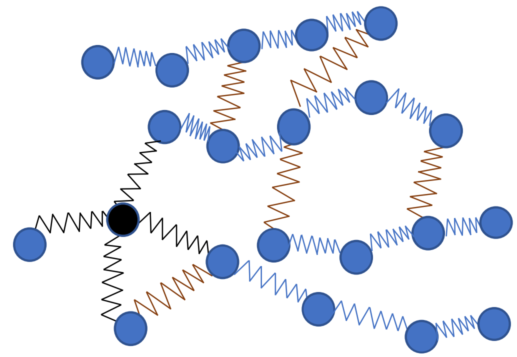


The change of free energy with varying Rs.

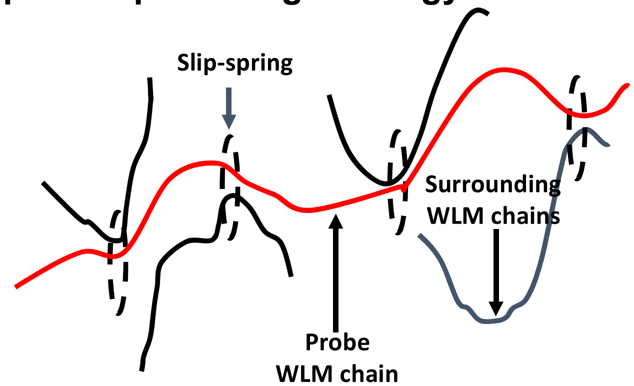
Progress and Current Status of Project

Novel coarse-grained Brownian dynamics(BD)/kinetic Monte Carlo (kMc) model developed for predicting rheology of DBCs

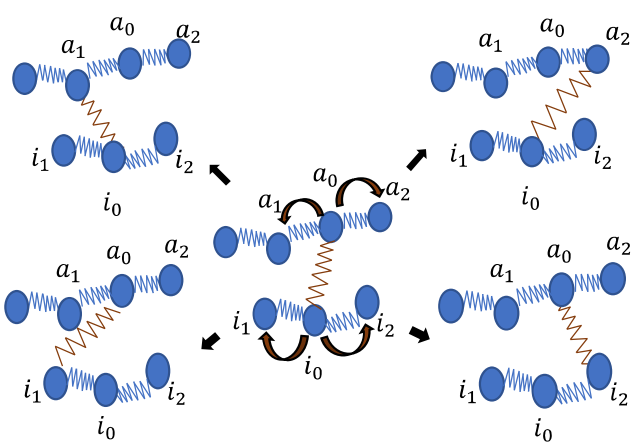
- In this model, DBC chains are represented by springs and beads while the entanglements are represented by slip-springs.
- Simulation of stress relaxation is modeled through mechanisms like reptation, contour length fluctuations, constraint release, and dynamic union and scission, which are executed by the kMC method using the standard metropolis algorithm.
- The kMC algorithm simulates the reptation mechanism by the process of slip spring hopping.



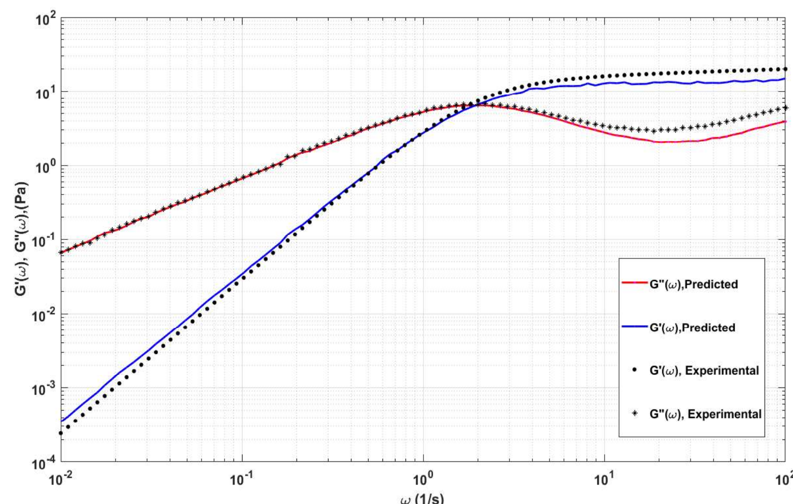
Coarse-grained representation of WLM melt



Entanglements in WLMs modeled with slip springs



Considered kMC events to model reptation in WLMs



Validation of model with experimental data

The Coarse grained BD/kMC rheology model simulations are compatible with the experimental data, which demonstrates that reptation, constraint release, contour length fluctuations, and dynamic union and scission are the major relaxation mechanisms in the WLMS.

Progress and Current Status of Project

Impact of using VES fluids

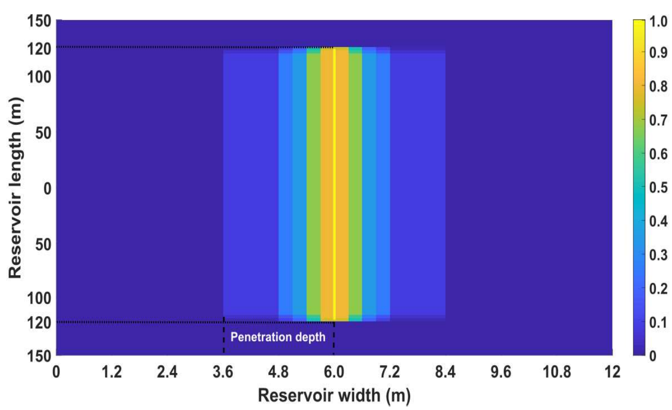
A three-dimensional, multiphase production simulator is developed to predict the production from a reservoir, hydraulic fractured with VES fluids, by considering the impact of formation damage, fracture geometry, and fluid flowback.

Determine optimal viscosity

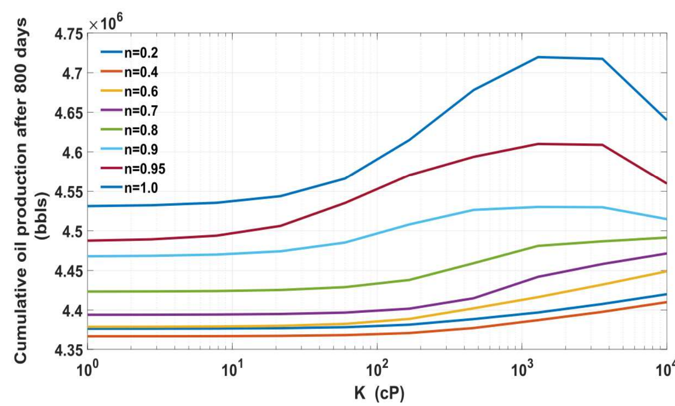
The production simulator is used to carry out the sensitivity analysis for determining the optimal viscosity of fracturing fluids, for a specific reservoir.

Obtaining a pumping schedule

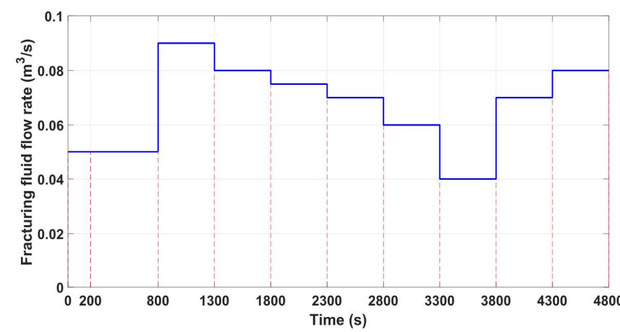
A closed-loop optimization problem is formulated and solved to obtain the optimum pumping schedule necessary for obtaining the final fracture geometry with uniform proppant concentration inside the hydraulic fractures.



The 2D view of the production simulator



Sensitivity analysis to determine optimal viscosity prediction



Optimal pumping schedule to attain target fracture geometry

Plans for Future Testing/Development/Commercialization

Scale-up and Commercialization

- As a first step in scale-up, **Incendium Technologies** has obtained kinetical parameters for reactions of the most promising three formulations.
- Pilot reactor has been built based on the kinetical parameters.
- The sourcing of raw materials for pilot scale production are being established.
- The energy consumption and operational costs is being monitored to be able to estimate the cost of novel viscosifiers.
- After confirming enhanced fracturing efficiency and pilot scale production, Incendium Technologies and **Eastman Chemicals** will establish agreements for large scale production.

Summary

- Novel gelling agents with super-adjustable viscosity have been developed.
- Nanoarchitecture of building blocks of DBCs can tuned to alter the target pH for stimuli-responsiveness
- DBCs have demonstrated high-tolerance against temperature.
- Salinity has a weak influence on the viscosity of DBCs.
- One particular formulation has been discovered to have increased viscosity with increasing salinity.
- DBCs have demonstrated exceptional ability to suspend proppants.
- Synergistic influence of viscosity and intermolecular interactions (DBC mesh adhering to proppant particles) are responsible for enhanced proppant stability.

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Appendix

Organizational Chart