Development of Nanoparticle-Stabilized Foams to Improve Performance of Water-less Hydraulic Fracturing

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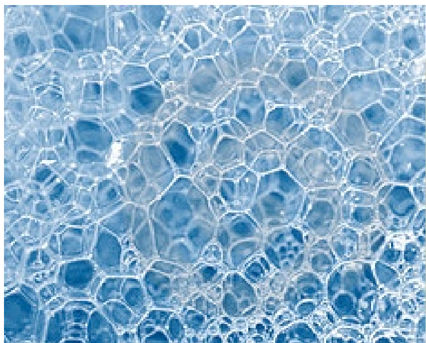
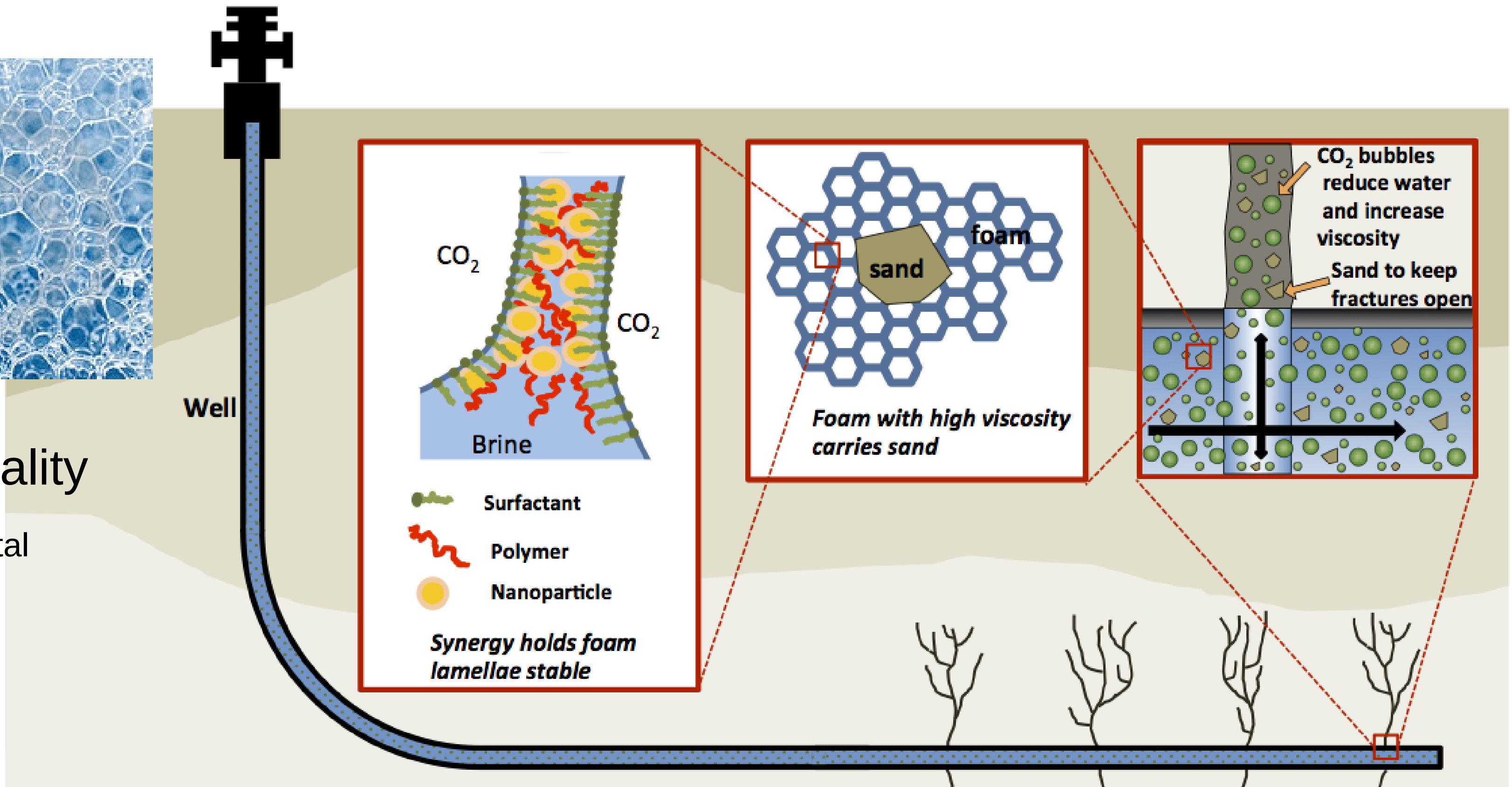
Goal: Establish Novel CO_2/water and N_2/water Ultra Dry Foams Frac Fluids to Reduce Water Consumption and Improve Performance



Foam quality

$=V_{gas}/V_{total}$



Water usage in hydraulic fracturing could be reduced by over 90% by using ultra-dry foams. The foams are stabilized using nanoparticles, surfactants and polymers.

Background and Motivation

- Drivers
  - Hydraulic fracturing essential technology for current, future hydrocarbon production
  - Unconventional oil and gas reservoir development requires
    - Dense well spacing
    - Many frac stages per well
- Standard base fluid for hydraulic fracturing is fresh water
  - Water usage and disposal (mini earthquakes)
  - Water and additives that reduce leak-off form gel on fracture face impede oil and gas production

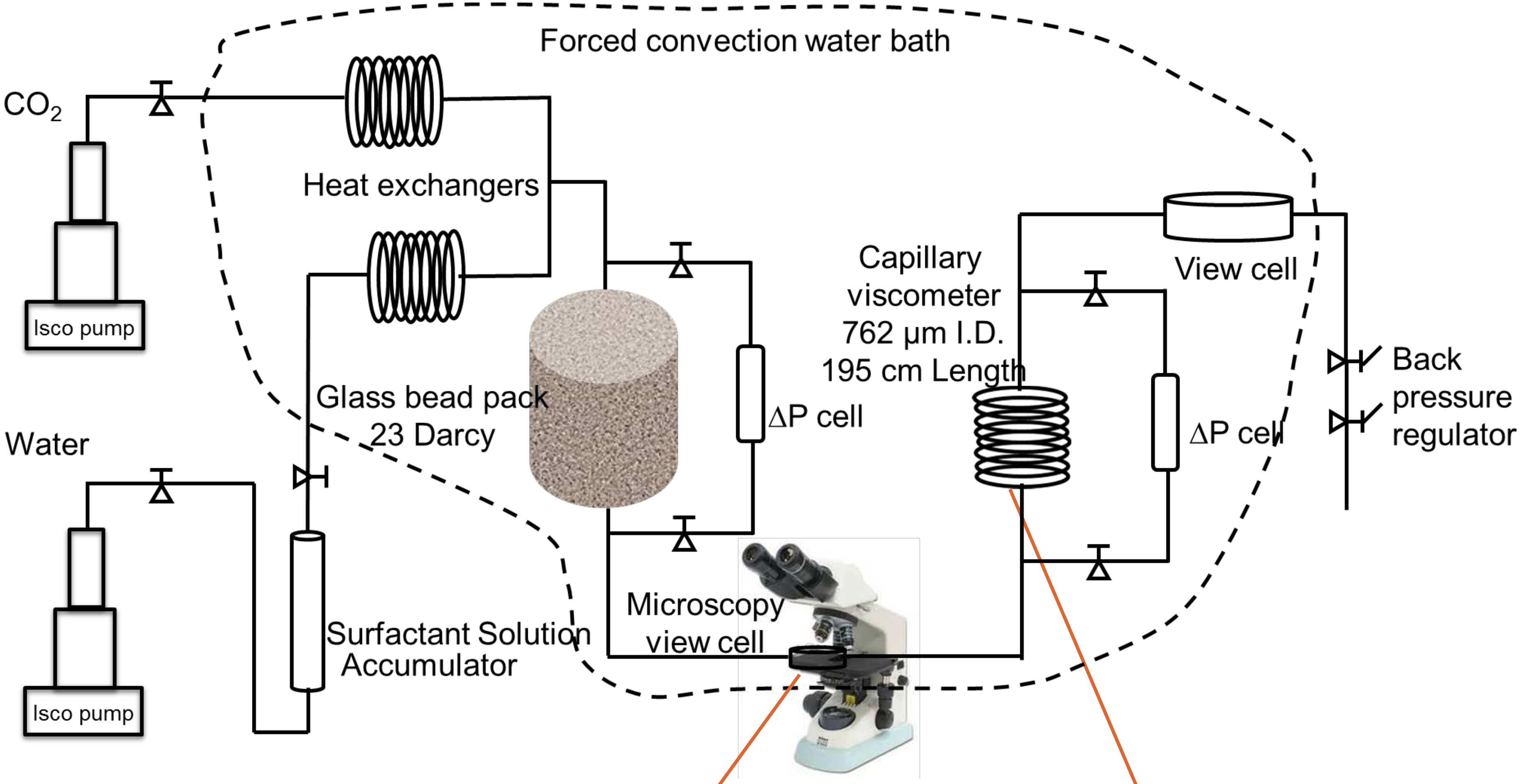
Key finding 1: ultra dry foams with NPs and surfactant

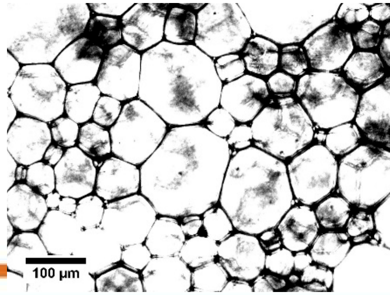
- Very low water ("ultra dry") supercritical CO_2-in-water foams:
  - 90% - 98% CO_2 by volume
  - with high viscosity on the order of 100 cP to carry proppant
  - long lifetime of hours
- Stabilized with mixtures of:
  - silica nanoparticles
  - lauramidopropyl betaine (LAPB) surfactant and
  - partially hydrolyzed polyacrylamide (HPAM) polymer
- Foams at typical conditions of hydraulic fracturing of 2 % KCl brine and 50 ^{o}C could potentially reduce water consumption for fracturing by 50 fold

- High continuous phase and surface viscosities produced as a result of interactions of nanoparticles with surfactant and polymer

- Xue, Prodanovic, Johnston et al, J. Coll. Int. Sci. (16)

Apparatus for Foam Viscosity Measurements





Hagen–Poiseuille equation

$$\mu_{app,capillary} = \frac{\pi \cdot \Delta P \cdot R^4}{8 \cdot q \cdot L}$$

Key finding #2: Ultra Dry Foams with Viscoelastic Surfactant Only

- **Simplified,** ultra dry foams formed with **viscoelastic surfactants and no polymer or NPs**
  - **high viscosity (100 cP at 100 s^{-1}),**
  - **high quality (> 0.9)** C/W foams
  - with **long lifetime (>3 hrs)**
  - **high temperature to 120 C, salinity, pressure**

- With sodium lauryl ethoxylated sulfate (SLES) –cationic surfactant mixture

  - *“Ultra dry carbon dioxide-in-water foams with viscoelastic aqueous phases”, Zheng Xue, Andrew J. Worthen, Ali Qajar, Isiah Robert, Chun Huh, Maša Prodanović, Keith P. Johnston, Langmuir, 2016*

- With single zwitterionic amidopropylcarbobetaines
  - $R\text{-}ONHC_3H_6N(CH_3)_2CH_2CO_2$, where R is varied from $C_{12–14}$ (coco) to C_{18} (oleyl) to C_{22} (erucyl)

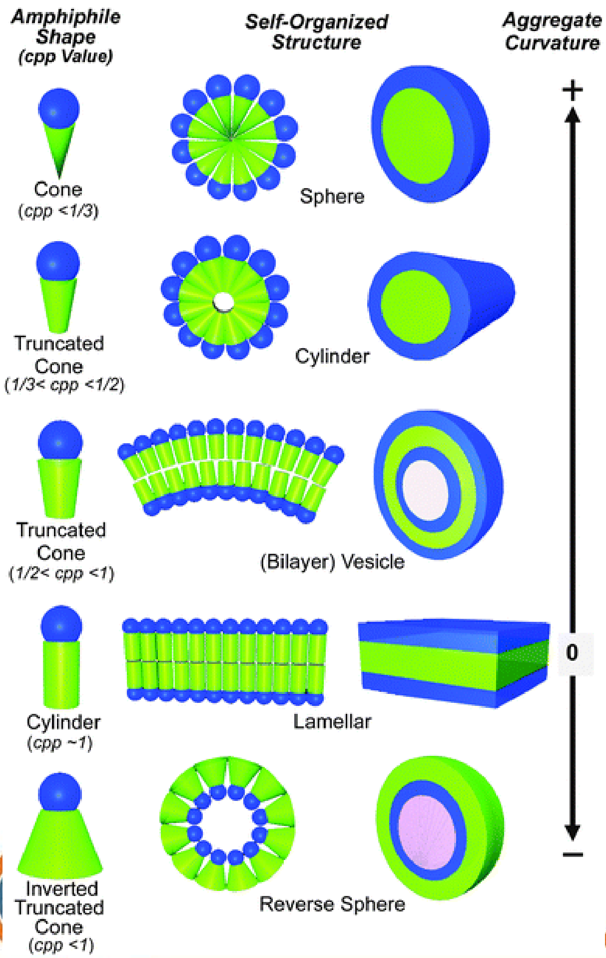
  - *S. Alzobaidi, C. Da, V. Tran, M. Prodanović, and K. P. Johnston, “High temperature ultralow water content carbon dioxide-in-water foam stabilized with viscoelastic zwitterionic surfactants,” Journal of Colloid and Interface Science, vol. 488, pp. 79–91, Feb. 2017.*

Entanglement of Wormlike Micelles Imparts Viscoelasticity

$p = v/a_0 l_c$

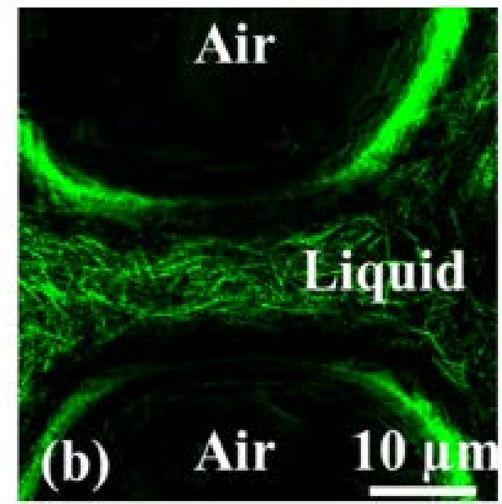
v/l_c area of surfactant tail
a_0 area of head group

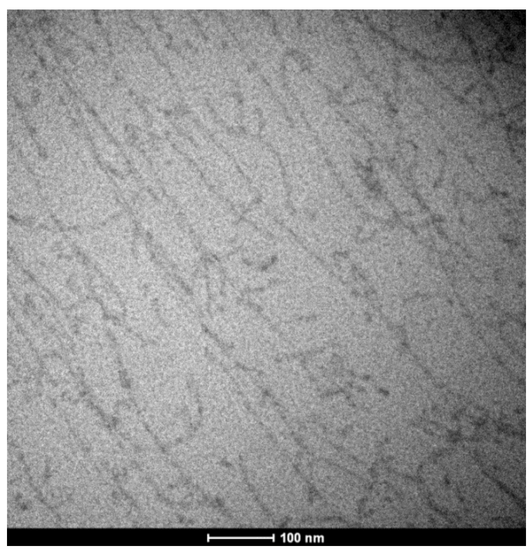
$$V = -\frac{dh_f}{dt} = \frac{2h^2}{3\mu_e R_f^2}\left(P_c - \Pi(h)\right)$$



Very dry foams, high ϕ gives high P_c
Rapid lamellae drainage

$$P_c = \gamma / R_f (1-\phi)^{0.5}$$





Catanionic micelles:
2:1 $C_{13}COO^-$: $C_{16}(CH_3)_3NH_4^+Cl$

Jamming: slow drainage maintains thick lamellae

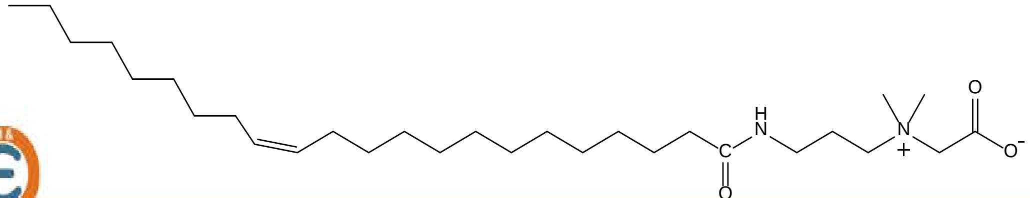
Fameau et al., Ang. Chem. (11)

Objective: Design High Internal Phase CO_2-in-Water Foams with a Viscoelastic Aqueous Phase

- Stabilize **high viscosity (>100 cP at 200 s^{-1}), high quality (> 0.9)** C/W foams with **long lifetime (>12 hrs)**

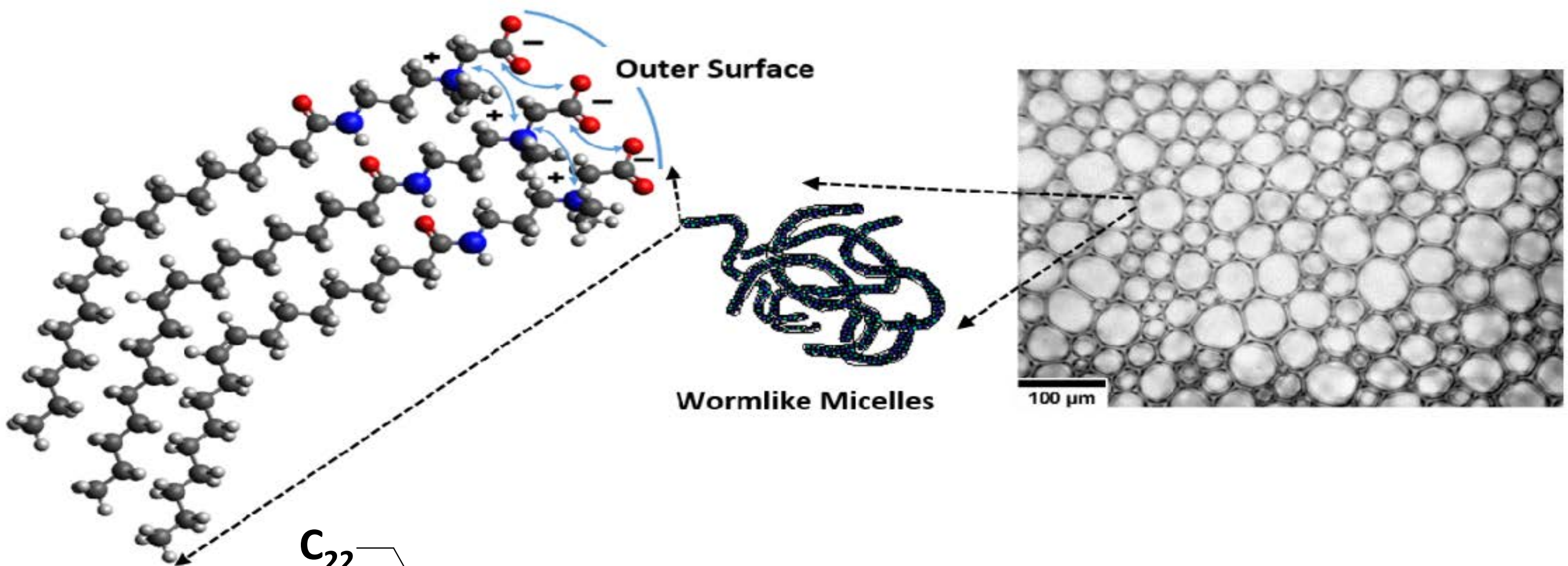
- Characterize rheology of aq. phases of zwitterionic amidopropylcarboxybetaine surfactants with long tails
  - Viscoelastic aq. phase composed of wormlike micelles (high packing fraction)
  - Single **environmentally responsible surfactant at low concentration**
  - Efficacy over a wide range in salinity (up to 22% TDS), pH and T up to 120^{o}C

- Understand stability of C/W foams with only 1 wt.% surfactant
  - Role of slow lamellar drainage even at high qualities where cap. P is high
  - Thicker lamellae: slow down Ostwald ripening (microscopy)
  - Contrast three different tail lengths for fixed amidopropyl betaine headgroup (C12-14, C18, C22)



Adjusting Packing Fraction for Viscoelastic Wormlike Micelle Aqueous Phases

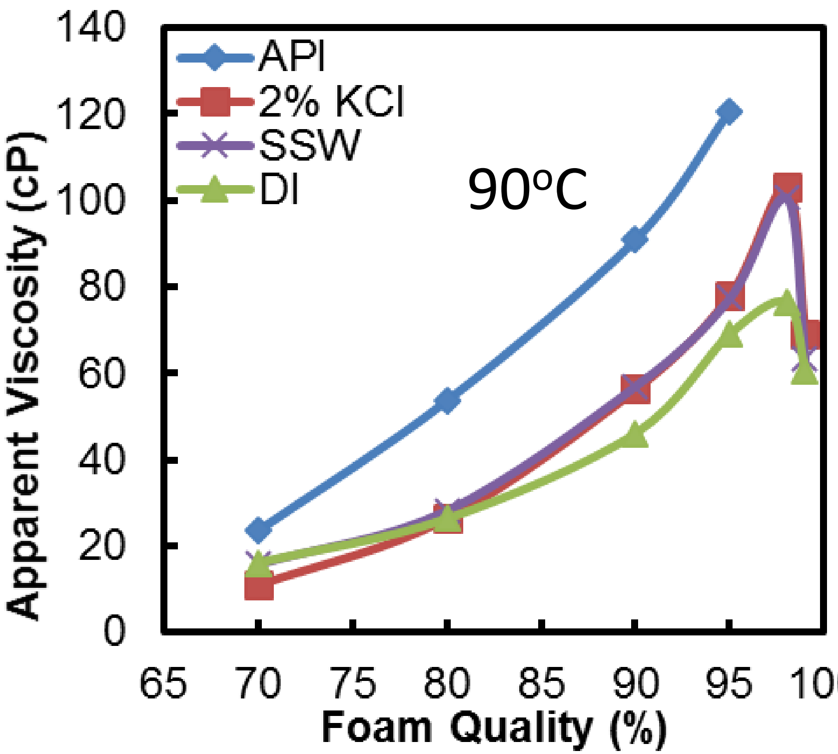
- Small headgroup area even with alignment of charges in headgroup: still less electrostatic repulsion than for ionic surfactants
- C_{18} and C_{22} tails to raise numerator of p

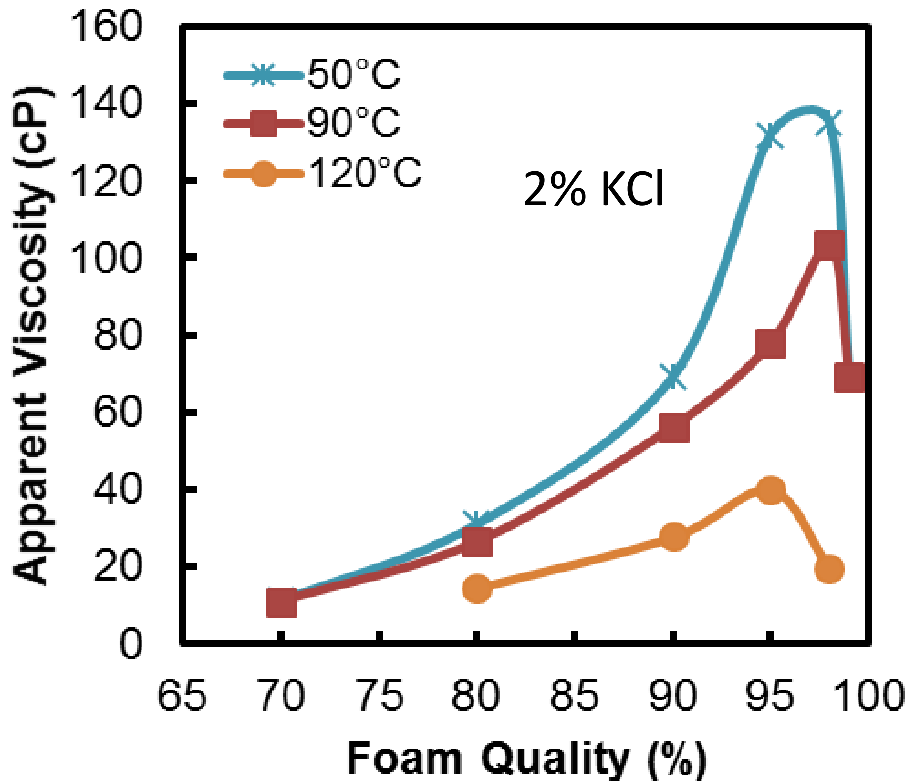


EAPB	erucyl
OAPB	oleyl
CAPB	coco

$p = v/a_0 l_c$

Foam Generated with 1% w/v C18Amidopropylbetaine Surfactant at a Shear Rate of 200 s-1 (3000 psig)

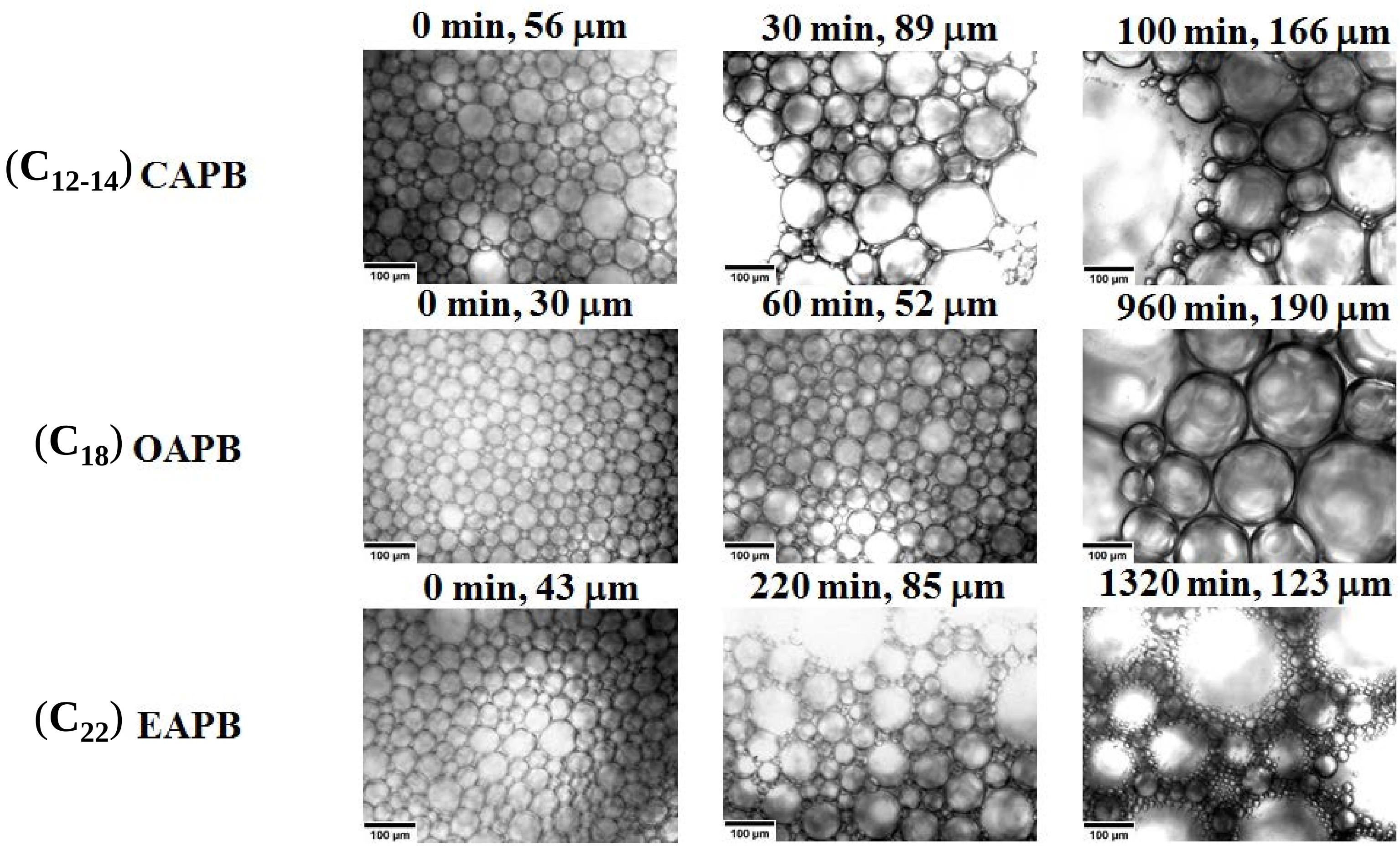




$$\mu_{foam} = \frac{\tau_0}{\dot{\gamma}} + f(\emptyset_i)\mu_e(\frac{\mu_e \dot{\gamma} R}{\gamma})^{-1/2}$$

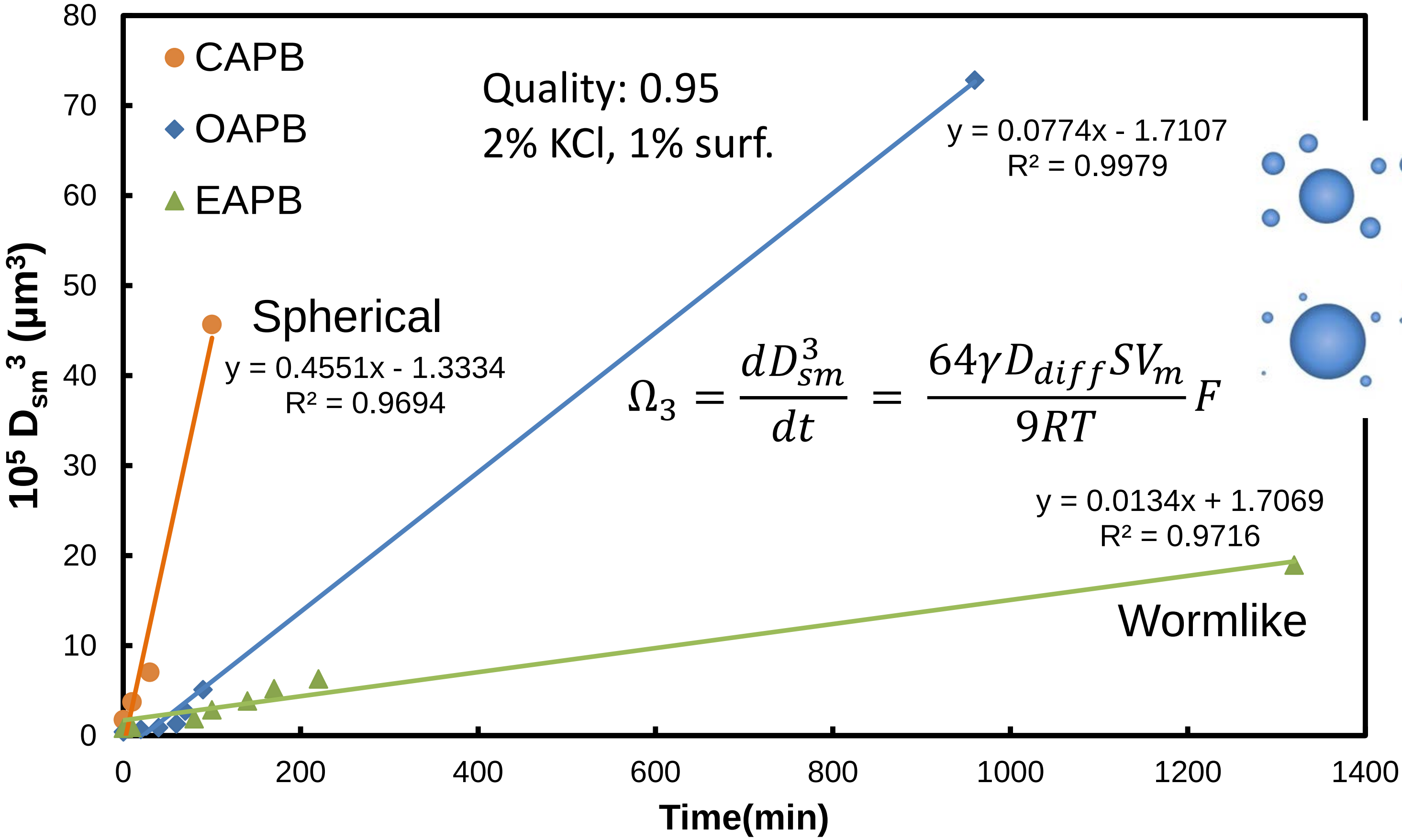
- Aq. phase visc. raises C/W foam visc.
- Stable foams maintained up to 120°C even with very high foam quality:
  - reduced lamellae drainage with viscoelastic wormlike micelles
  - thicker lamellae resist Ostwald ripening and coalescence

Foam Texture Micrographs of 1% w/v C_{12-14}, C_{18} and C_{22} Surfactant Over Time

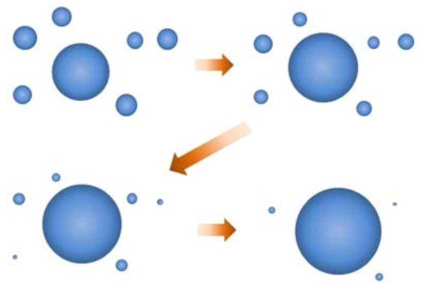


- Limited gas diffusion, strong wormlike micelles entanglement (EAPB).

Slowest Ostwald Ripening for C22 tail given most entangled wormlike micelles and most viscous aq phase



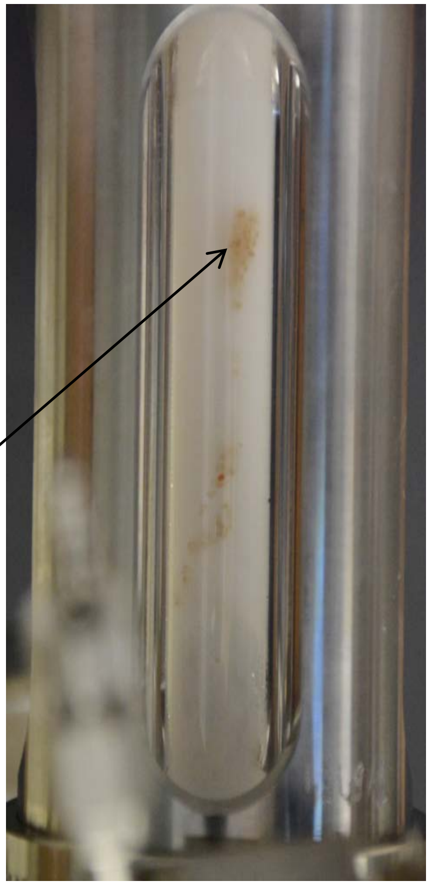
$$\Omega_3 = \frac{dD_{sm}^3}{dt} = \frac{64\gamma D_{diff} S V_m}{9RT} F$$



- Long term stability is dominated by Ostwald ripening (const. polydisp.)
- Ω_3 decreased by a factor of ~30 upon formation of wormlike micelles
- Thicker lamellae will slow down Ostwald ipening

High Pressure Foam Suspends Sand

Proppant
particles



Right after foam generated

One day later

- Presence of the proppant grains does not affect the foam stability
- The dry foam has enough strength and stability to carry the proppant in potential fracturing applications

C. Da, Z. Xue, A. J. Worthen, A. Qajar, C. Huh, M. Prodanovic, and K. P. Johnston, "Viscosity and Stability of Dry CO2 Foams for Improved Oil Recovery," in SPE Improved Oil Recovery Conference Proceedings, Tulsa, OK, 2016, p. Paper number 179690.

Conclusions: Finding 2

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- Single zwitterionic surfactants with C_{18} or C_{22} tails formed wormlike micelles at on 1 wt. % over a wide range of salinity, pH and T.
- High app. foam viscosity >100 cP at 0.9-0.98 quality (ultra dry), 200 s^{-1} sufficient to carry proppant
  - high aq. phase viscosity
  - small bubble size of ~30 µm at 90ºC
- Long term stability of hours to days
  - Reduced Ostwald ripening rate by a factor of 30 upon formation of wormlike micelles
    - Slow drainage rates with viscoelastic aqueous phases
    - Thicker lamellae and slower CO_2 diffusion
- Potential for improved oil and gas recovery as water often inhibits flow through porous media

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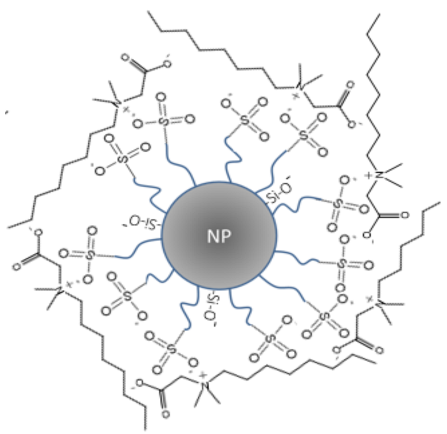
Viscous C/W foam with salt tolerant sulfonated ligands and zwitterionic surfactant up to 80 C

OB Surfactant + SA12



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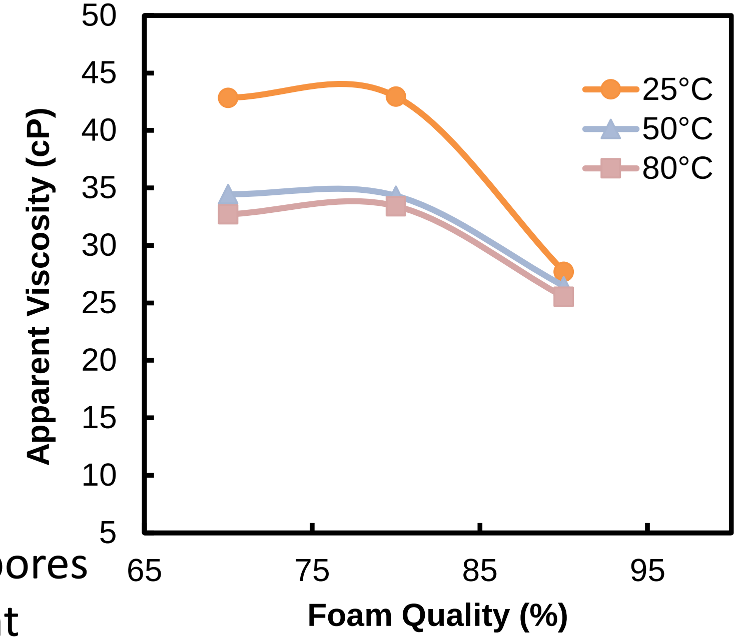
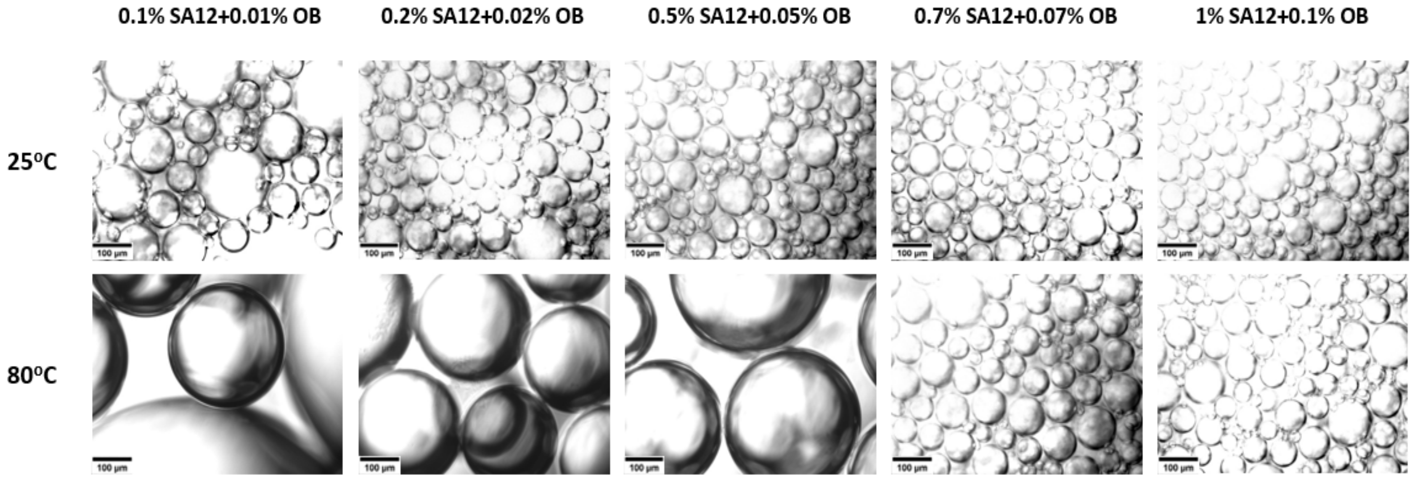


Nanoparticles may prevent water invasion into pores
Stabilize foams at low conc. of nps and surfactant



Novel CO_2/oil emulsions with no H_2O

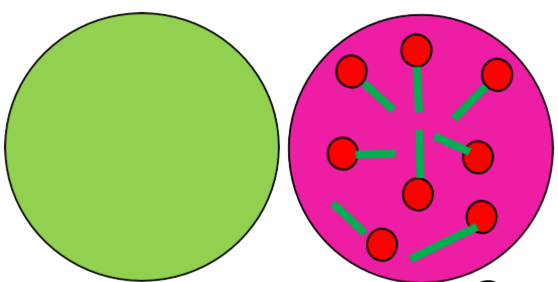
CO_2 and oil are not completely miscible, even at extreme pressures: low polarizability/volume for CO2

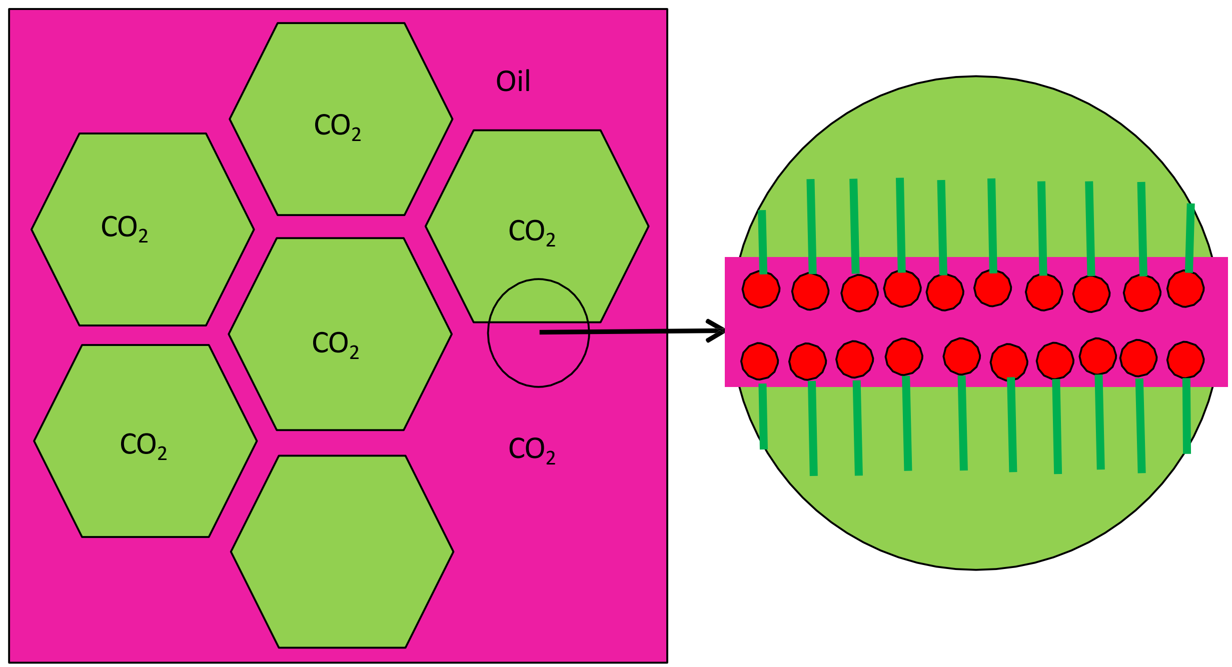
Oil-phobic CO_2 philic

Polypropylene glycol
Oligovinyl acetate
Sugar acetate
Polydimethyl-siloxane

Oil-philic CO2-phobic

Alkyl chains C14-C40



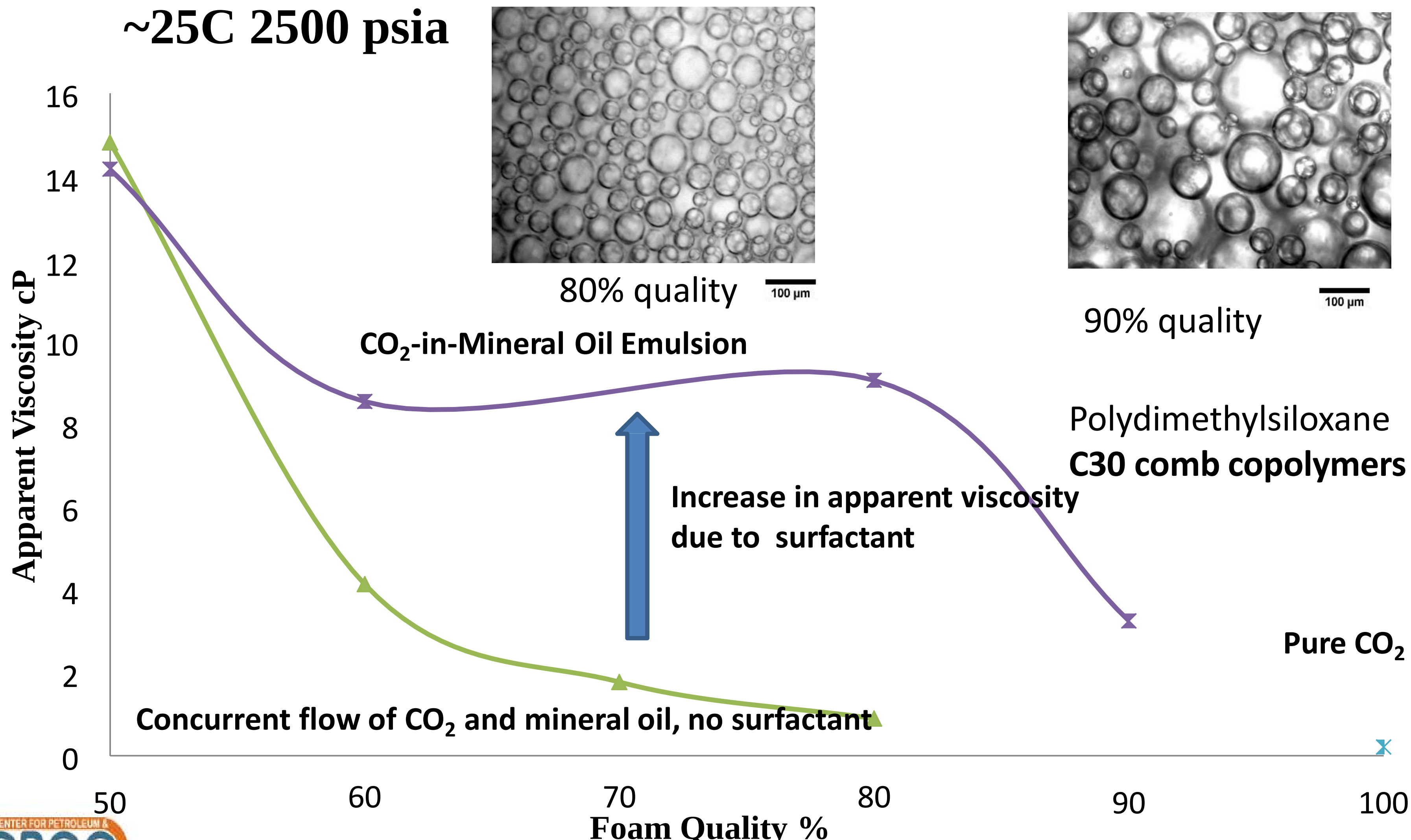


Crude oil, mineral oil, vegetable oil

Surfactant favors oil but does not gel the oil

With Robert Enick University of Pittsburgh and Bob Perry, GE Global Res.

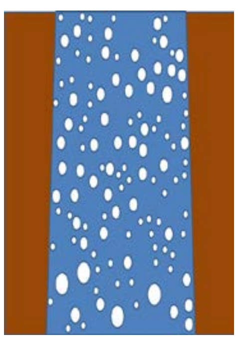
C/O Emulsions without gelling oil with PDMS:HC surf. Emulsion generated at 400/s shear rate in 22D bead pack



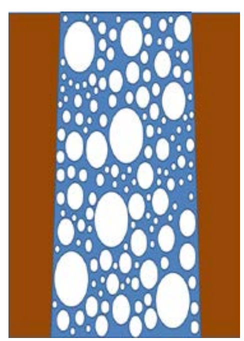
Accomplishments to Date

- Successful creation and characterization of viscous, ultra dry CO_2- and N_2-in-water foams with surfactants or nanoparticles and surfactants
  - Stable at high temperature (120 C), salinity and pressure
  - Can carry proppant with significant reduction in water use down to 2% water!
  - Environmentally friendly surfactants
- Mechanistic understanding of foam stabilization used to relate foam rheology and stability to foam texture and interfacial properties
  - Used to minimize amphiphile and water requirements
  - Contrast nanoparticle and surfactant and nanoparticle/surfactant stabilized energized foams
- Foam behavior in fractures and leak-off: numerical assessment
  - Larger viscosity foams create wider fracture with shorter half-length
  - Less leak-off, less clean-up
  - *“Modeling fracture propagation and cleanup for dry nanoparticle-stabilized-foam fracturing”, Qajar,*

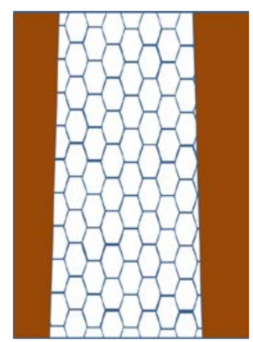
Energized Fluids (Q <40%)



High Quality Foam (Q>60%)



Ultry Dry Foam (Q>90%)



Thank you!

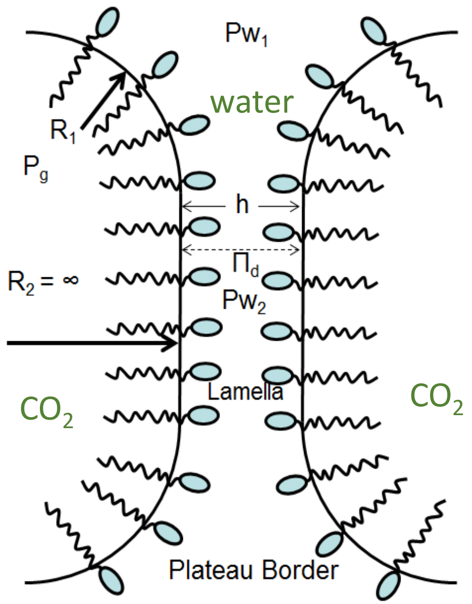
- Participants:
  - Prof. Steven L. Bryant
  - Prof. Chun Huh
  - Dr. Ali Qajar
  - Dr. Andrew J. Worthen
  - Dr. Zheng Xue
  - Chang Da
  - Shehab Alzobaidi

- Funding
  - DOE Grant DE-FE0013723
  - Welch Foundation F-1319

Key finding #1: Mechanisms

- High continuous phase and surface viscosities produced as a result of opposite charge between surfactant and polymer
- CO_2/brine IFT reduced from 20 mN/m to 5 mN/m at 50 ^oC, 3000 psia
- Low lamellae drainage rates and low coalescence
- Small bubble size leads to high viscosity of 150-270 cP at 0.90-0.98 quality, at 200 s^{-1}
- NPs increase the apparent viscosity and stability of foam

Foam Stability: Lamellae Film Drainage and Coalescence



Lamella drainage (Reynolds)

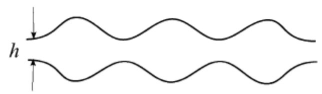
$$V = -\frac{dh_f}{dt} = \frac{h_f^2}{3\mu_e R_f^2}\Delta P_{film}$$

$$\Delta P_{film} = 2(P_c - \Pi_d)$$

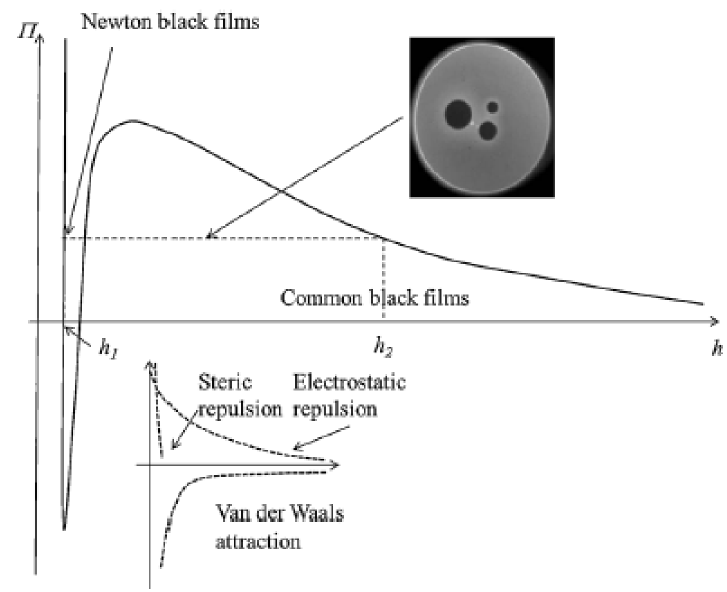
$$P_c \approx \frac{\gamma}{R_v\sqrt{1-\phi}}$$

Capillary pressure increases with foam quality

Rupture



$t \; \alpha \; \mu \gamma \; A^{-2} h^5$



- Lamellae thinning influences Ostwald ripening and coalescence
- Raise stability:

  lower P_c (lower IFT), incr. π_d , μ_e and h
- Micellar layering phenomena aids P_d (Wasan)

Ivanov and Kralchevsky, 1997; Langevin, 2000
Adkins KPJ et al., 2010; Babak and Stebe, 2002, Israelachvili 3rd ed. (10)

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