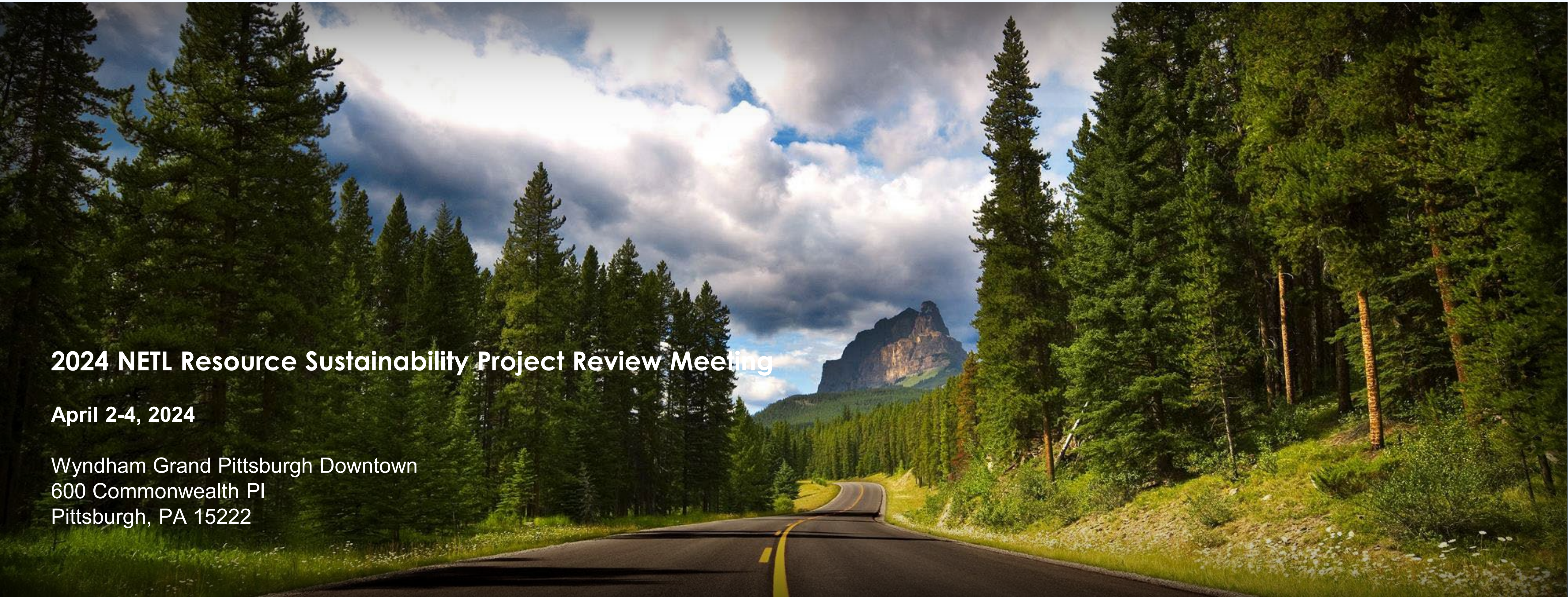
CO_2-EOR in Shale Resources

Angela Goodman[1], Bob Enick[2], Deepak Tapriyal[1], Lauren Burrows[1], Foad Haeri[1], Abdullah Shaheer[2], Eilis Rosenbaum[1]

[1]National Energy Technology Laboratory, 626 Cochran Mill Road, Pittsburgh, PA 15236, USA

[2]University of Pittsburgh, Pittsburgh, PA 15261, USA



2024 NETL Resource Sustainability Project Review Meeting

April 2-4, 2024

Wyndham Grand Pittsburgh Downtown
600 Commonwealth Pl
Pittsburgh, PA 15222

Barriers to Enhanced Oil Recovery (EOR) and CO_2 Storage

Meeting the world's growing energy needs in the face of climate change is one of the greatest scientific challenges of our time

1. **Barriers in increasing recovery and improving operational efficiency**
   - Primary oil recovery from fractured unconventional formations **is typically less than 10%.**
   - Environmental damage inflicted by hydraulic fracturing and fossil fuel emissions is problematic
   - EOR in **unconventional is far more challenging** than conventional formations (Extremely low permeability and mixed wettability)
2. **How the barriers are being addressed**
   - Challenges associated with **water-based EOR techniques** leads to investigating several nonaqueous injection fluids (**CO_2, rich natural gas,** and nitrogen).
     - lower viscosity than water, allows easier access to **shale nanopores**
   - If anthropogenic CO_2 is injected, some of the CO_2 will be trapped in the subsurface offsetting the CO_2 emissions that result from combustion of the produced hydrocarbons
3. **The extent the barriers have been/are being addressed by the project**
   - Field tests with CO_2 and natural gas in the Bakken and Eagle Ford formations
   - **Our project examines CO_2 and surfactants dissolved in CO_2 to increase EOR by changing the wettability**
   - **Also examining if we can address conformance issues by creating foams**

Project Goals – Enhancing Oil Recovery with CO_2

End Product and Benefits:

- ✓ Determine viability of CO_2 as an enhanced recovery agent for unconventional oil with and without surfactants
- ✓ Determine if foams could help with conformance issues
- ✓ Adding surfactants directly to CO_2 offers an advantage because it does not require additional water injection
- ✓ If anthropogenic CO_2 is injected, some of the CO_2 will be trapped in the subsurface offsetting the CO_2 emissions that result from combustion of the produced hydrocarbons
- ✓ Surfactants all commercially-available, cost approximately $1-3 per pound, and anticipated to be effective at concentrations of 0.1 wt% or less.
- ✓ Would add approximately $2-6 to the cost of one ton of CO_2.

CO_2 for EOR in Unconventional Formations

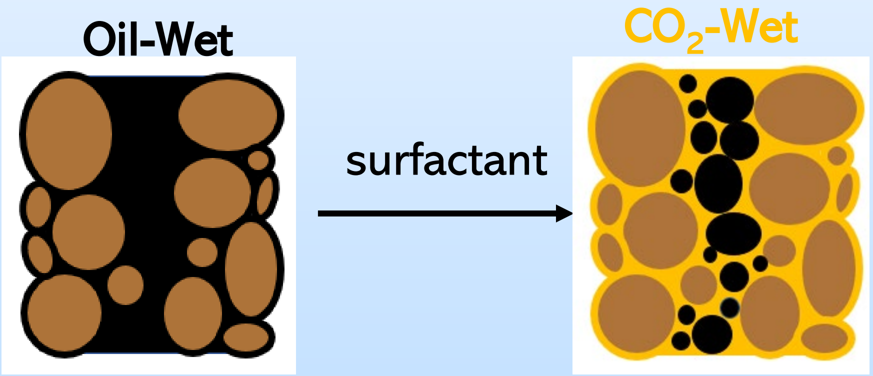
Previously Established Oil Recovery (EOR) Mechanisms During CO_2 Huff 'n Puff

- CO_2 diffusion into oil
- Oil swelling
- Solution gas drive
- Pressure support
- Solution gas drive
- CO_2 extraction of oil
- Oil diffusion into CO_2
- Oil viscosity reduction
- Low CO_2-oil interfacial tension (IFT)
- Relative permeability hysteresis

New proposed mechanism

Wettability alteration from oil-wet toward CO_2-wet during soaking (huff part of huff 'n puff) caused by the nonionic surfactants dissolved in the injected CO_2

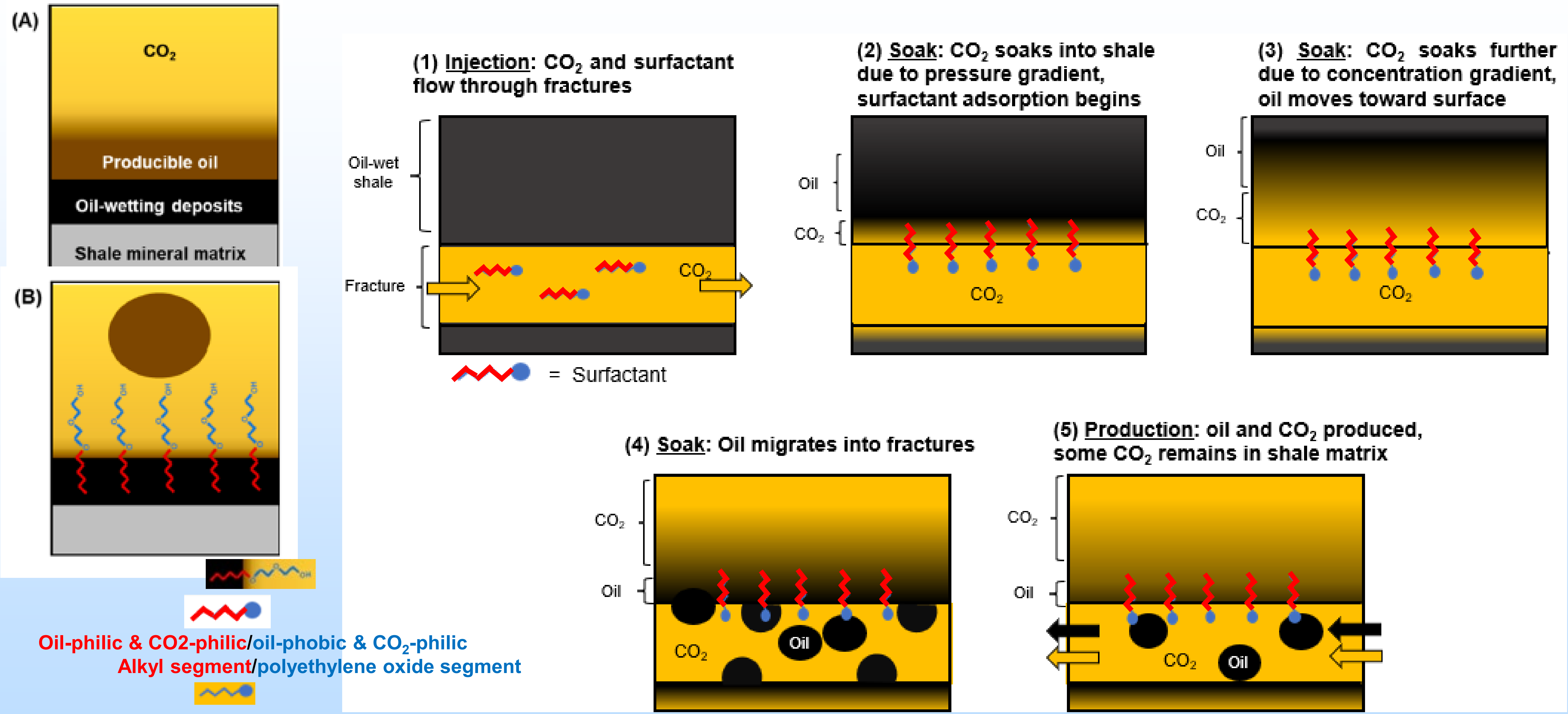
In the oil-filled, oil-wet pores...during huff 'n puff



Oil-Wet:
Oil coats rock surfaces in oil-saturated pores

CO_2-Wet:
CO_2 wets the rock during huff 'n puff

Potential wettability alteration mechanism - adsorption

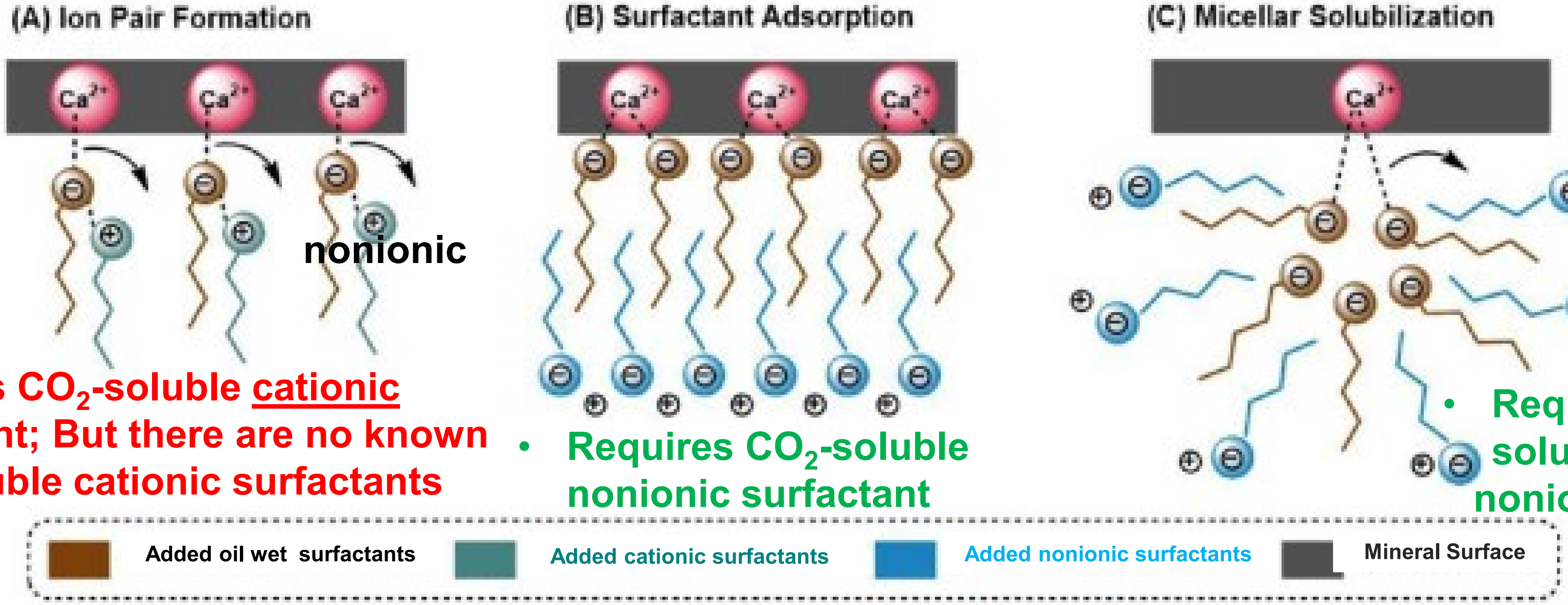


Oil-philic & CO2-philic/oil-phobic & CO_2-philic

Alkyl segment/polyethylene oxide segment

Other potential wettability alteration mechanisms

Ion pair formation | **Adsorption** | **Oil Emulsification**



- Requires CO_2-soluble <u>cationic</u> surfactant; But there are no known CO_2-soluble cationic surfactants (yet)
- Requires CO_2-soluble nonionic surfactant
- Requires CO_2-soluble nonionic surfactant

Figure 18. Mechanisms of wettability alteration by surfactants.

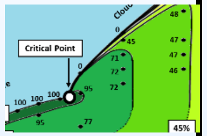
Our experimental approach

Surfactant Selection ✓ CO_2-soluble ✓ Oil-soluble
✓ Inexpensive ✓ Environmentally benign

Hydrophilic “head”
Hydrophobic “tail”

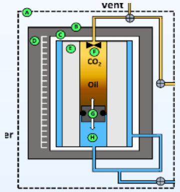
CO_2-Oil Phase Behavior

High pressure, high temperature Pressure-composition of CO_2 and Eagle Ford oil



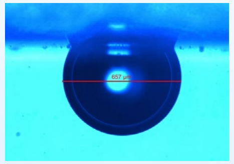
CO_2 Surfactant Solubility

High pressure, high temperature solubilities of the surfactants in CO_2



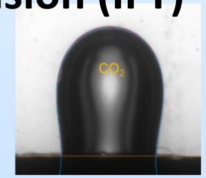
CO_2 + Surfactant + Shale Wettability Alteration

Air Water
Ambient contact angles



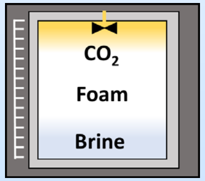
CO_2 + oil + Surfactant Interfacial Tension (IFT)

High pressure,
high temperature
CO_2-Oil IFT



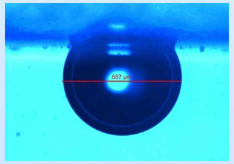
CO_2 + oil + Surfactant Foaming

High pressure
high temperature
CO_2-Oil foaming



CO_2 + Surfactant + Oil + Shale Wettability Alteration

High pressure, temperature CO_2-oil contact angles

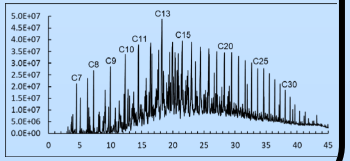


Huff-n-puff Experiments

- Immersed and confined cores

Gas Chromatography

Extracted oil analysis



✓ **Target experimental conditions:** 27.6 MPa and 80 °C

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Hydrophilic “head”
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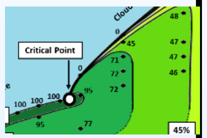
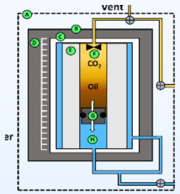


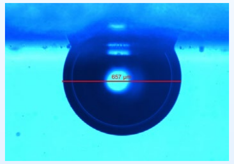
CO_2 Surfactant Solubility

High pressure, high temperature solubilities of the surfactants in CO_2



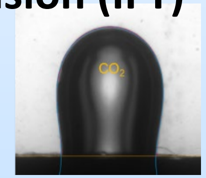
CO_2 + Surfactant + Shale Wettability Alteration

Air Water
Ambient contact angles



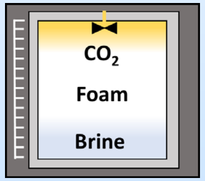
CO_2 + oil + Surfactant Interfacial Tension (IFT)

High pressure,
high temperature
CO_2-Oil IFT



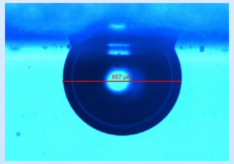
CO_2 + oil + Surfactant Foaming

High pressure
high temperature
CO_2-Oil foaming



CO_2 + Surfactant + Oil + Shale Wettability Alteration

High pressure, temperature CO_2-oil contact angles



NMR *in situ* Huff-n-puff Experiments

- Immersed and confined cores

✓ **Target experimental conditions:** 27.6 MPa and 80 °C

Conclusions from Prior Work

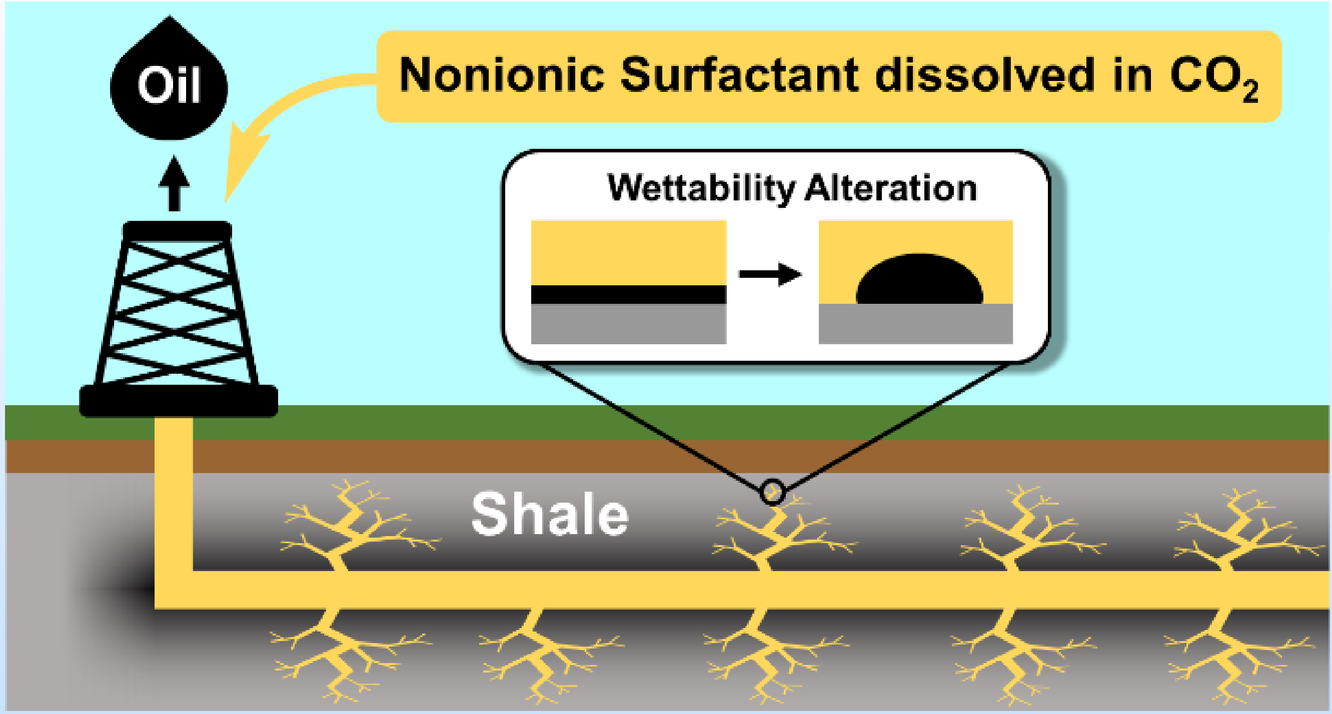
- **Improving CO_2 EOR is possible** by surfactant-induced wettability alteration

  - ***Phase behavior:*** CO_2 and oil are not completely miscible at reservoir conditions
  - ***CO_2-solubility of surfactants:*** Nonionic surfactants are soluble in CO_2 to ~1 wt% at typical CO_2 EOR conditions
  - ***CO_2-oil-rock contact angle:*** CO_2-soluble surfactants can alter shale wettability from oil-wet toward CO_2-wet
  - ***IFT experiments:*** surfactant had no effect on the CO_2-oil IFT
  - ***Foam experiments*****:** surfactant also did not generate a CO_2-oil or oil-CO_2 foam
  - ***GC analysis:*** CO_2-dissolved surfactant recover a higher proportion of heavier oil in the first puffs than pure CO_2.
  - ***Huff n' puff experiments:*** In the best case, oil recovery increase by a surfactant dissolved in CO_2 was modest (e.g. 71% to 75%, by 0.1% of a branched tridecyl ethoxylate with 9 EO units), other surfactants had little effect or detrimental effect
  - ***Cost:*** surfactants were inexpensive ($1-3/pound), commercially-available, liquid, and used in dilute amounts (0.01-0.1 wt%).

Current Direction

- Surfactants in prior study were relatively large, with lengths between 3.82-4.26 nm, about the size of *n*-C30
- Reviewed 60 papers with the latest information on surfactants.
- Selected three classes of best surfactant based on literature review
- Will age cores in fracture fluid prior to aging in oil
- Will engage with field test operations
- Will examine conformance control with CO_2 and surfactants
- Will add NMR to quantify the amount of CO_2 stored and oil extracted from cores

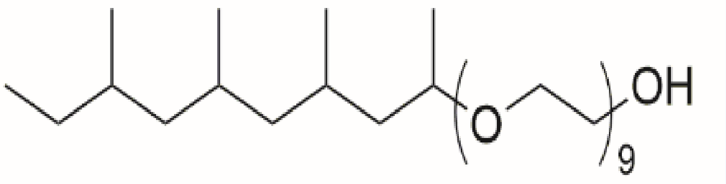
- As anthropogenic CO_2 becomes more available through CO_2-capture efforts, CO_2 EOR in unconventional reservoirs will provide an important economic driver for anthropogenic CO_2 capture and result in more CO_2 being stored permanently in the subsurface



Prior CO_2-Soluble Surfactants

3 water-soluble, essentially oil-insoluble, slightly CO_2-soluble nonionic ethoxylated alcohols were selected.

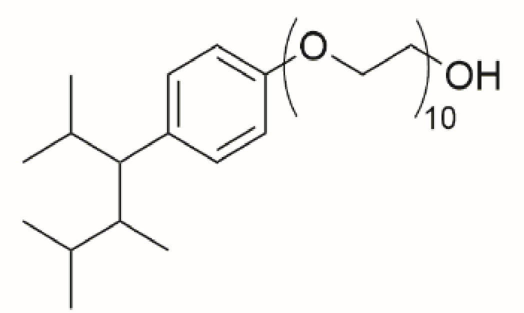
Indorama SURFONIC® TDA-9



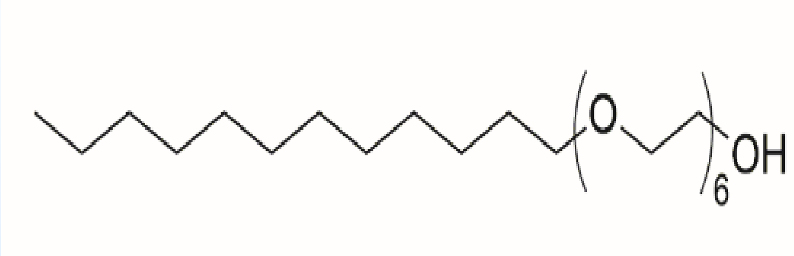
Strongly oil-philic
Somewhat CO_2-philic

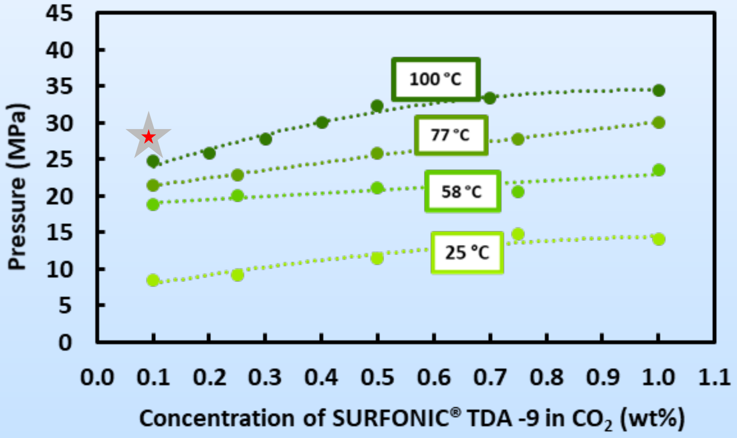
Strongly oil-phobic
Somewhat CO_2-philic

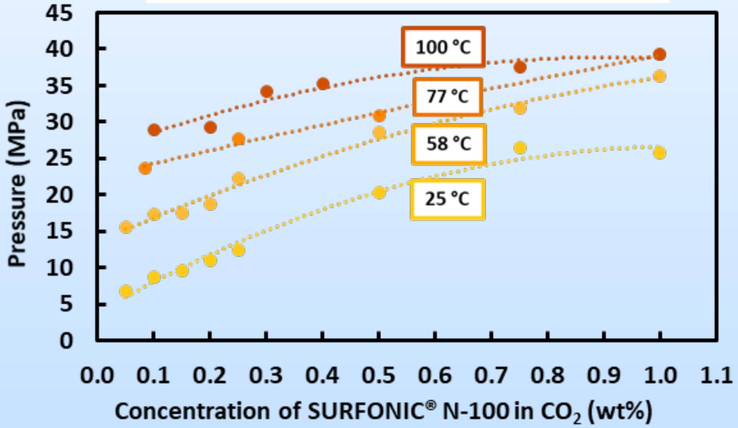
Indorama SURFONIC® N-100

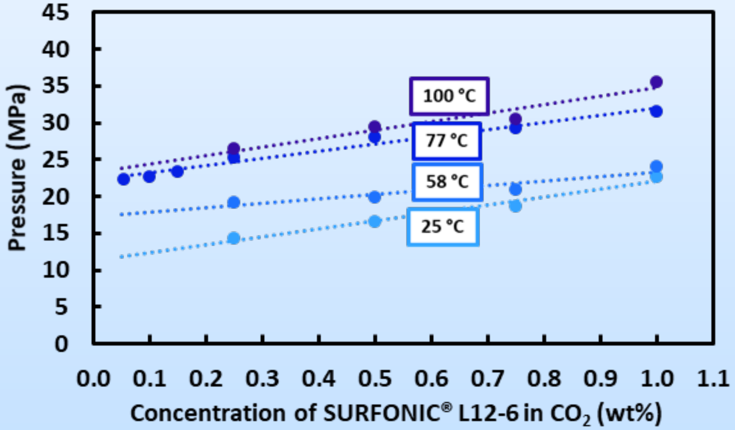


Indorama SURFONIC® L12-6







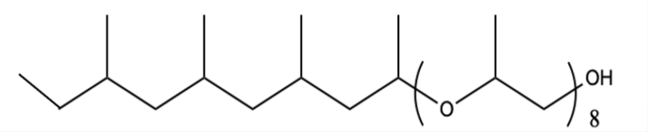


★ **Experimental conditions in subsequent tests were chosen to ensure the surfactant is completely dissolved in the CO_2 (27.6 MPa and 80 °C)**

New Candidates: CO_2-Soluble Surfactants

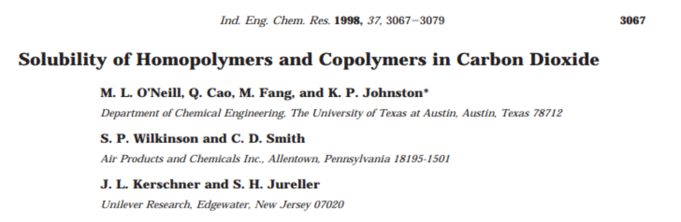
An oil-miscible, slightly CO_2-soluble, nonionic, water-insoluble propoxylated alcohol. PPO is more CO_2-philic than PEO (O'Neill 1998), but this surfactant is ~30 wt% soluble in oil, so much will partition into oil.

Indorama SURFONIC® TDA-8PO-0.1EO
i.e. C13(PO)8



Strongly oil-philic Somewhat CO_2-philic

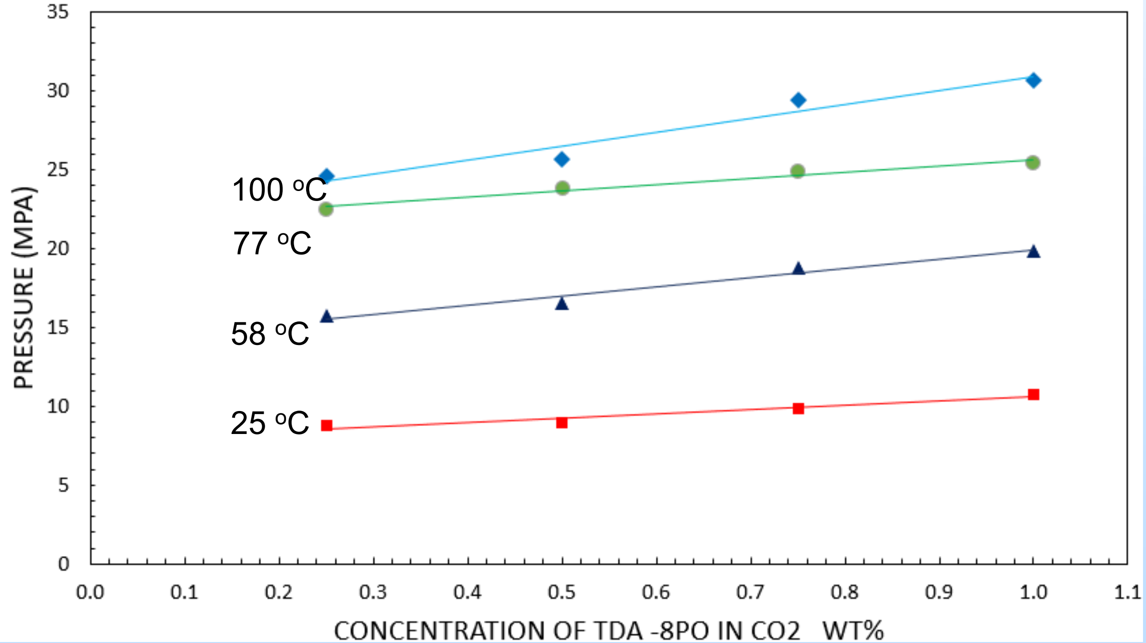
Slightly oil-phobic Strongly CO_2-philic


Ind. Eng. Chem. Res. 1998, 37, 3067−3079 3067

Solubility of Homopolymers and Copolymers in Carbon Dioxide

M. L. O'Neill, Q. Cao, M. Fang, and K. P. Johnston*
Department of Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712
S. P. Wilkinson and C. D. Smith
Air Products and Chemicals Inc., Allentown, Pennsylvania 18195-1501
J. L. Kerschner and S. H. Jureller
Unilever Research, Edgewater, New Jersey 07020

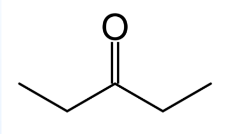
PPO more CO2philic than PEO



A small molecule purported to induce wettability change (from oil-wet to water-wet) was selected.

3-pentanone

Oil-miscible, 1 wt% water soluble, very CO_2-soluble



Hsieh C., Vrabec J. "Vapor–liquid equilibrium measurements of the binary mixtures CO2 + acetone and CO2 + pentanones". The Journal of Supercritical Fluids, Volume 100, 2015.

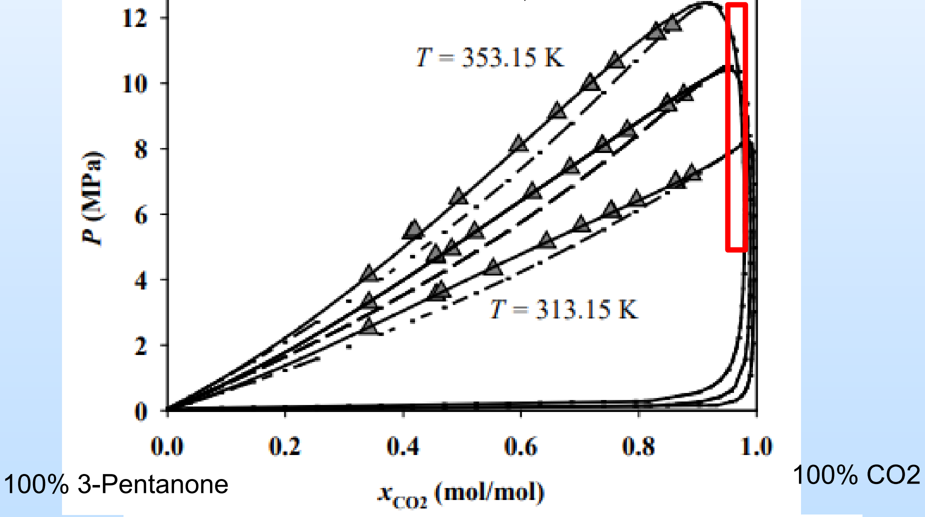
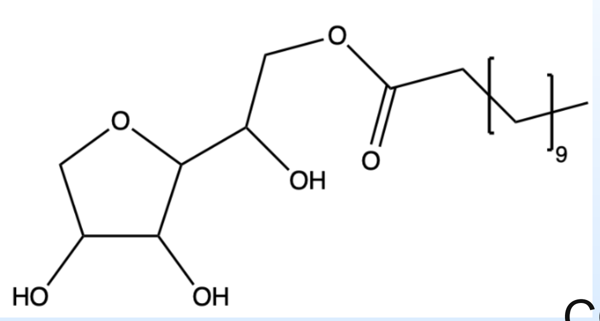


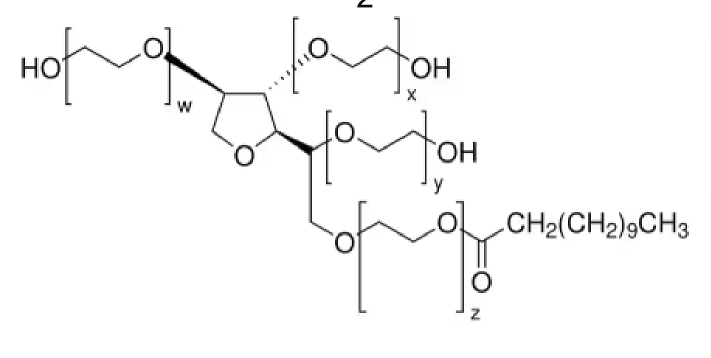
Fig. 5. Comparison of vapor–liquid equilibria of CO_2+3-pentanone at 313.15 K, 313.15 K, and 353.15 K from experimental data measured in this work (▲), correlation by PR+HV+UNIQUAC (–), and prediction by PR+VDW (–).

New Candidates: Sorbitan laurate

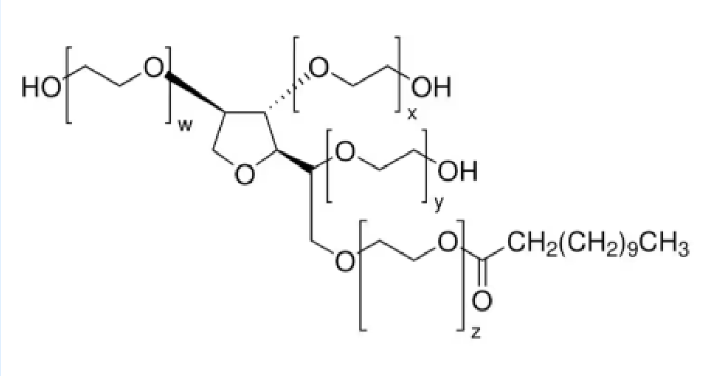
SPAN 20
Nonionic sorbitan laurate
Oil-soluble, water-insoluble
CO_2-solubility not yet determined

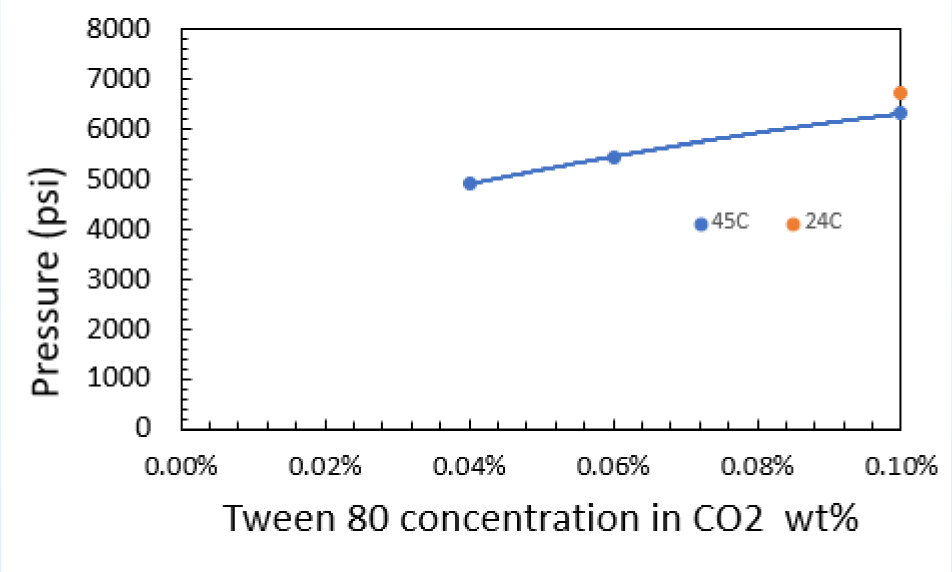


TWEEN 20 w + x + y + z = 20
CO_2-solubility not yet determined
Expected to be more CO_2-soluble than Tween 80



TWEEN 80 w + x + y + z = 80
CO_2-solubility determined (to the right)
Very high pressures





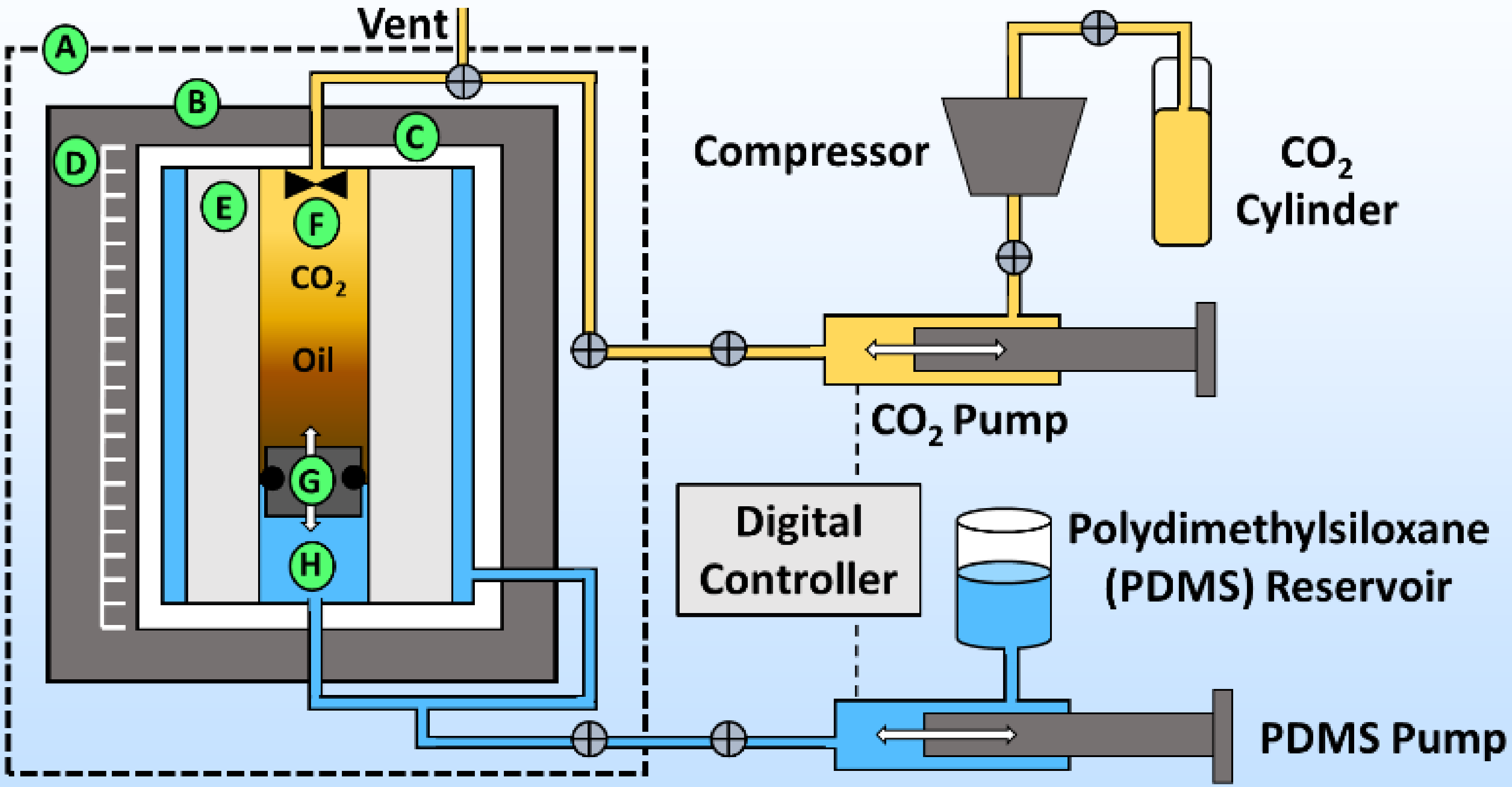
Occurrence of Two Fluid Phases

This surfactant can only work if there are two fluid phases, an oil-rich phase and a CO_2-rich phase, present in the initially oil-wet pores even at pressures at or slightly above the minimum miscibility pressure (MMP).

Emphasis is placed on commercially available surfactants that are non-fluorous liquids to facilitate eventual application at field-scale.

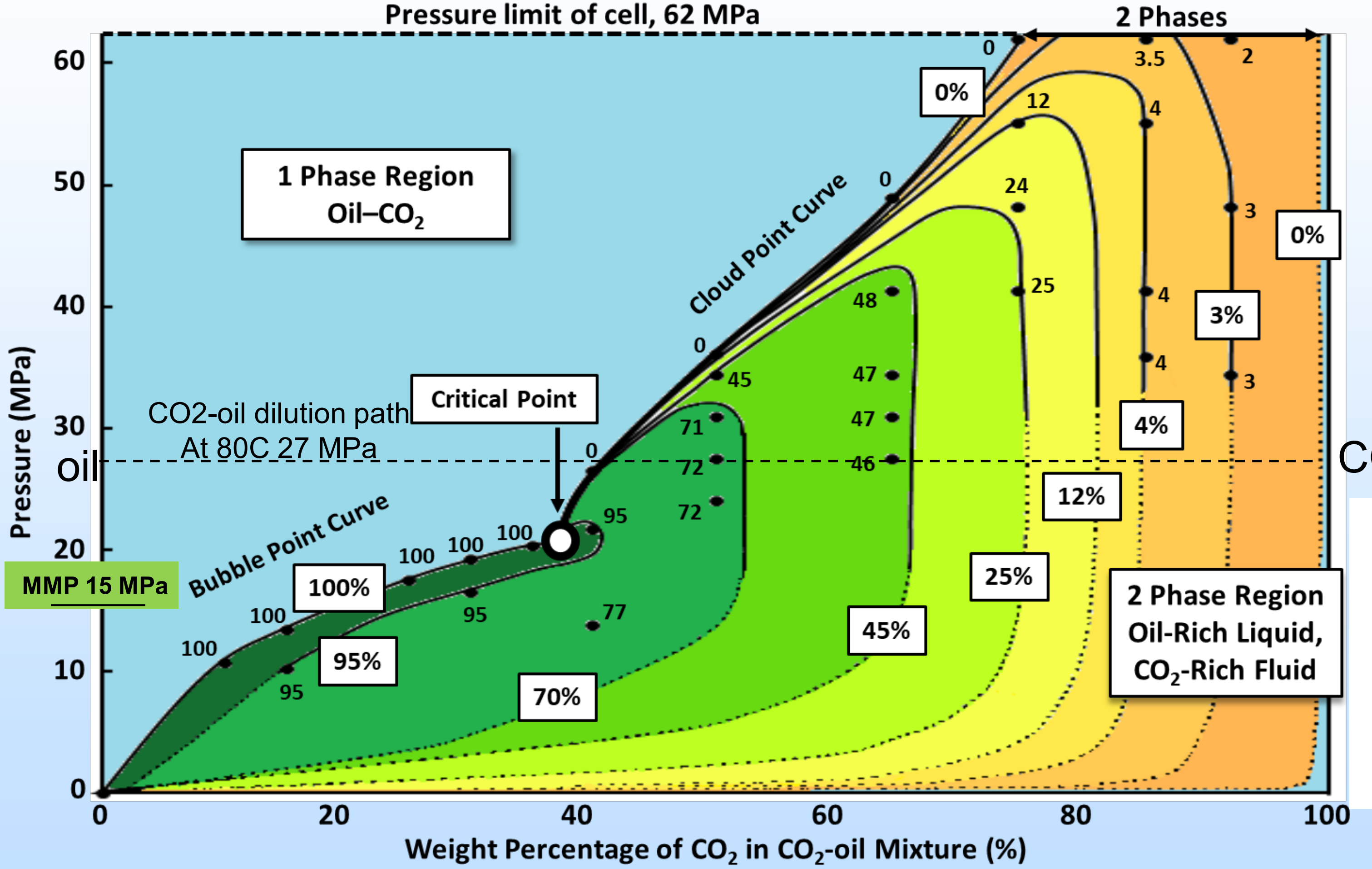
Phase Behavior Apparatus for CO_2-Oil PX Diagrams and Surfactant Solubility in CO_2

- (A) Boundary of Air Bath
- (B) Cell Body
- (C) Window
- (D) Ruler
- (E) Thick-Walled Pyrex Tube
- (F) Magnetically-Driven Impeller
- (G) Sliding Piston and O-Ring
- (H) PDMS Overburden Fluid



CO_2-Oil Pressure-Composition (Px) Diagram

The Px diagram for CO_2-Eagle Ford oil mixtures at 77 °C ranging from 0-100% CO_2



Even though CO_2 is considered a very good solvent for oil, **there are still a wide range of conditions in which two fluid phases co-exist, especially for CO_2-rich mixtures at pressure well above the MMP of 15 MPa**

With two phases present, CO_2-EOR may be improved using surfactants by wettability alteration. However, surfactants may also cause reductions in CO_2-oil IFT and may also promote the formation of CO_2-in-oil foams.

Current Direction

- Reviewed 60 papers with the latest information on surfactants.
- Selected three classes of best surfactant based on literature review
- Will engage with field test operations
- Will examine conformance control with CO_2 and surfactants
- Will add NMR to quantify the amount of CO_2 stored and oil extracted from cores

- As anthropogenic CO_2 becomes more available through CO_2-capture efforts, CO_2 EOR in unconventional reservoirs will provide an important economic driver for anthropogenic CO_2 capture and result in more CO_2 being stored permanently in the subsurface

energy&fuels

pubs.acs.org/EF Review

A Literature Review of CO_2, Natural Gas, and Water-Based Fluids for Enhanced Oil Recovery in Unconventional Reservoirs

Lauren C. Burrows, Foad Haeri, Patricia Cvetic, Sean Sanguinito, Fan Shi, Deepak Tapriyal, Angela Goodman,* and Robert M. Enick*

Cite This: *Energy Fuels* 2020, 34, 5331–5380 Read Online

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pubs.acs.org/EF Article

CO_2-Soluble Nonionic Surfactants for Enhanced CO_2 Storage via In Situ Foam Generation

Lauren C. Burrows, Foad Haeri, Deepak Tapriyal, Parth G. Shah, Dustin Crandall, Robert M. Enick,* and Angela Goodman*

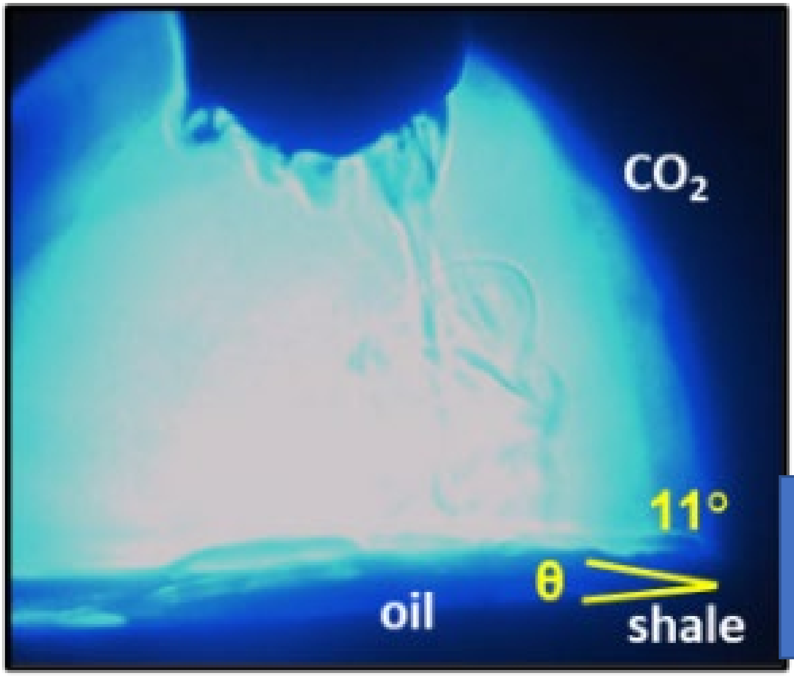
Cite This: *Energy Fuels* 2023, 37, 12089–12100 Read Online

High-Pressure Shale-Oil-CO_2 Contact Angles

- Direct test of the central hypothesis of this work:

  CO_2-dissolved surfactants (0.1 wt%) can alter the wettability of shale from oil-philic toward CO_2-philic

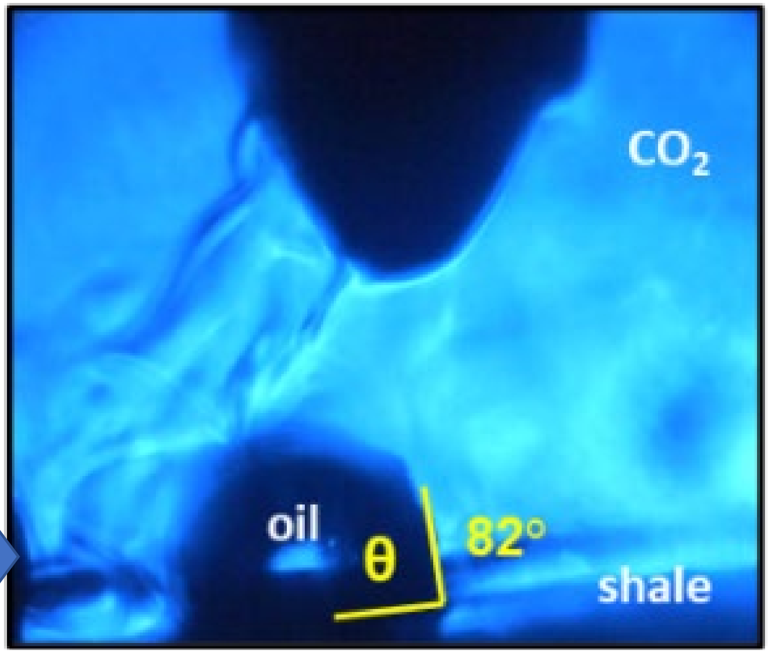
(A) Oil-aged shale chip, CO_2 soak



Oil-wet initially

+71° in contact angle

(C) Oil-aged shale chip, CO_2 + TDA-9 soak



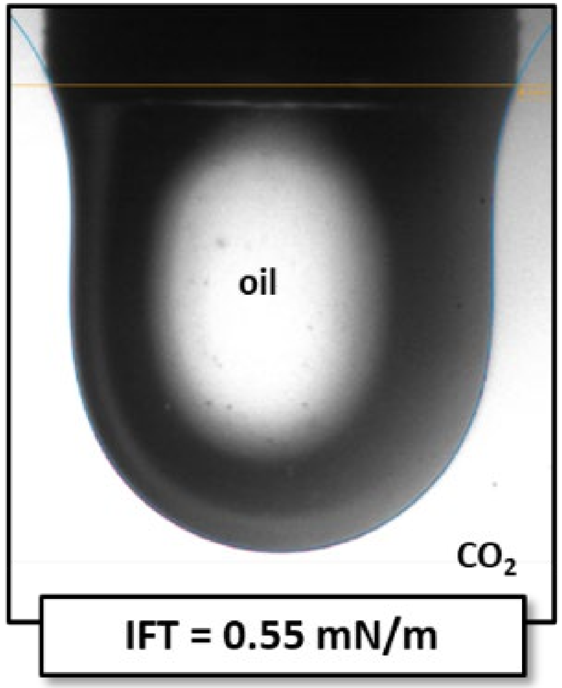
Intermediate oil/CO_2-wet

80 °C
27.6 MPa

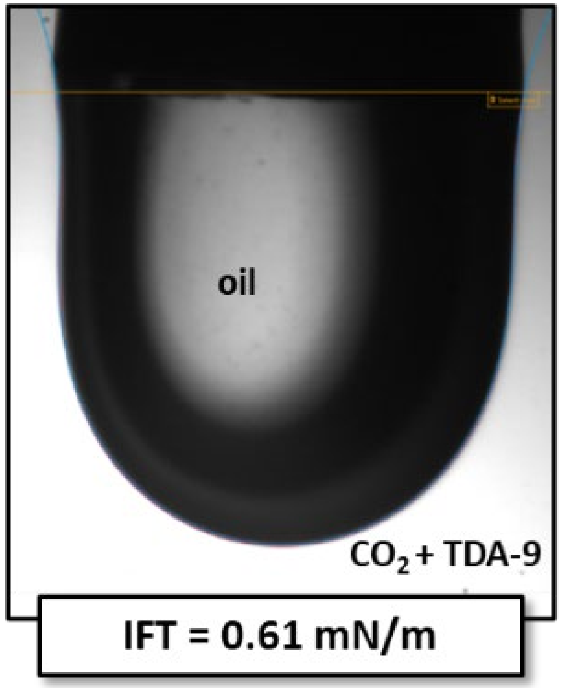
CO_2-Oil Inter-Facial Tension Measurements

CO_2 + dead Eagle Ford oil, 80 °C, 27.6 MPa (4000 psi)

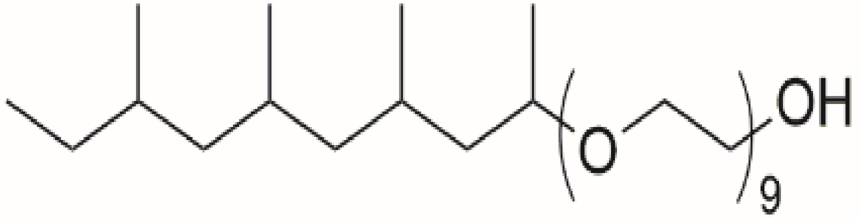
CO_2-oil IFT



CO_2+SURFONIC®
TDA-9 (0.1 wt%)-oil IFT



Note: These tests are done at much lower surfactant concentration (0.1wt%) than those reported by groups (0.5wt% who did measure IFT reduction



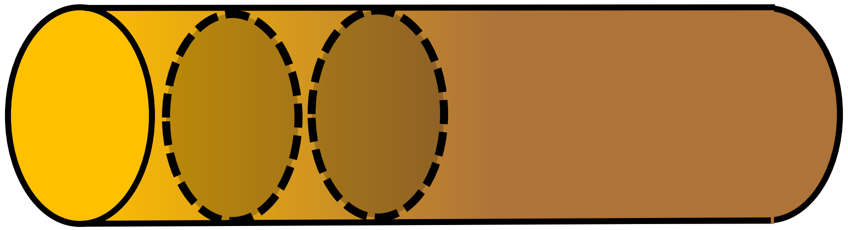
TDA-9 dissolved in CO_2 did not reduce CO_2-oil IFT
CO_2-oil IFT is already very low

The slight increase in IFT may be due to experimental uncertainties

IFT reduction is NOT the occurring at these concentrations and is NOT the mechanism by which CO_2 EOR is expected to improve using nonionic surfactants at 0.1wt%

NMR Imaging: CO_2-EOR in shale

Spatially resolved fluid measurements

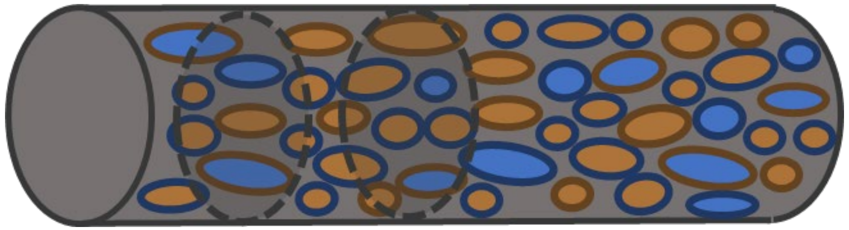


- How far does CO_2 penetrate shale?
- Which EOR gases (CO_2, nat gas, ethane) penetrate farthest?
- **How much CO_2 is stored during EOR?**

Spatially resolved pore measurements

- **What size pores is oil produced from?**
- **Which pores store CO_2?**
- How does CO_2 effect pore size? Kerogen content?

Spatially resolved wettability measurements



- How far does surfactant penetrate?
- Is wettability altered throughout the core?
- Is oil produced by water wet or oil wet pores?