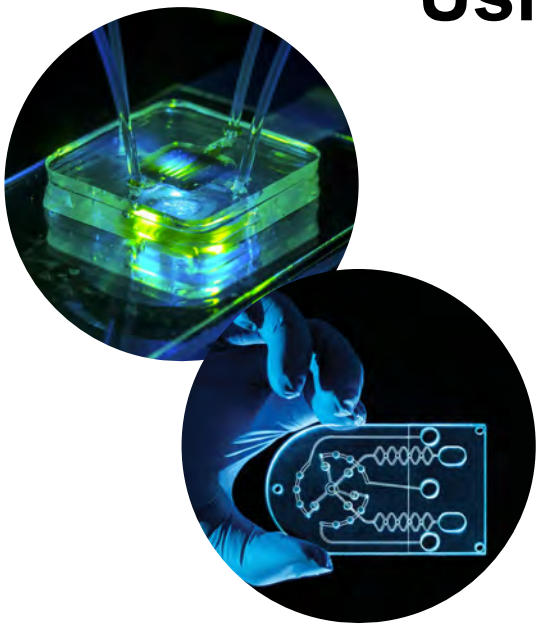
RICE UNIVERSITY
School of Engineering
Department of Chemical and Biomolecular Engineering

Physicochemical Characterization of Asphaltenes Using Microfluidic Porous Media



Sibani Lisa Biswal

William M. McCardell Professor and Chair

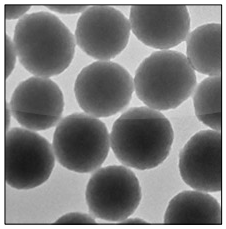
Chemical and Biomolecular Engineering

Rice University

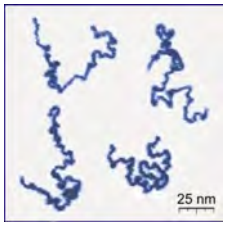
Engineering Soft Matter

Advanced Materials:

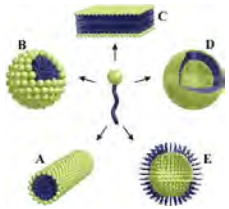
- Superparamagnetic Colloidal Crystals
- Flexible magnetic filaments
- Micromechanical sensors



Colloids



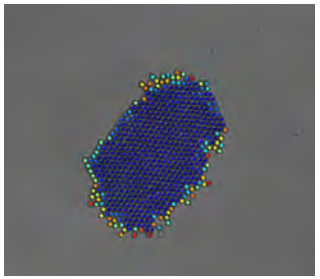
Polymers

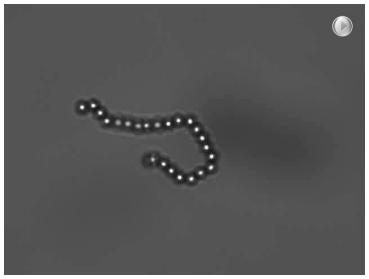


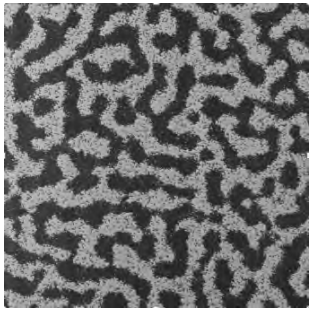
Surfactants

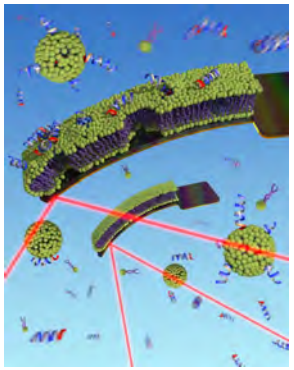
Energy Applications:

- Bubbles and Foams for CO_2 sequestration
- Emulsions for remediation
- Silicon Anodes for Lithium-Ion Batteries
- Electrochemical separation of lithium from geothermal brines

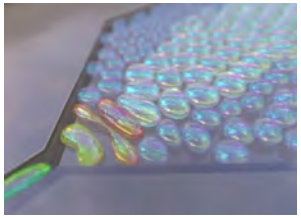


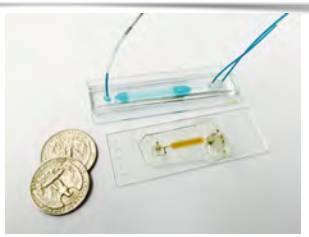


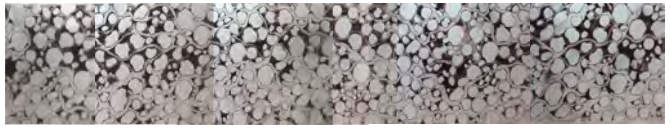


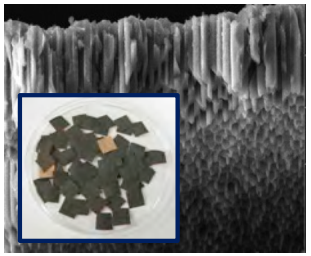


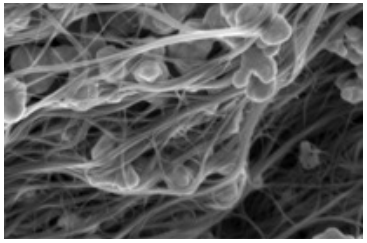
- Directed Paramagnetic Colloidal Assemblies
- Multiphase Flows in Porous Media
- Lipid and Protein-Based Biosensors
- Porous Silicon Composites for Batteries





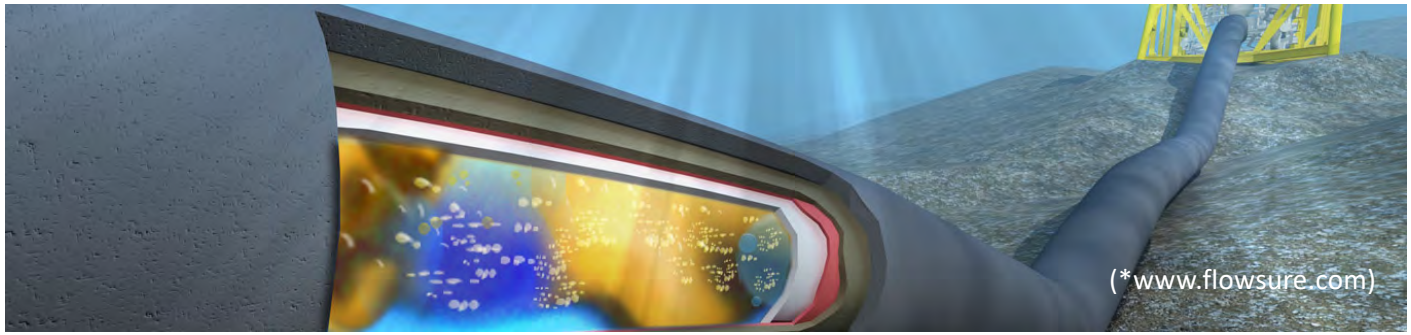


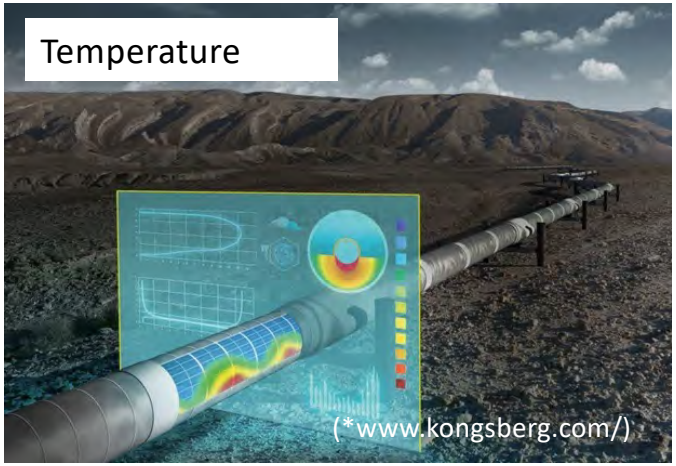




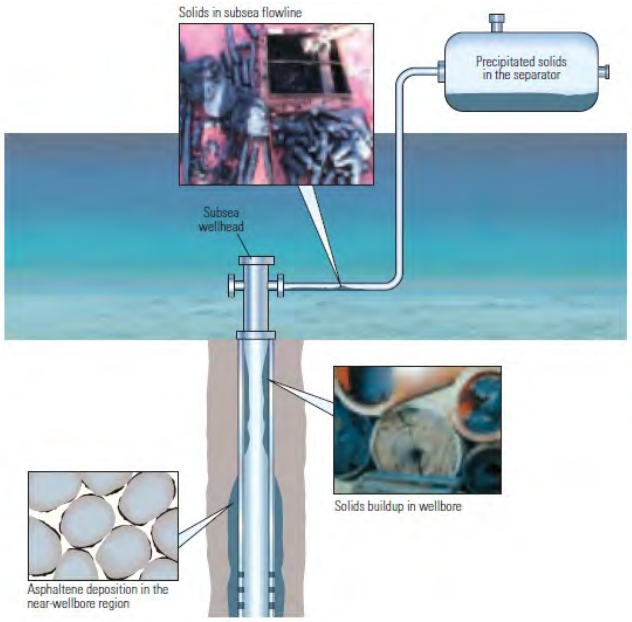
Multiphase Fluid Flows

Complexities of multiphase flows is fundamental to the success of oil and gas operations, impacting everything from production and transport to safety and environmental protection.





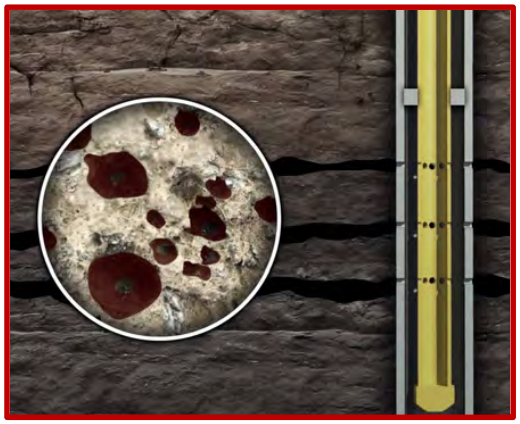
Coating Problem: Asphaltenes



High cost of remediation:
~ $500 k/well onshore
~ $3 MM/well offshore
~ 1.2 MM per day
(lost production)

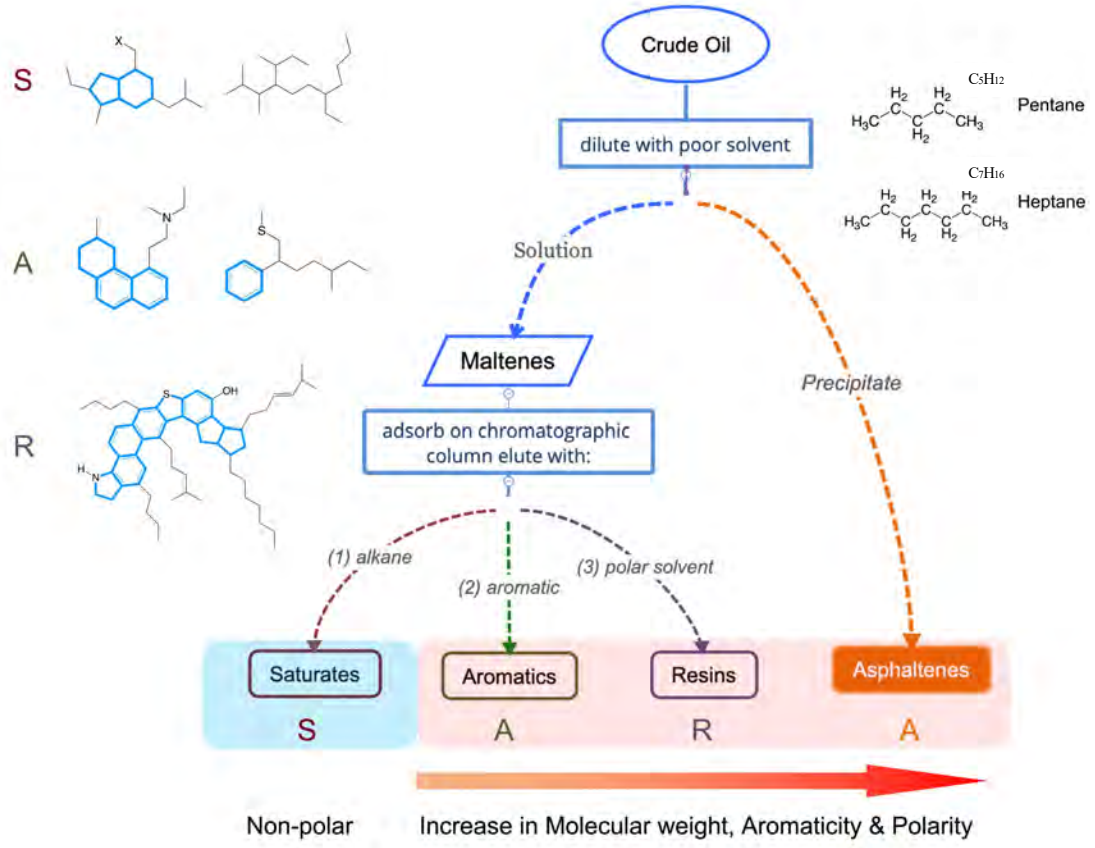
Plugging in the wellbore

Plugging in the porous media



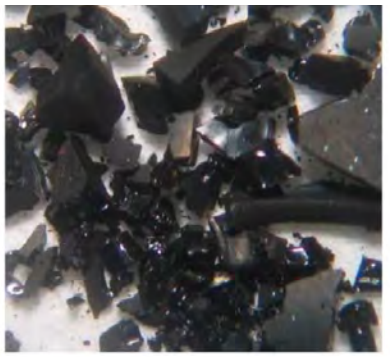
(**Oilfield review*, 2007)

What are Asphaltenes?



(*Jill Buckley's Lab, New Mexico Tech)

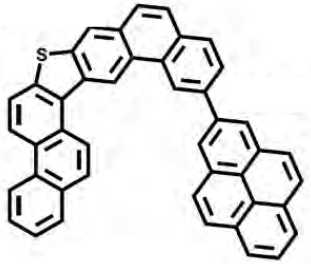
C5 Asphaltene



C7 Asphaltene

(**Oilfield review*, Summer 2007)

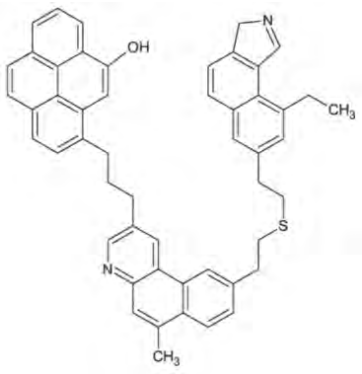
Island Motif

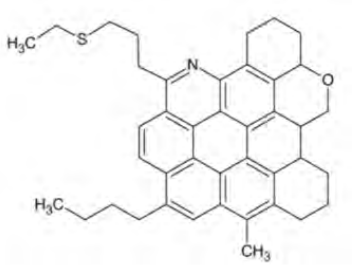


Archipelago Motif

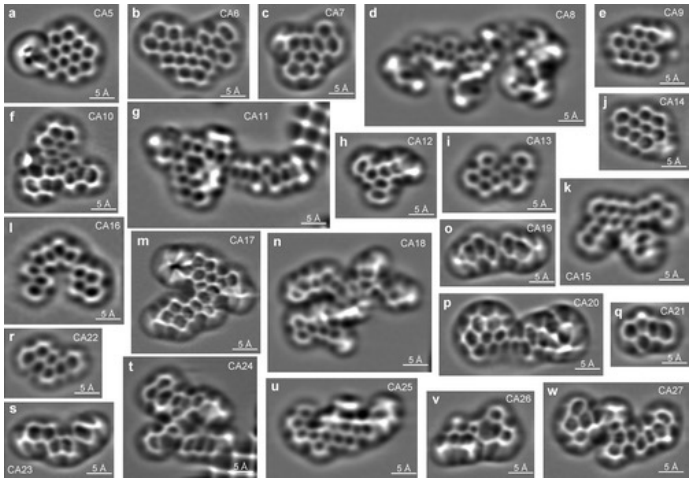
(*M. L. Chacon *et al.*, *Florida State University*)

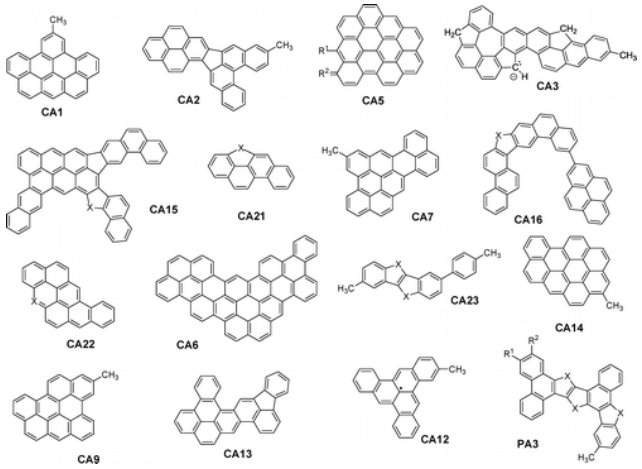
What are Asphaltenes?





- Asphaltene chemical structure generally contains:
  - Fused ring structures
  - Naphthenic rings
  - Aliphatic chains
    - Hydrogen and carbon
    - Heteroatoms (nitrogen, sulfur, oxygen)
    - Trace metals (vanadium, nickel)

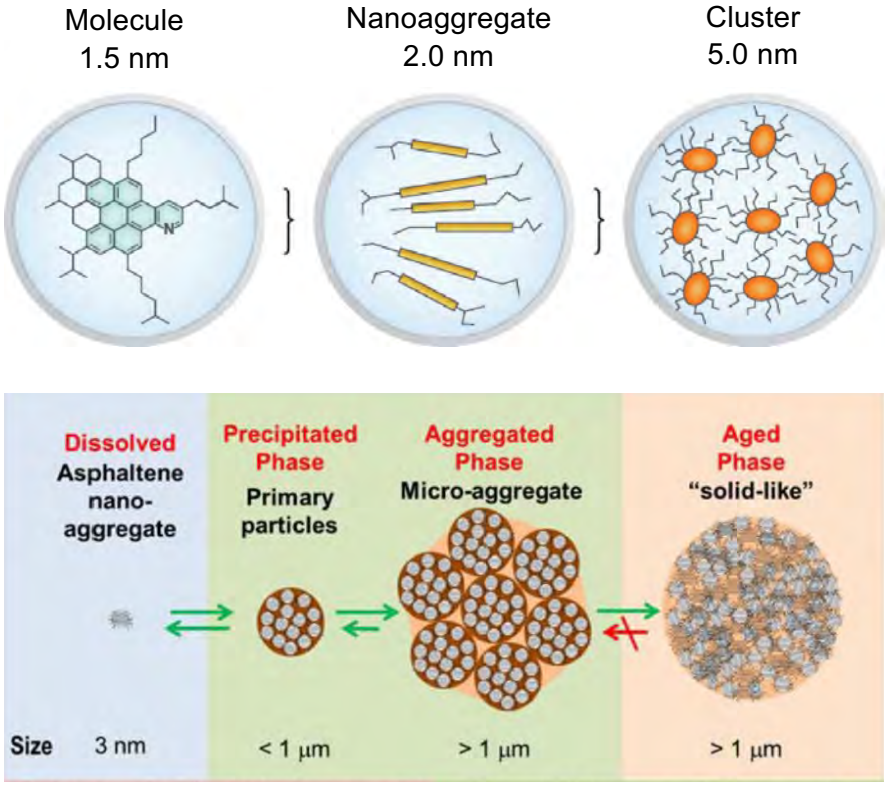




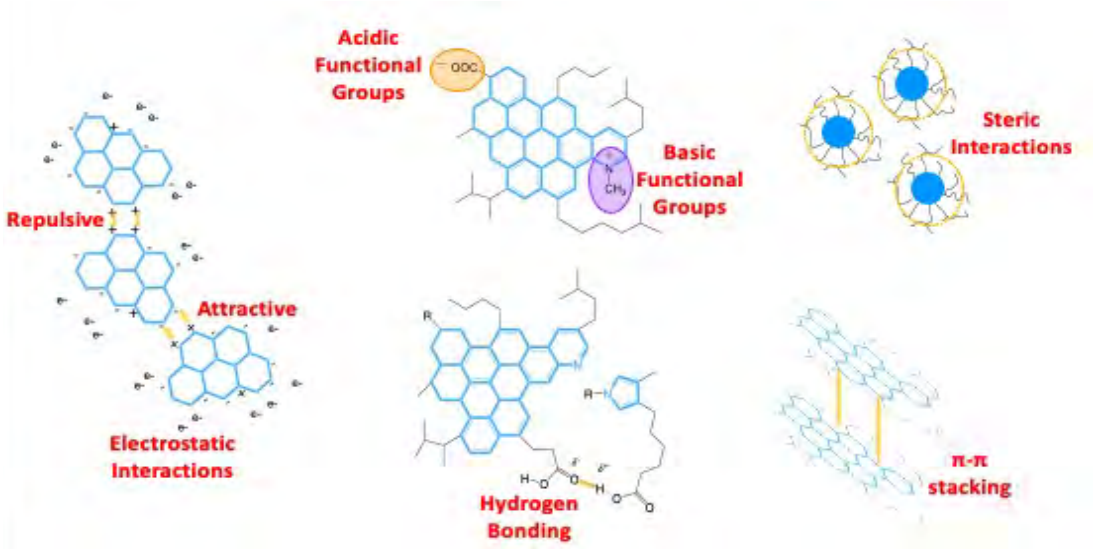
Majundar, 2015.
B. Schuler et al., JACS, 2015.

Asphaltene Physicochemical Properties

Colloidal behavior of asphaltenes

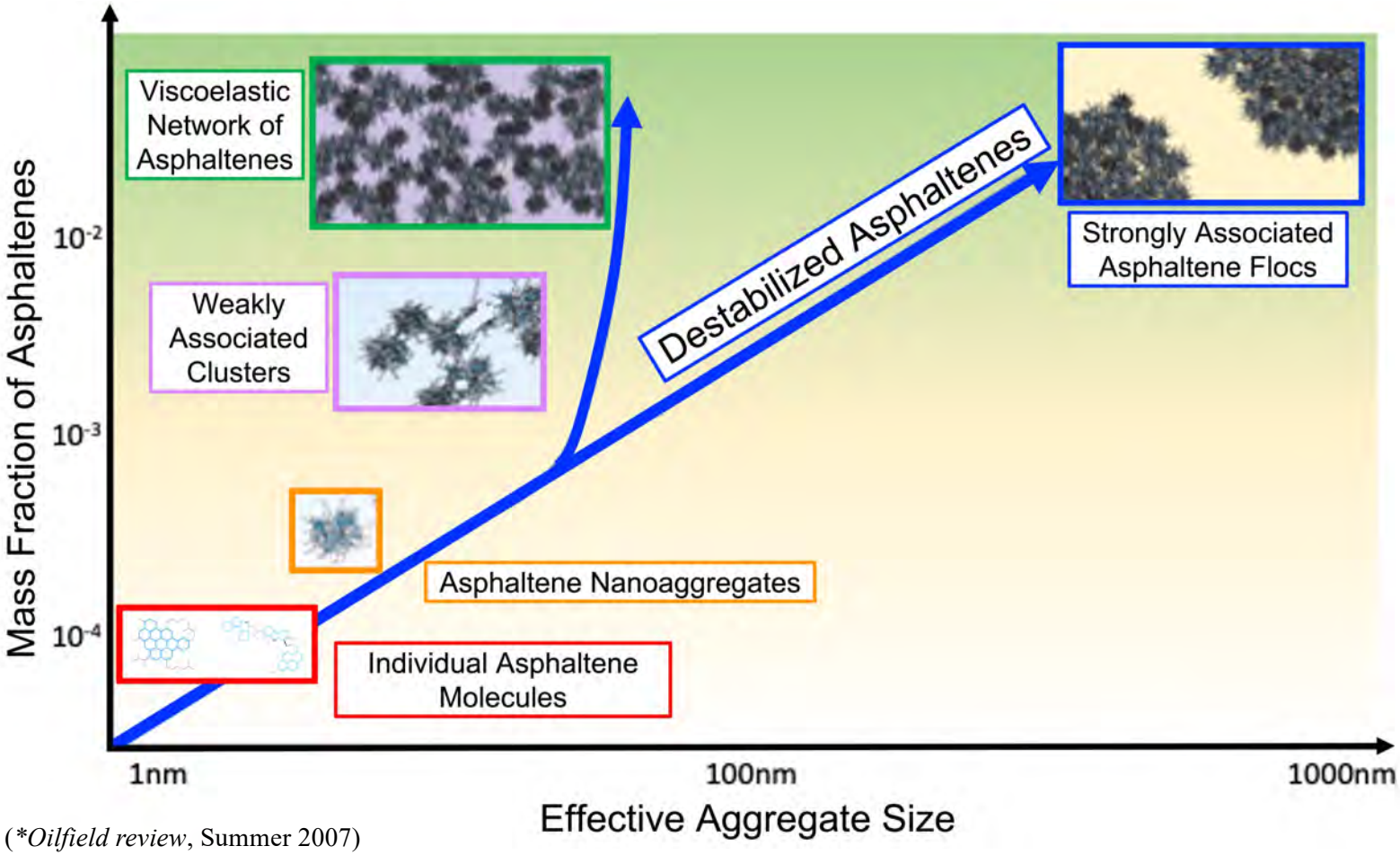


Key governing intermolecular forces



(*Mullins *et al.,* **Energy Fuels** 2012, 26, 3986−4003)

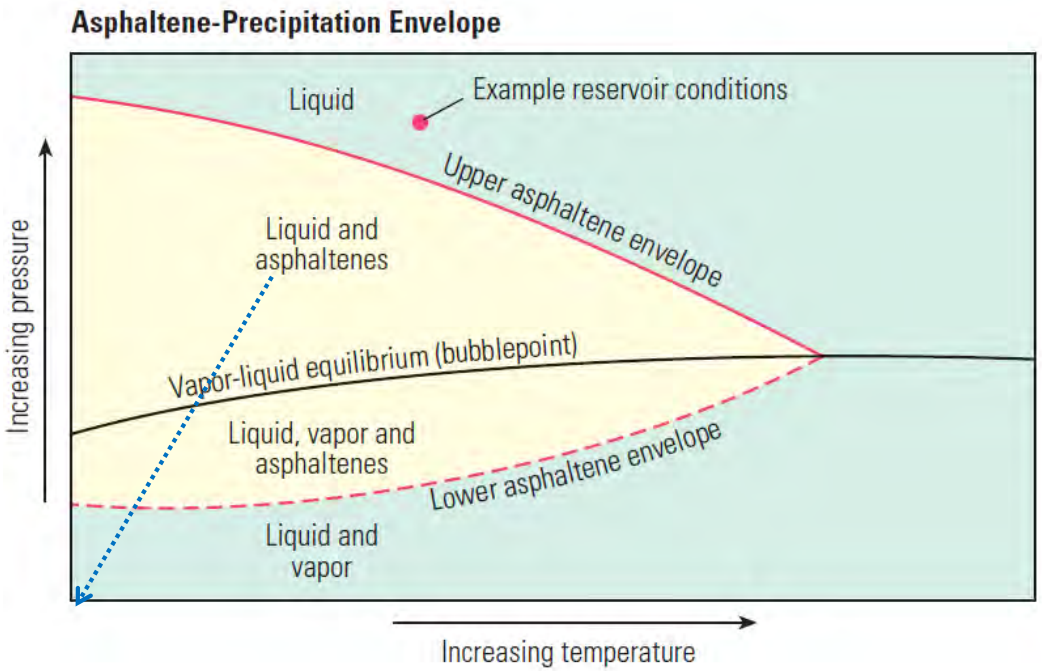
Asphaltene Physicochemical Properties

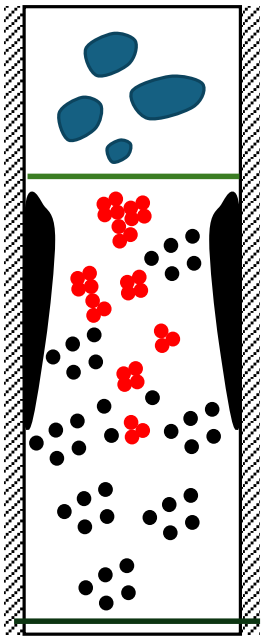


(**Oilfield review*, Summer 2007)

Asphaltene Destabilization & Precipitation

- Precipitate due to pressure, temperature, and composition change
- Insoluble: *n*-alkane (*n*-heptane and *n*-pentane)
  Soluble: aromatics (toluene and xylene)





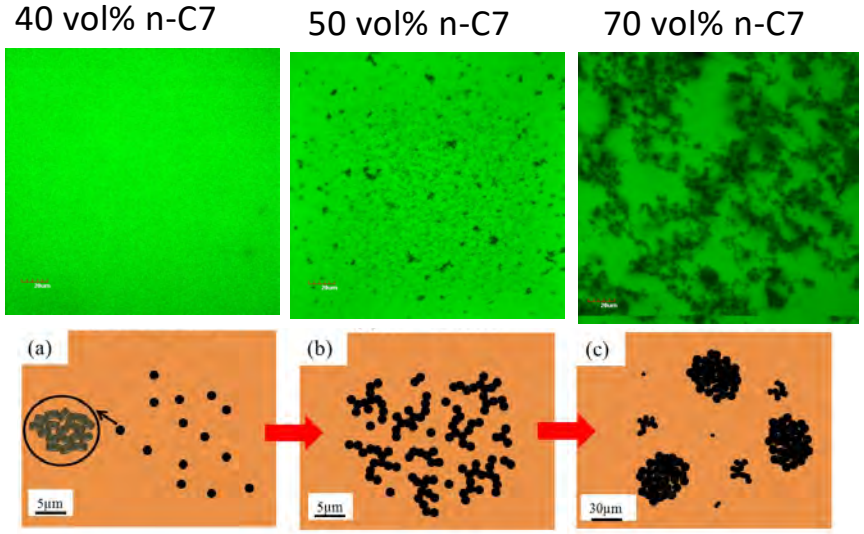
Bubble Point

AOP

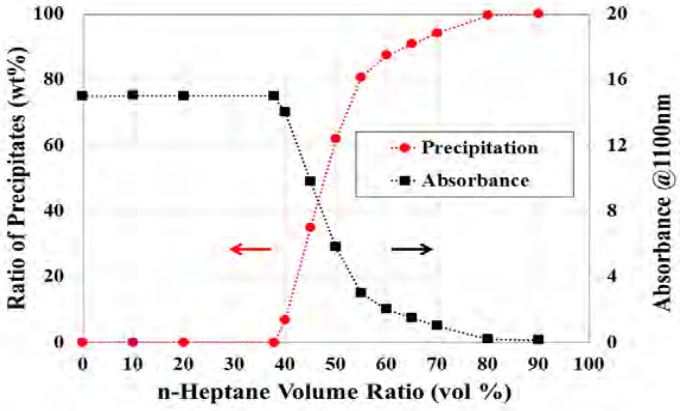
Asphaltene **O**nset **P**ressure

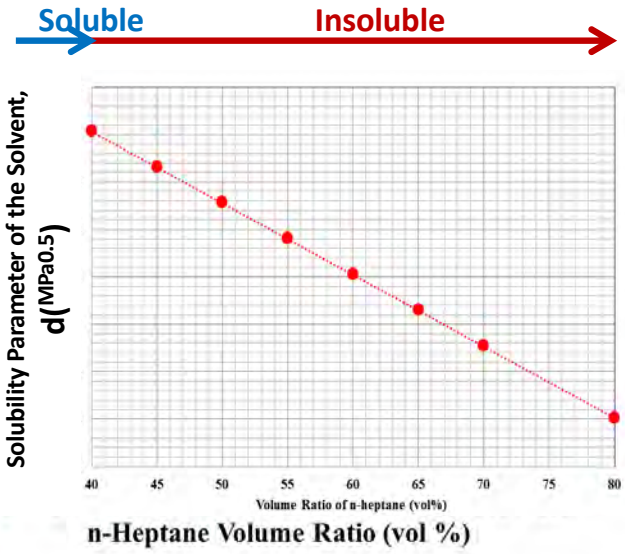
Vargas et al., Asphaltene Deposition: Fundamentals, Prediction, Prevention, and Remediation, 2018.

Asphaltene Aggregation Model



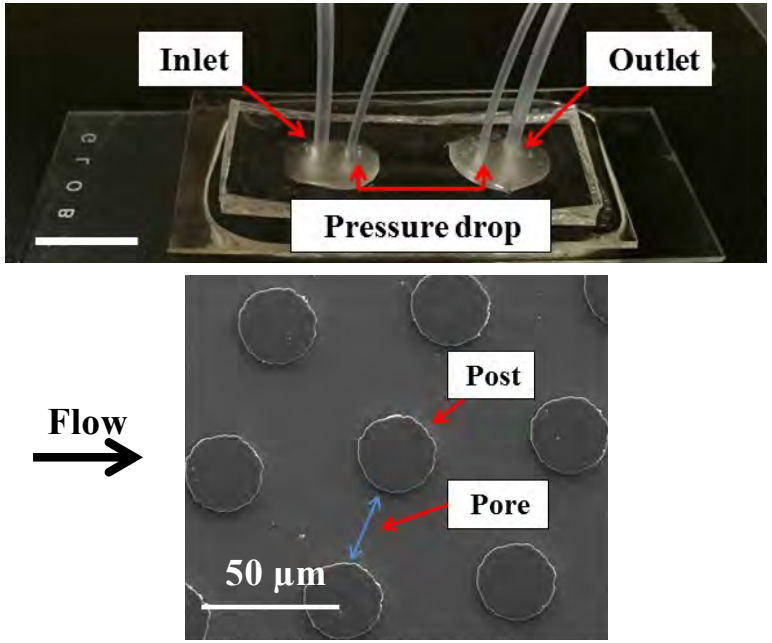
4.6wt% asphaltene in a model oil





(*Lin, Biswal, **Langmuir**, 2016)

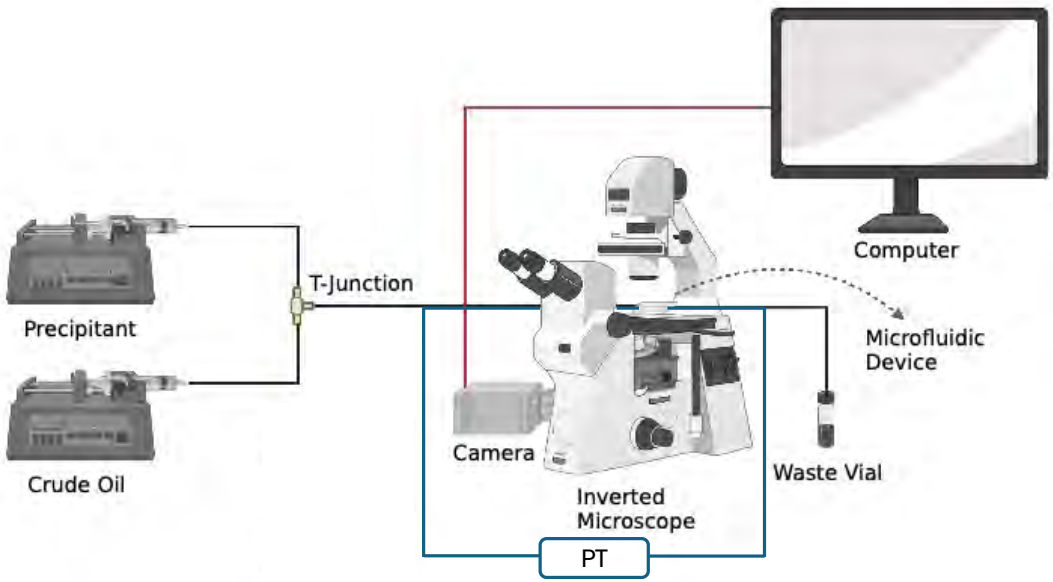
Microfluidic Model of Porous Media

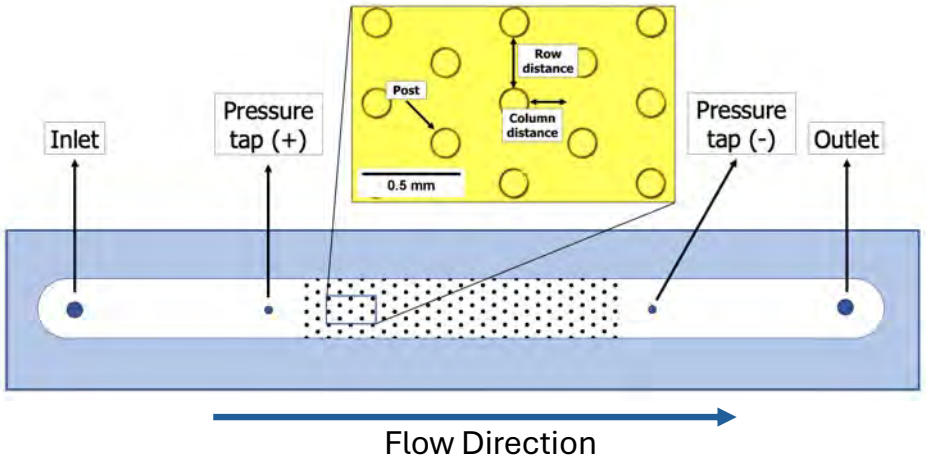


(*Yu-Jiun Lin *et al.*, **Langmuir**, 2016)

- Behavior of asphaltenes are detected both macroscopically (pressure drop) and in the pore scale (visualization).
- Knowledge of asphaltenes at the ***micro scale*** helps to solve related flow assurance issues at ***field scale***

Microfluidic Experimental Setup



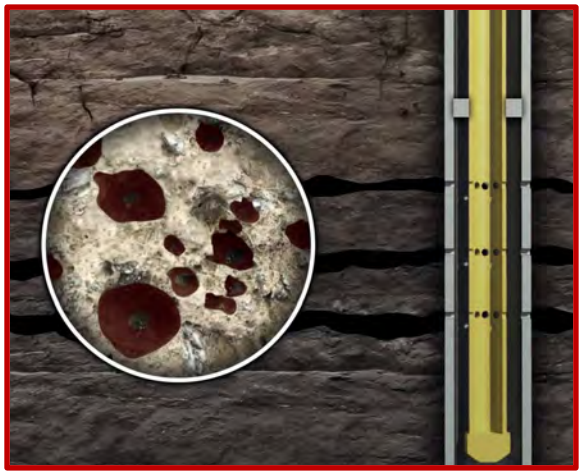


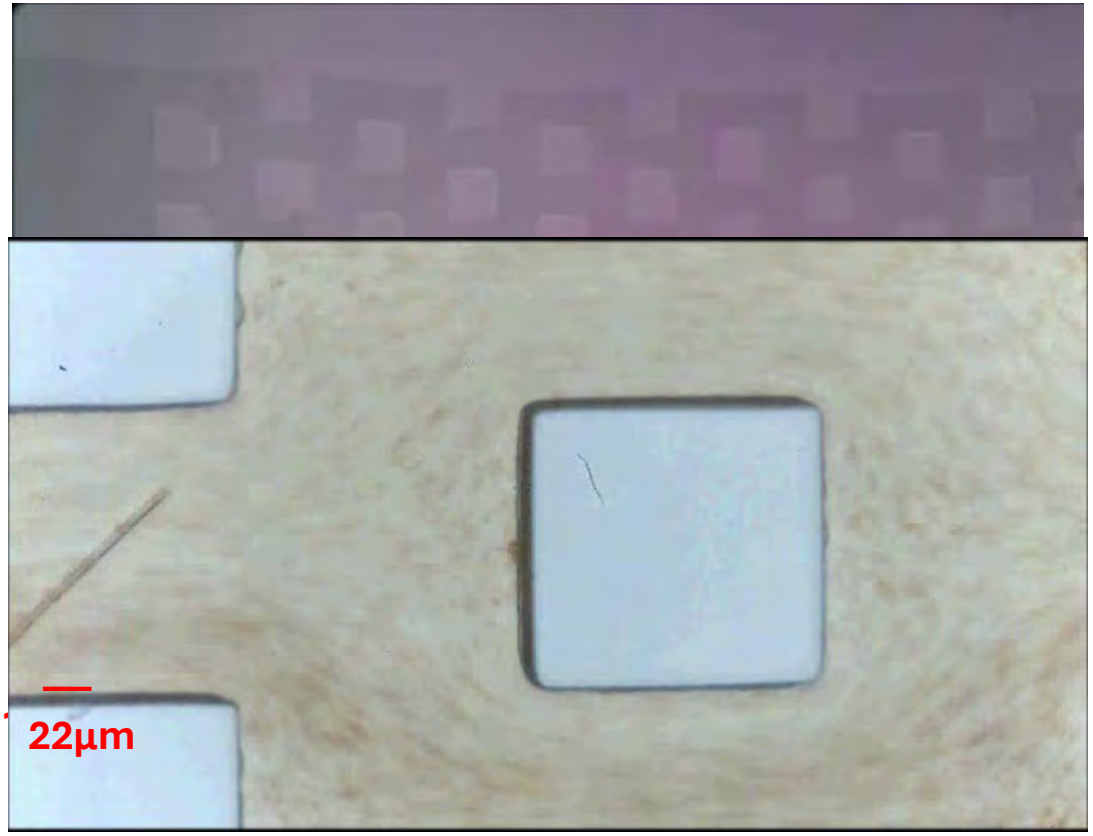
Porous media's length	1 mm
Porous media's width	0.2 mm
Porous media's thickness	40 μm
Post's diameter	120 μm
Row distance	280 μm
Column distance	220 μm
Porosity	91.6%
Permeability	40 Darcy

Nguyen et al., Energy Fuels, 2023.

Asphaltene Deposition in Porous Media

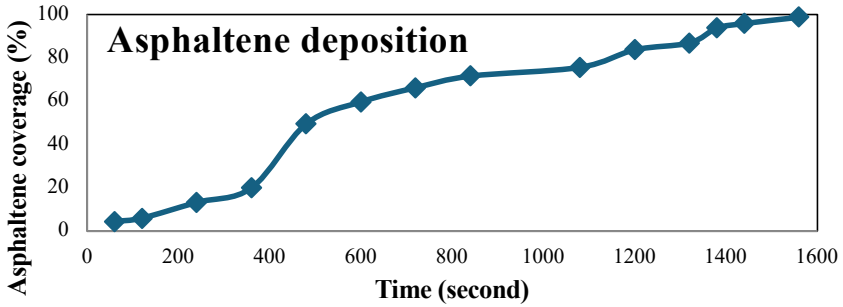
1. n-C7 70%, Oil 30%
2. Ambient Conditions

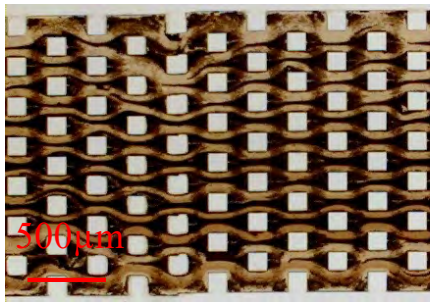




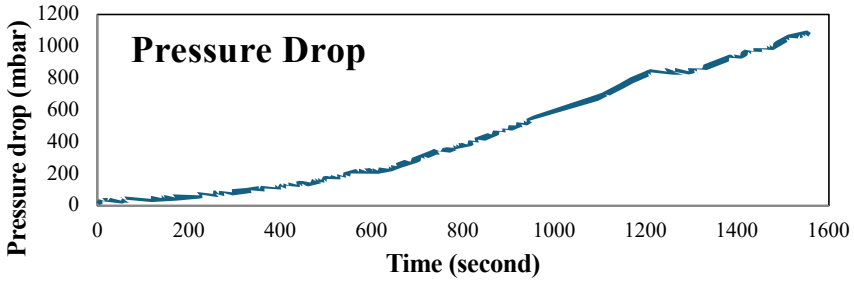
Asphaltene Data

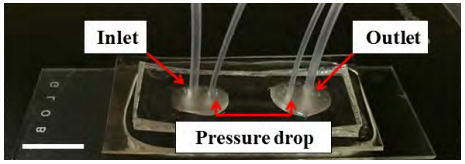
Imaging Process



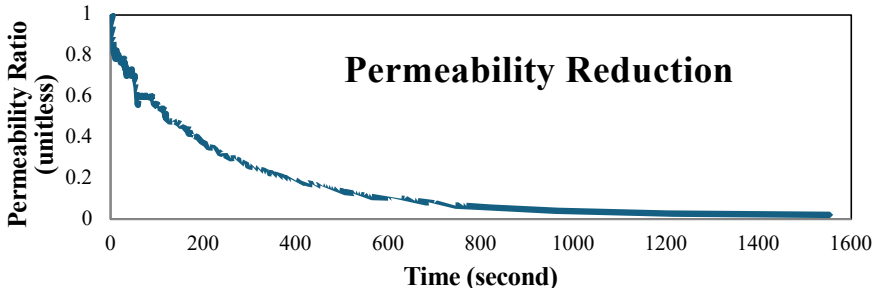


Pressure transducer





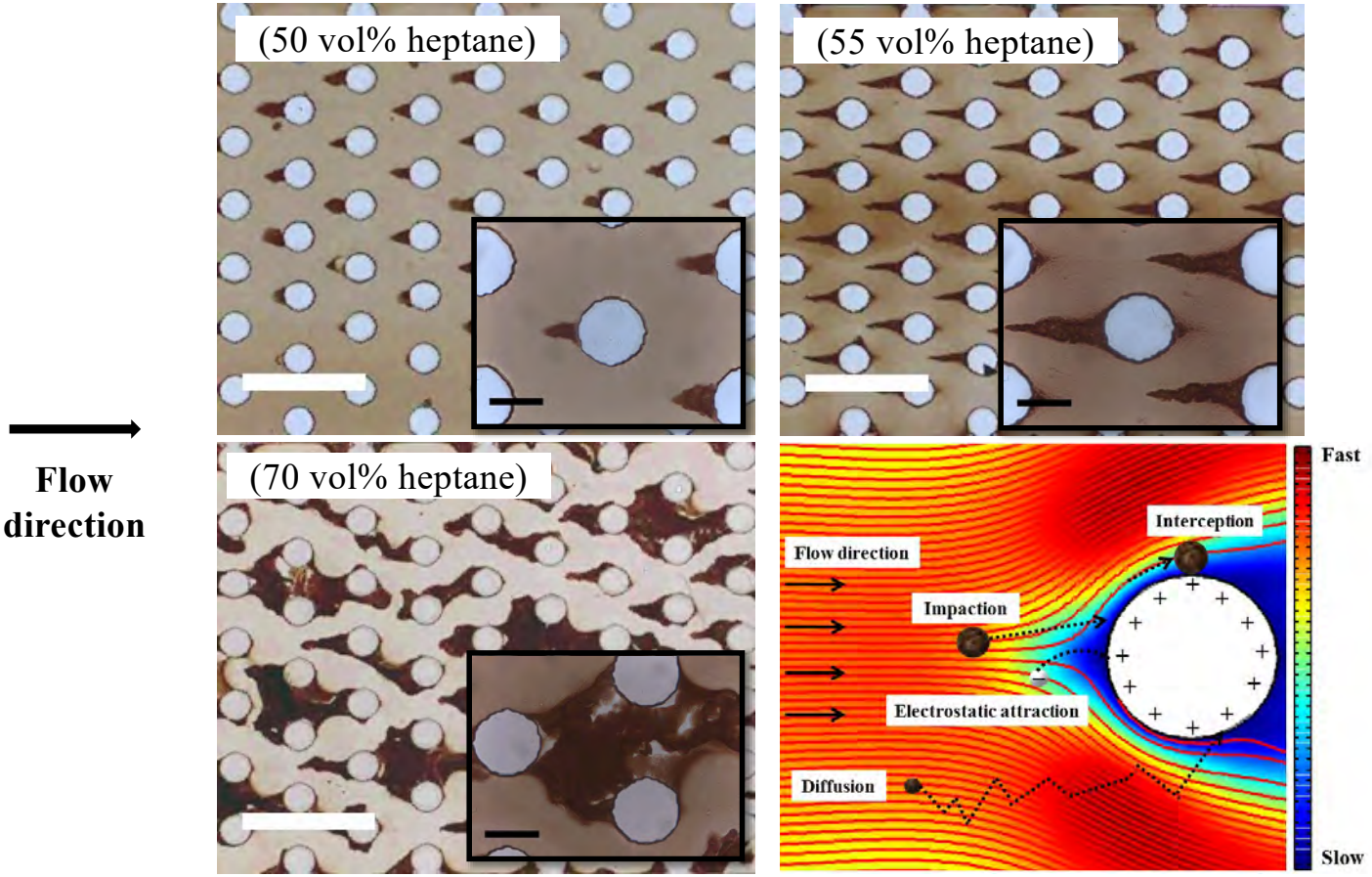
Calculation



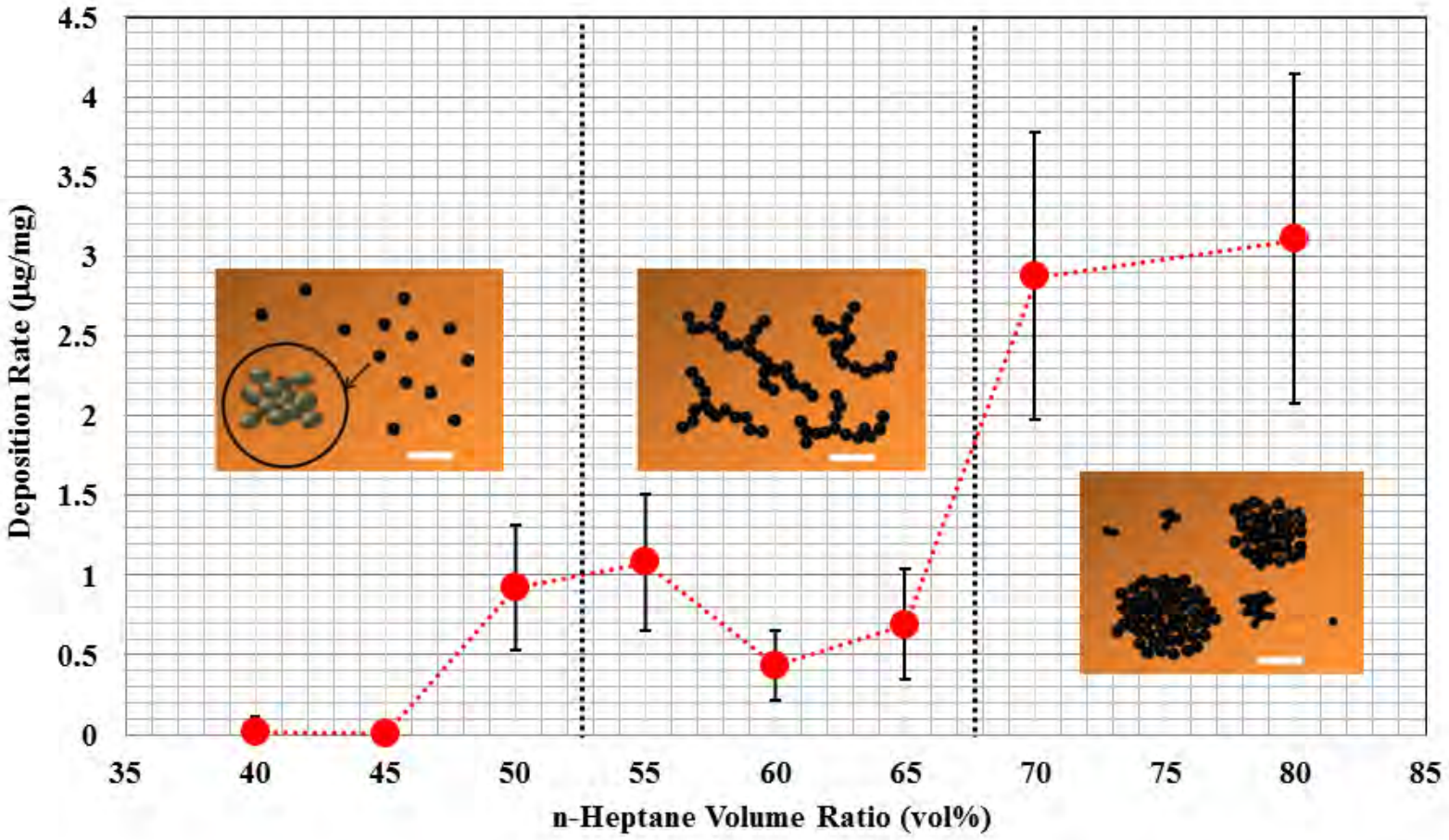
Darcy's Law:

$$Q = \frac{-kA\,\Delta P}{\mu L}$$

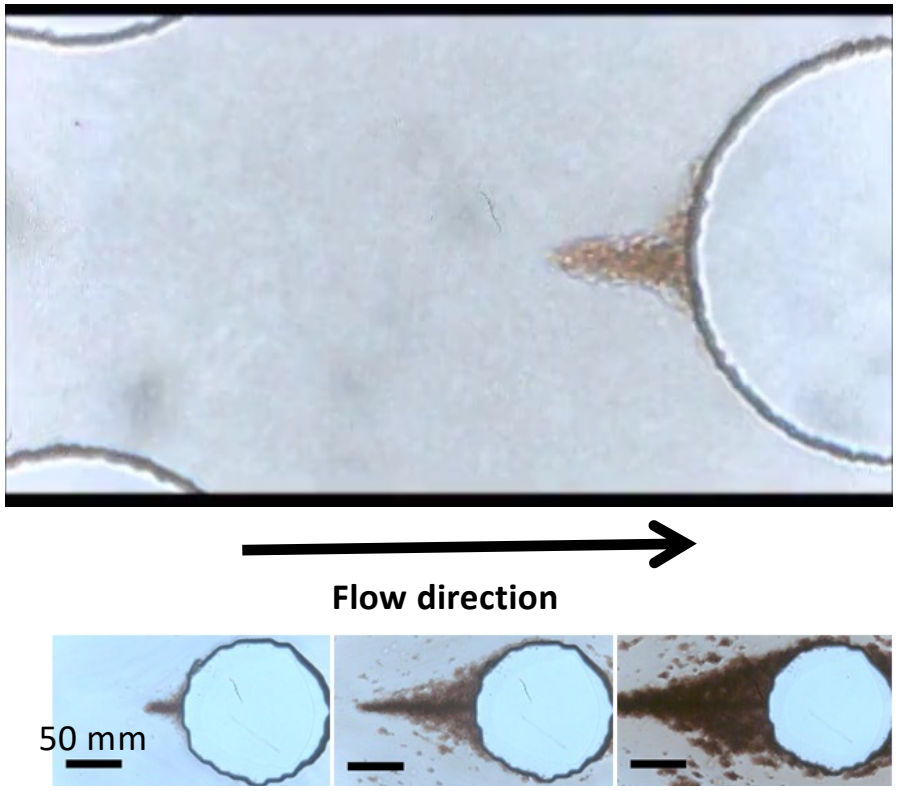
Asphaltene Deposition in Porous Media

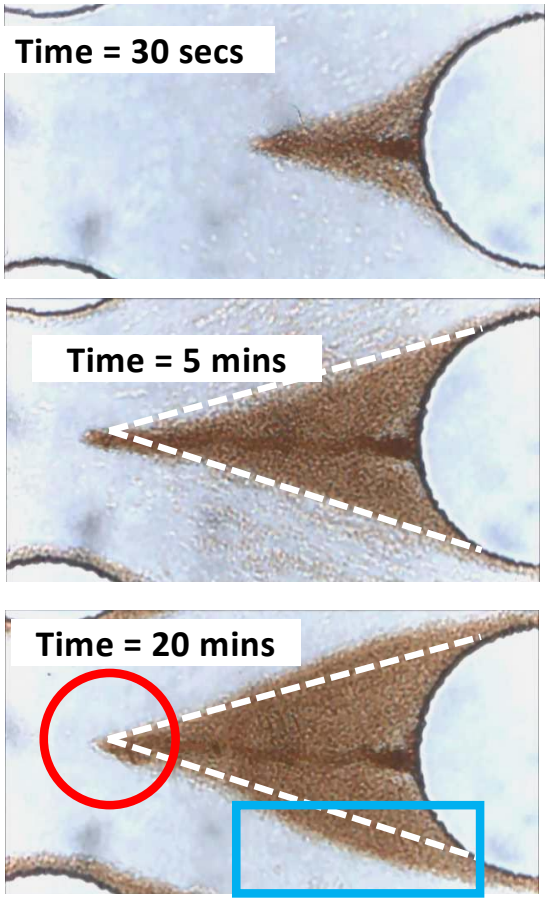


Asphaltene Deposition Rate



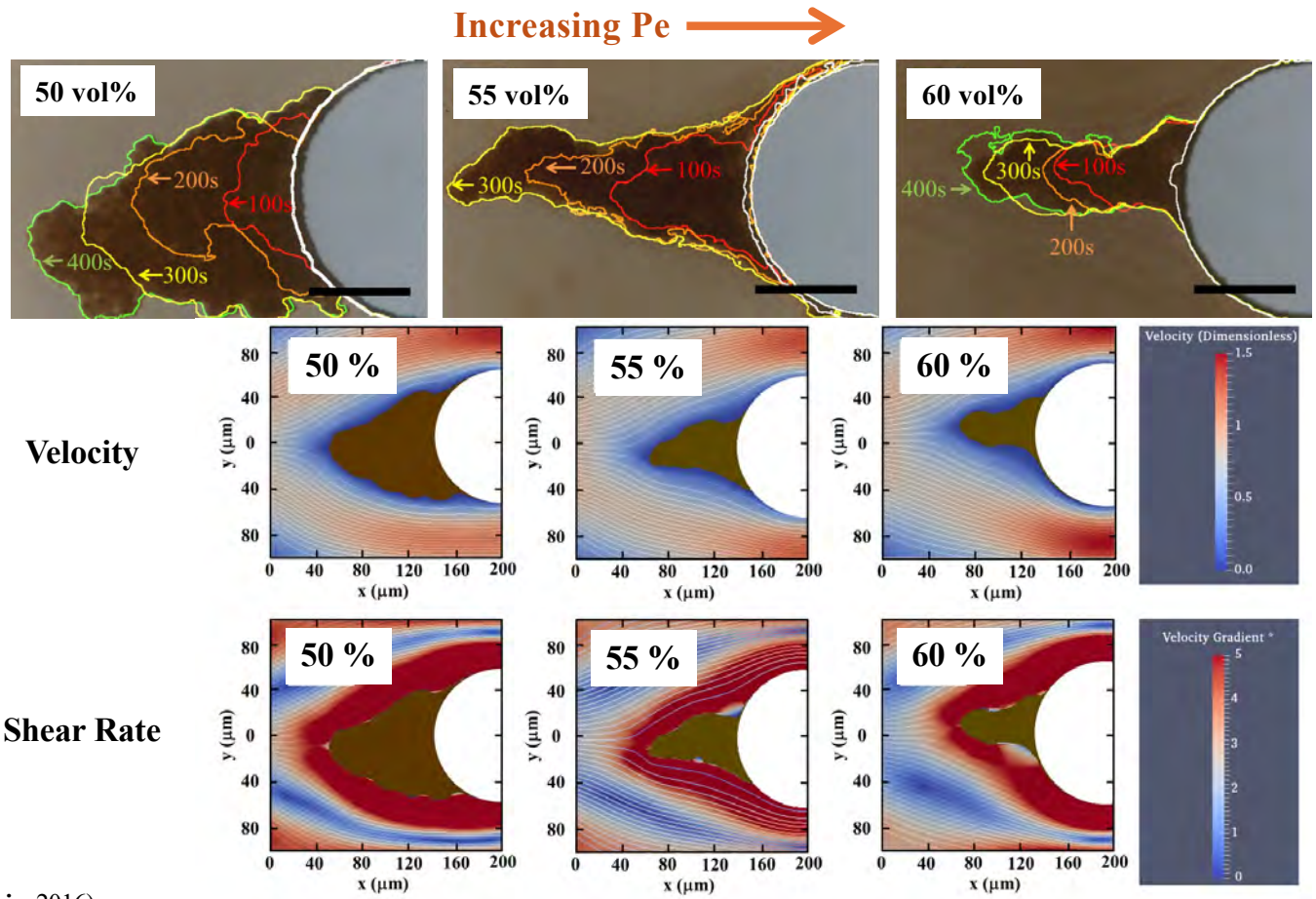
Asphaltene Deposition in Porous Media





- **The front of the deposition reaches a max growth at a critical shear rate**
- **However, the width of the deposition grows**

Pore Scale Velocity and Shear Rate

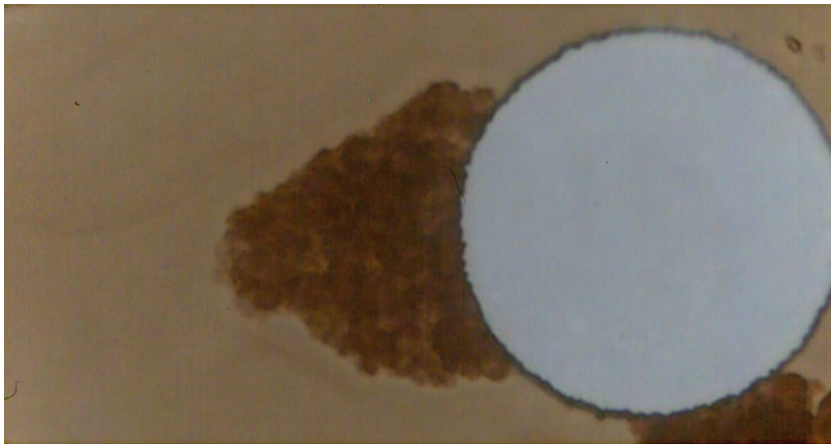


(*Yu-Jiun Lin *et al*., **Langmuir**, 2016)

Asphaltene Aggregation Structure

$$Pe = \frac{Convection}{Diffusion}$$

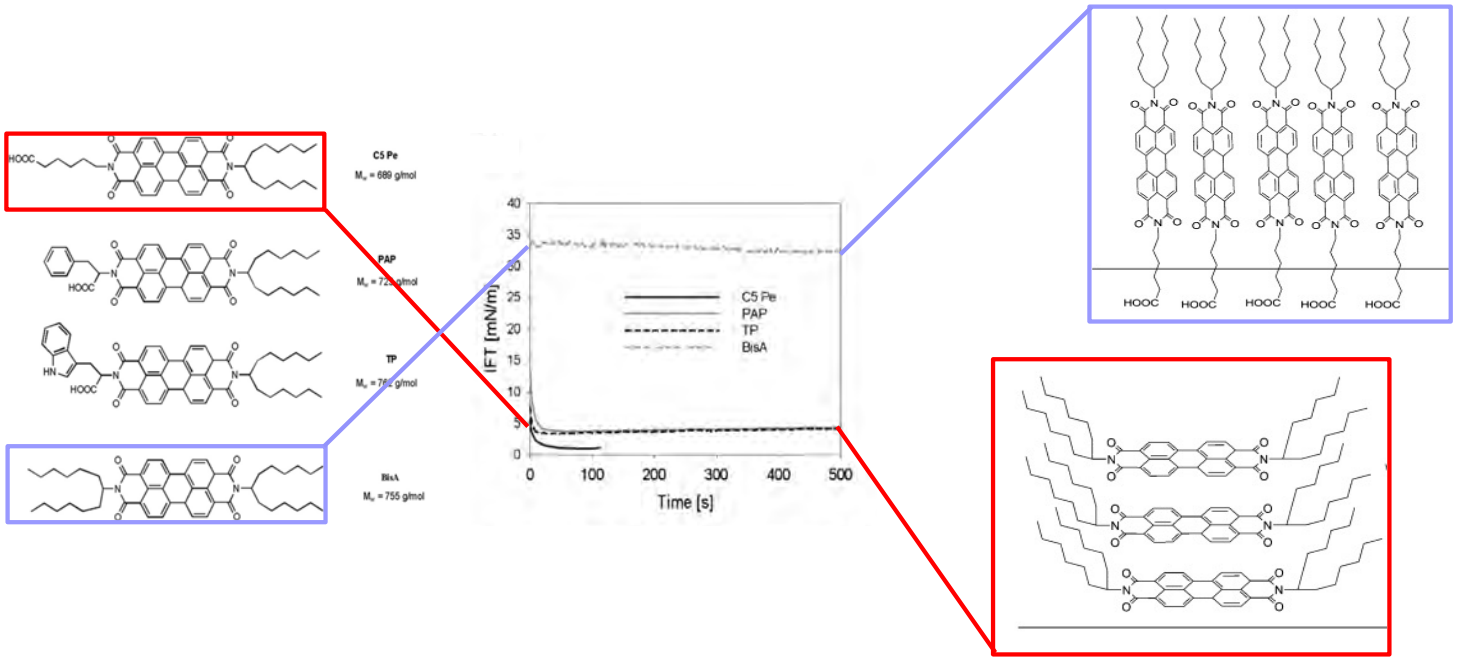
$\mathbf{Pe = 10^4 - 10^5}$



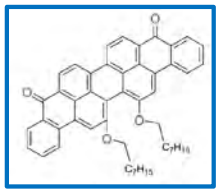
$\mathbf{Pe = 10^5 - 10^6}$

Deposition profile a function of Peclet number, which is a function of solubility

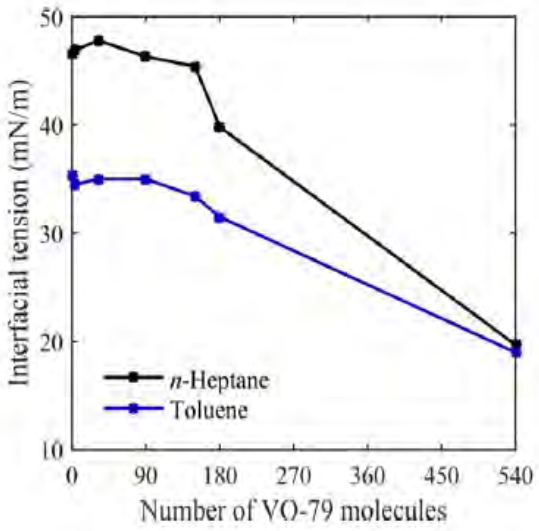
Model Asphaltene Molecules

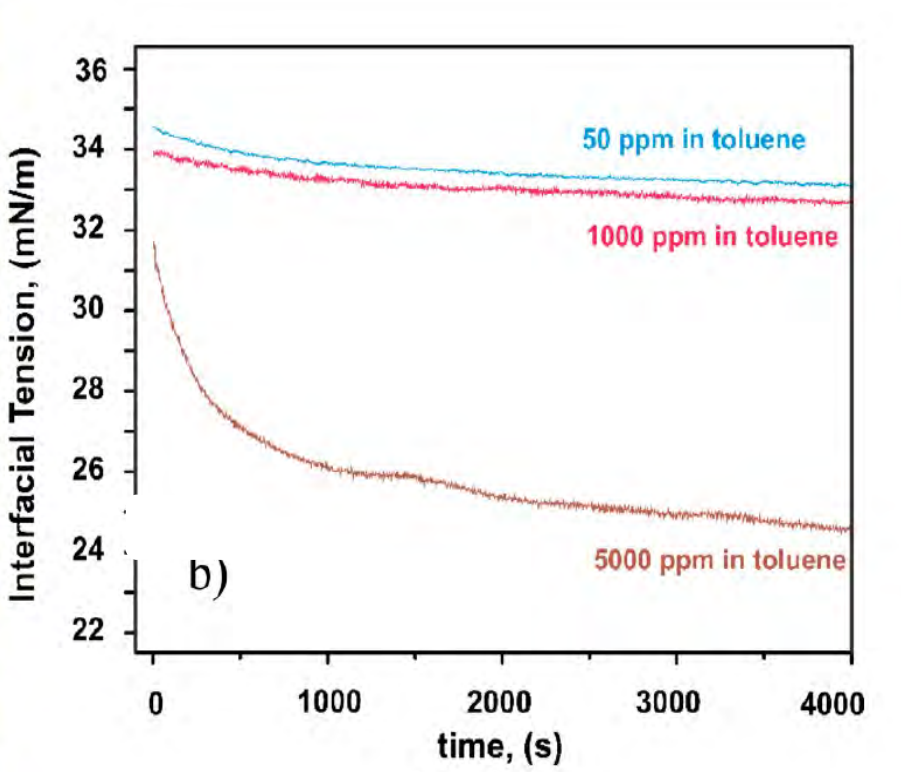


Nordgård et al Langmuir 2008 24(16) : 8742–51



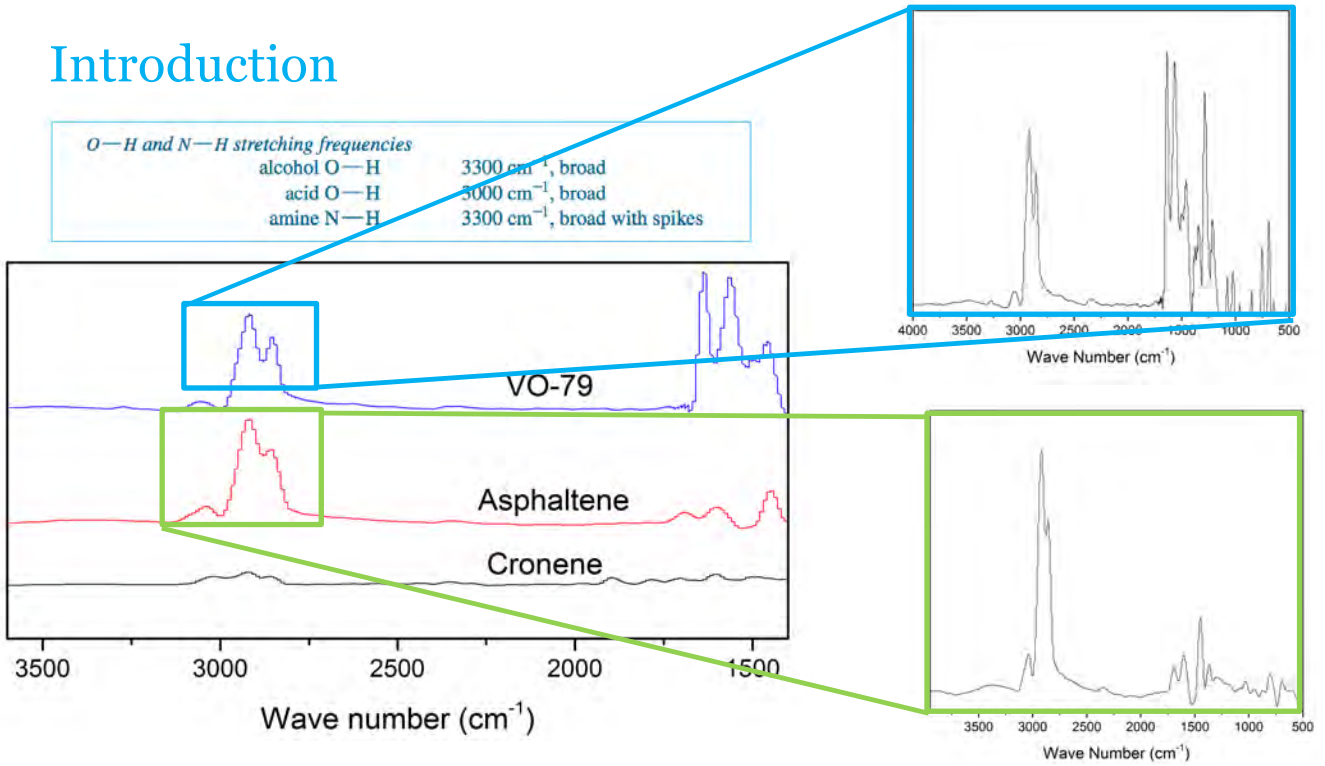
Vo-79


Interfacial tension (mN/m)
50
40
30
20
10
0
90
180
270
360
450
540
Number of VO-79 molecules
n-Heptane
Toluene

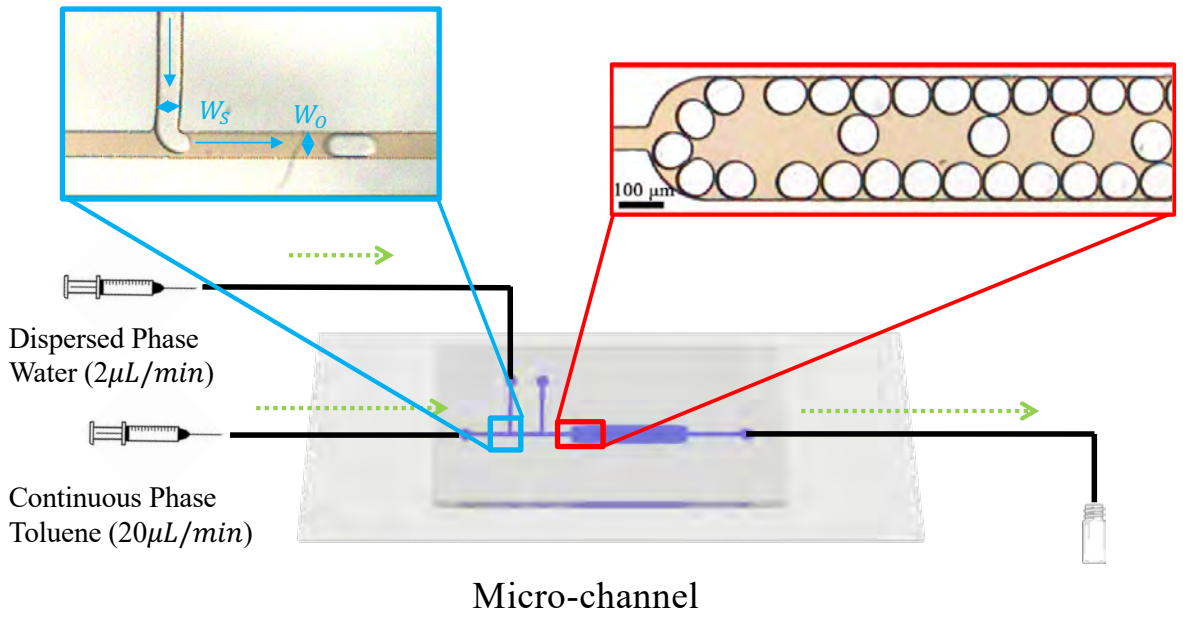

Interfacial Tension, (mN/m)
36
34
32
30
28
26
24
22
0
1000
2000
3000
4000
time, (s)
50 ppm in toluene
1000 ppm in toluene
5000 ppm in toluene
b)

Introduction

O—H and N—H stretching frequencies	
alcohol O—H	3300 cm^{-1}, broad
acid O—H	3000 cm^{-1}, broad
amine N—H	3300 cm^{-1}, broad with spikes

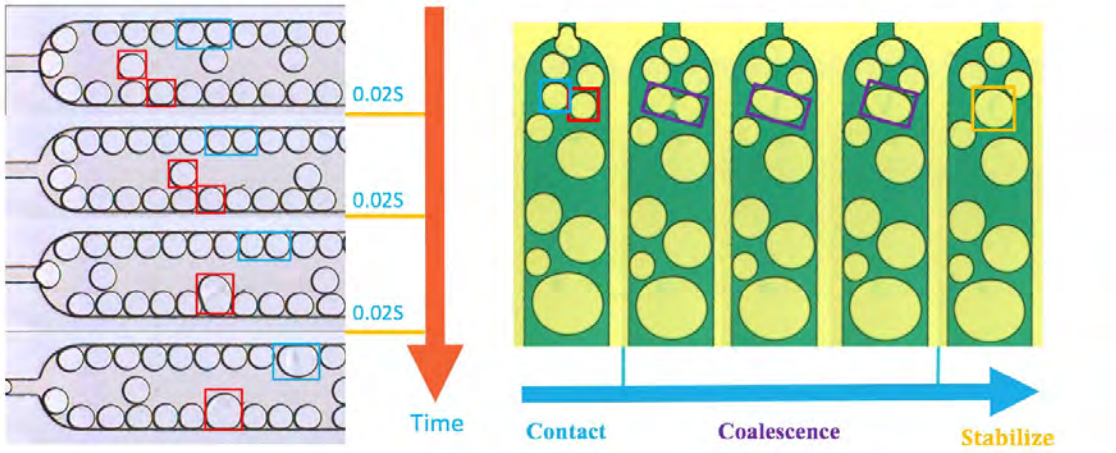


Probing Emulsion Stability Using Microfluidic Devices



Micro-channel

Coalescence Phenomenon Inside Micromodel



$$R_c = \frac{n_c}{A_c t_{exp} n_T}$$

$$n_c = \sum_{i}^{j} n_{c,ij}$$

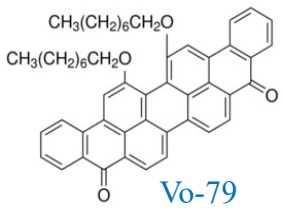
R_c - Coalescence rate ($m^{-2} \cdot s^{-1}$)

A_c- Monitored area (m^2)

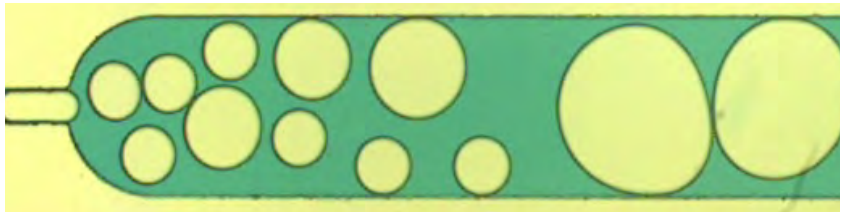
n_c -number of coalescence events

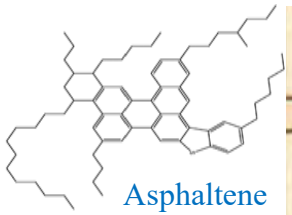
n_T – total number of initial emulsions

Coalescence Behavior Inside Collision Chamber

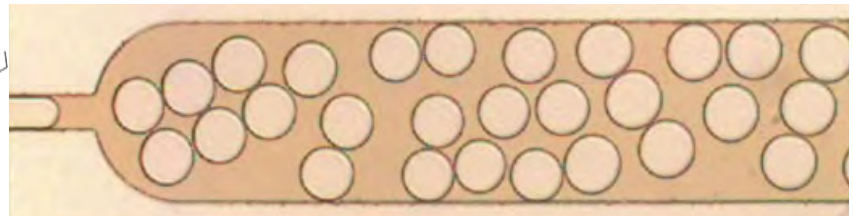


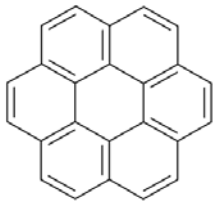
Vo-79



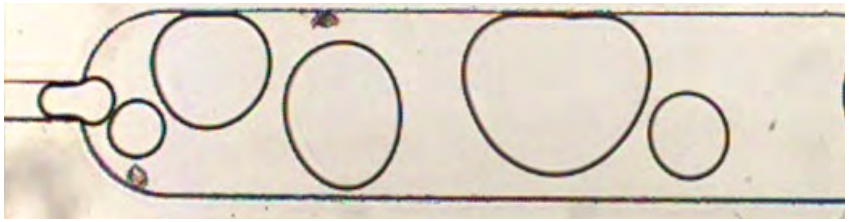


Asphaltene

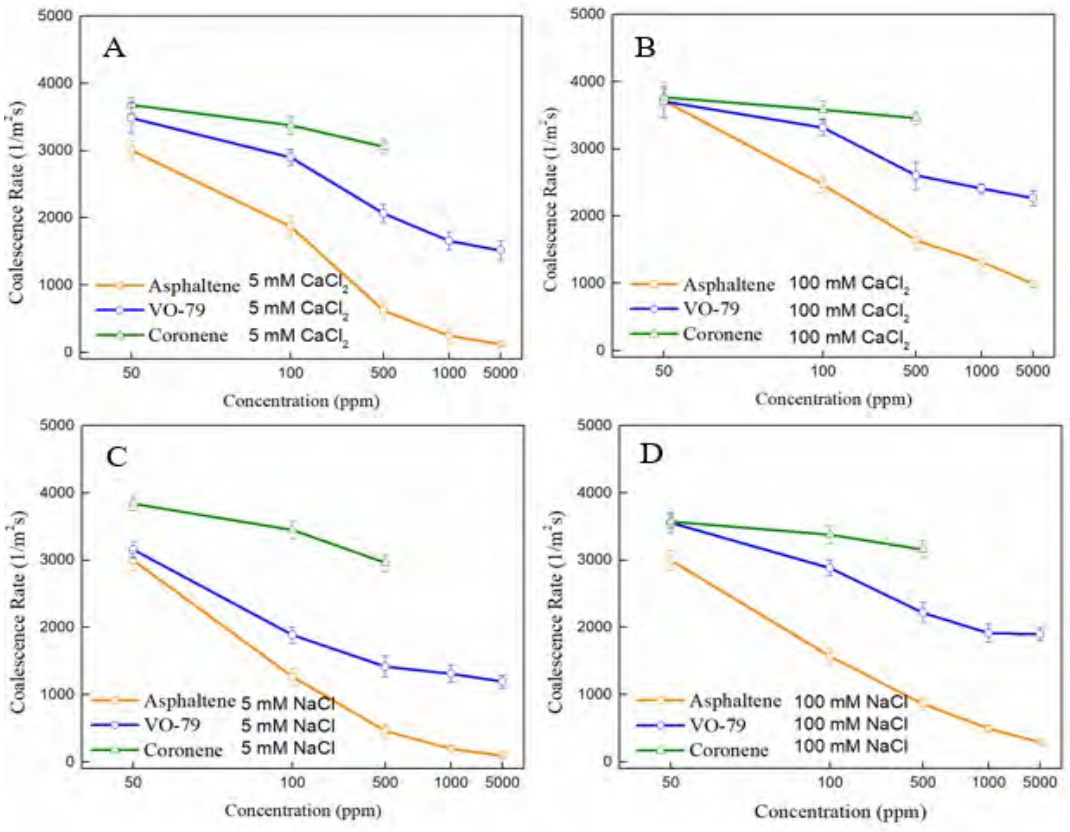




Coronene



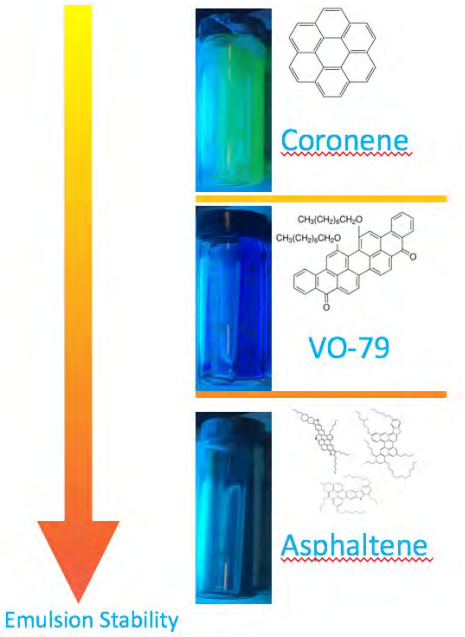
Effect of salt relate to emulsion stability

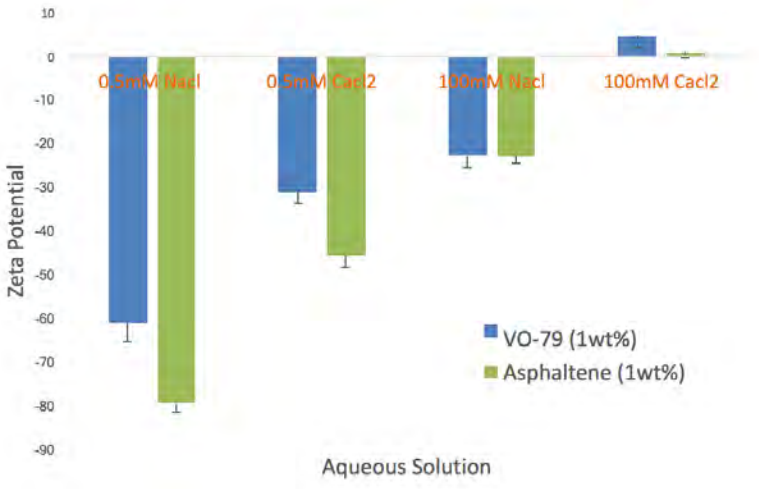


- Coronene stabilized emulsions are not affected by salt concentration
- Asphaltene stabilized emulsions are more sensitive to salt concentration
- Asphaltene stabilized emulsions are more stable than that of VO-79 in both high and low salt concentration

Emulsion Surface Characterization

Zeta Potential Measurement

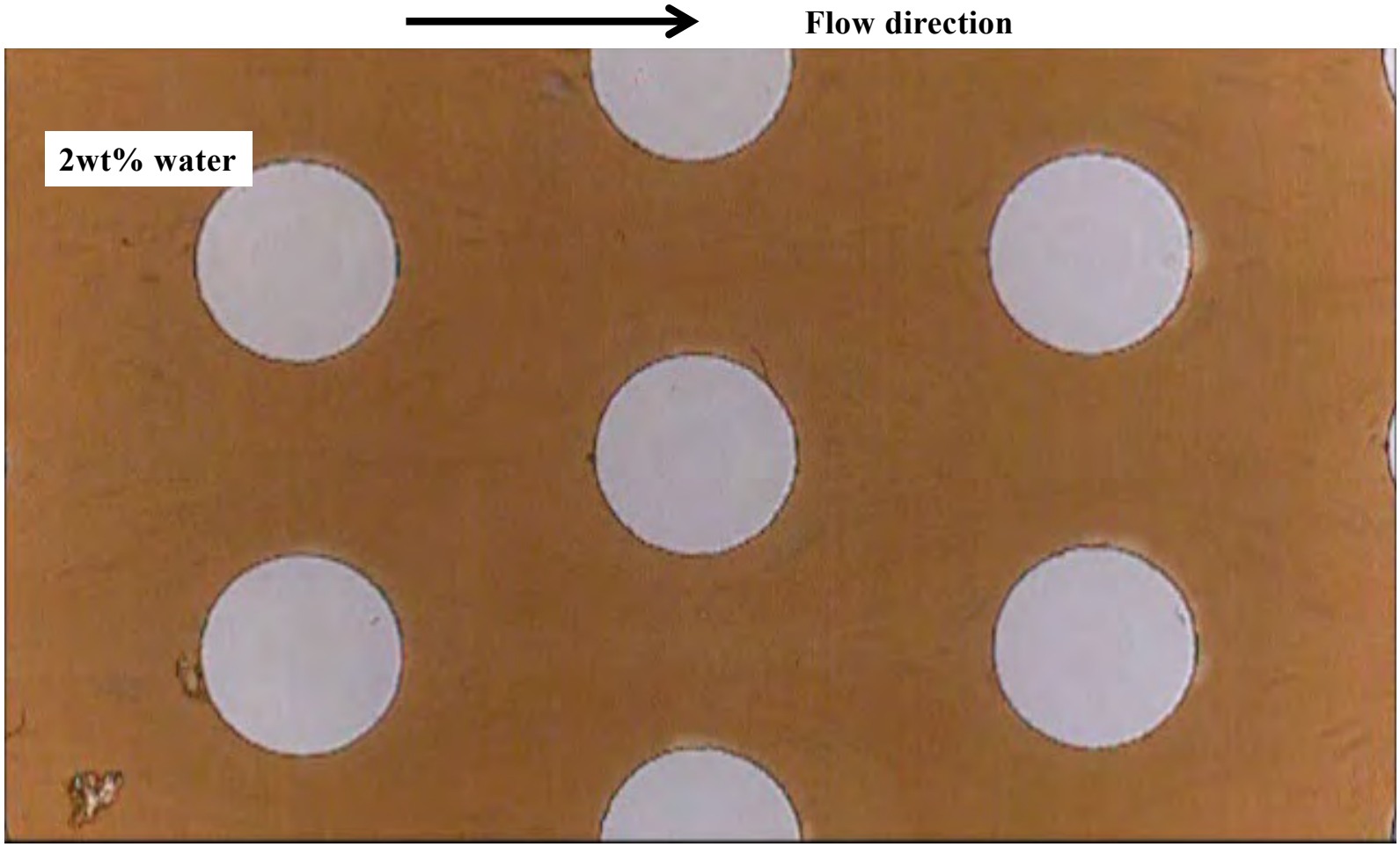




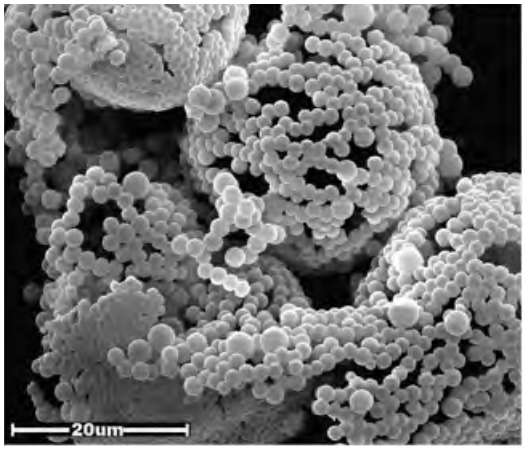
Asphaltene 1wt%	0.5mM Nacl	0.5mM $Cacl_2$	100mM Nacl	100mM $Cacl_2$
Zeta potential	-79.50	-45.64	-23.05	0.75
Standard deviation	2.16	2.55	1.51	1.38

VO-79 1wt%	0.5mM Nacl	0.5mM $Cacl_2$	100mM Nacl	100mM $Cacl_2$
Zeta potential	-60.94	-31.10	-22.73	4.55
Standard deviation	4.47	2.50	2.75	2.65

Asphaltene Stabilized Emulsions



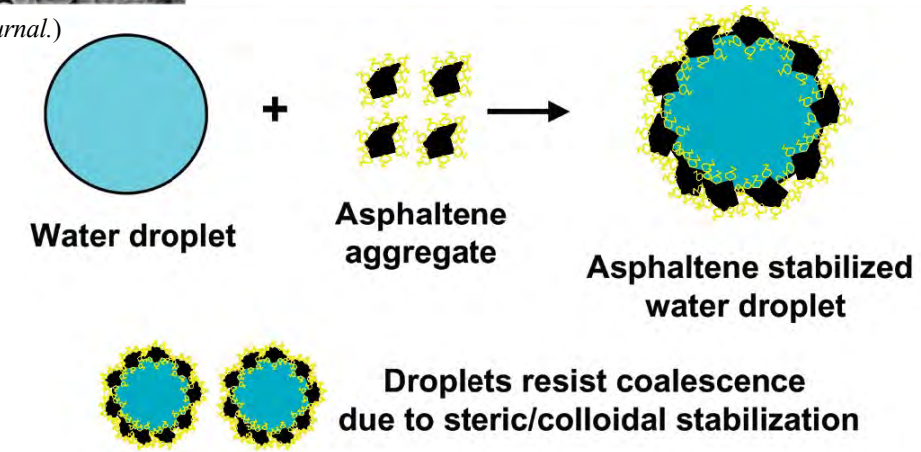
Pickering Emulsion



(*Zihua Chen et al. 2013. *Polymer Journal.*)

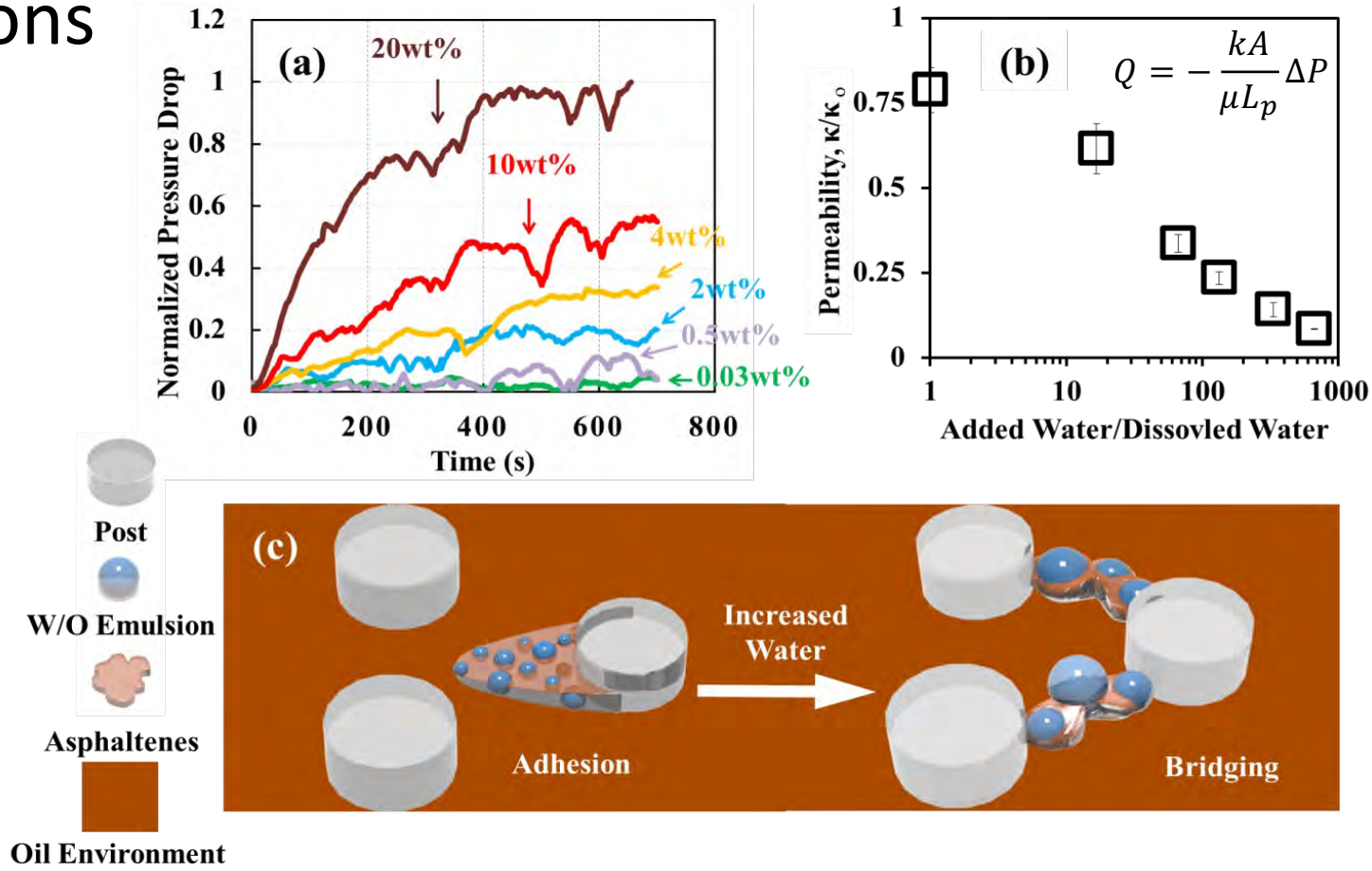
- Particle stabilized emulsions
  - Particle laden interface is viscoelastic
  - Particles provide steric repulsion
  - Particles provide mechanical protection

(*Oldroyd, J.G. *Proc. Royal Soc. London A* 1955)

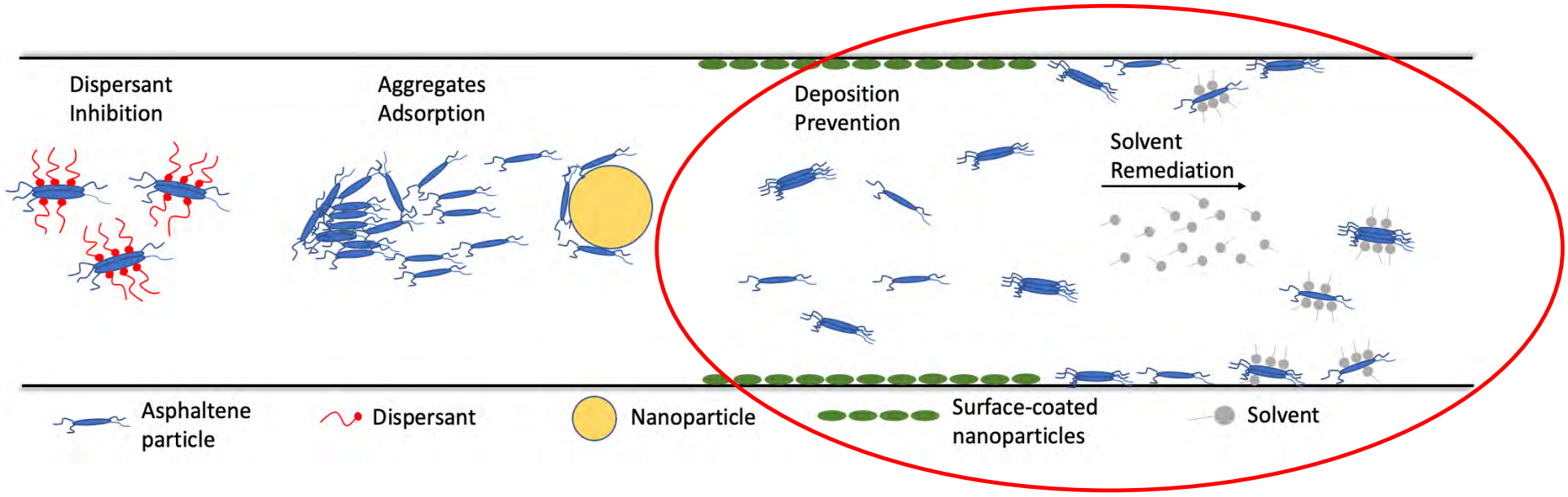


(*Tambe, D.E et al. 1993. *J. Colloid Interface Sci.*)

Plugging/Jamming of Asphaltene-Stabilized Emulsions

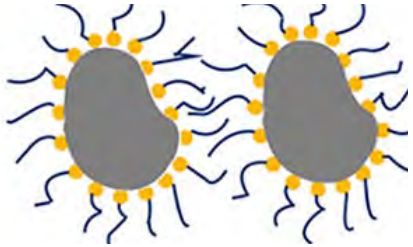


Asphaltene Solutions



Asphaltene Dispersants and Inhibitors

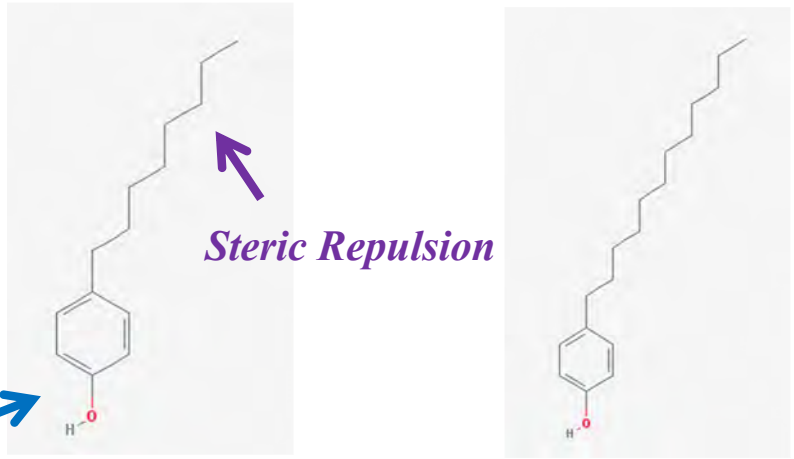
- Dispersant: suspend particles in the solution by reducing the size of the aggregates



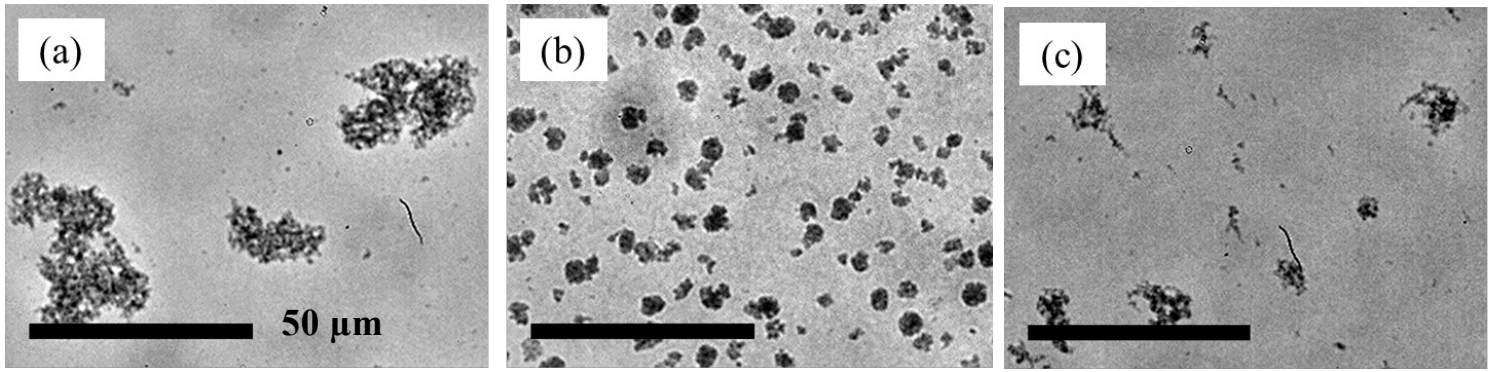
- Inhibitor: prevent asphaltene destabilization by shifting the onset of precipitation

Asphaltene Dispersant

- Dispersant: suspend particles in the solution by reducing the size of the aggregates
- Inhibitor: prevent the destabilization and shift the onset of precipitation (usually polymer)

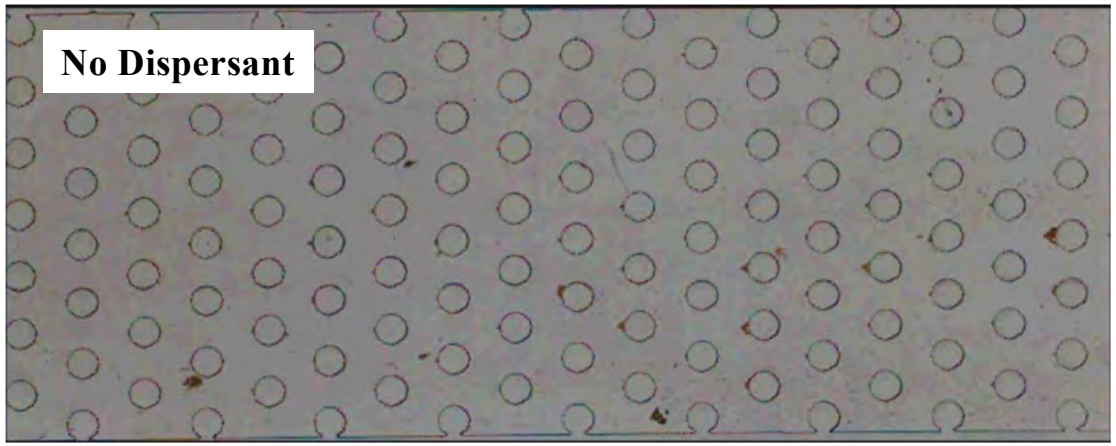


No Dispersant **_p_-Octylphenol (pC8)** **_p_-Dodecylphenol (pC12)**

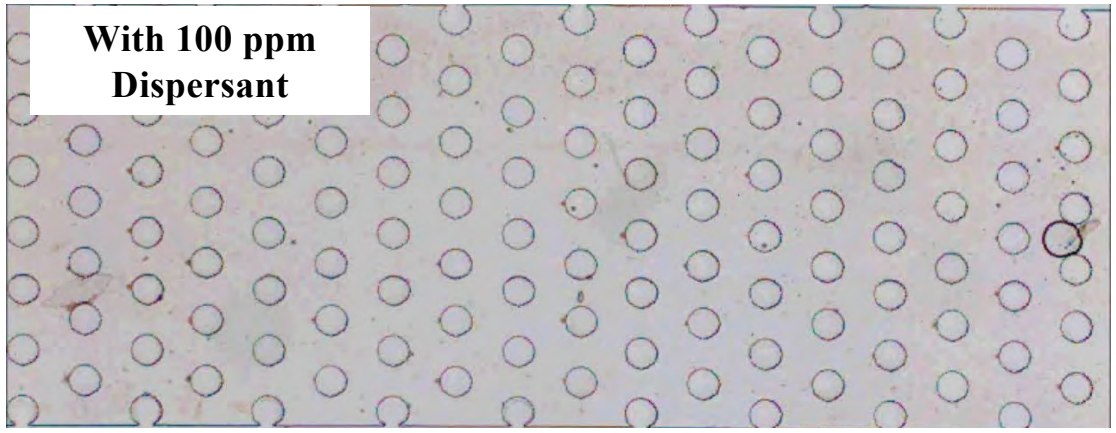


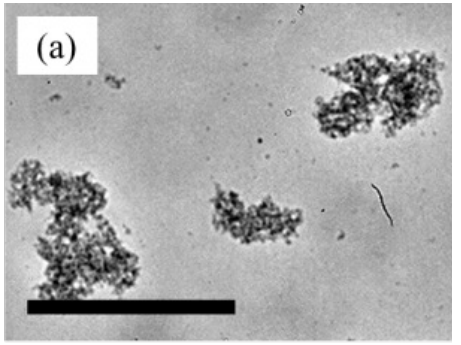
(*Yu-Jiun Lin *et al*., **EnergyFuels**, 2017)

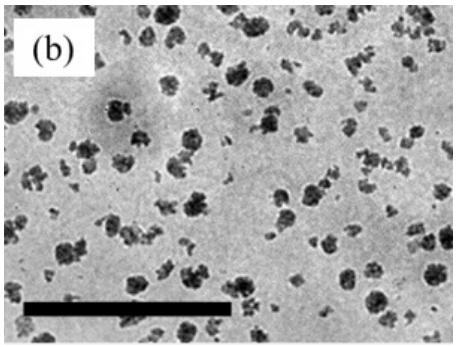
Dynamic Deposition Process



Flow



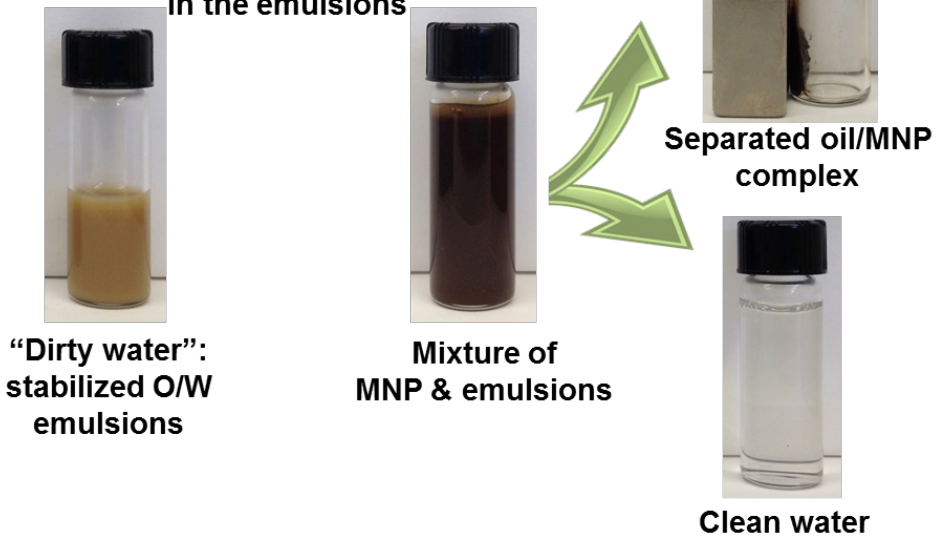


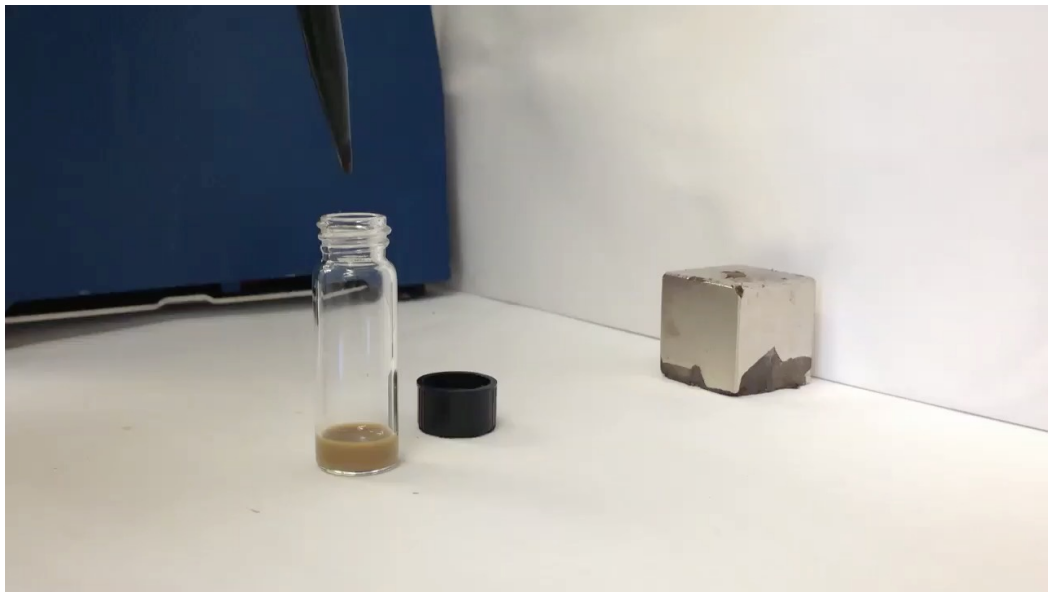


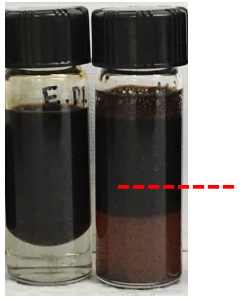
More Deposition but "Softer" Deposits

- **Particle Interaction is Important**

Polymer-Coated Nanoparticles







Emulsion layer

Contaminated water

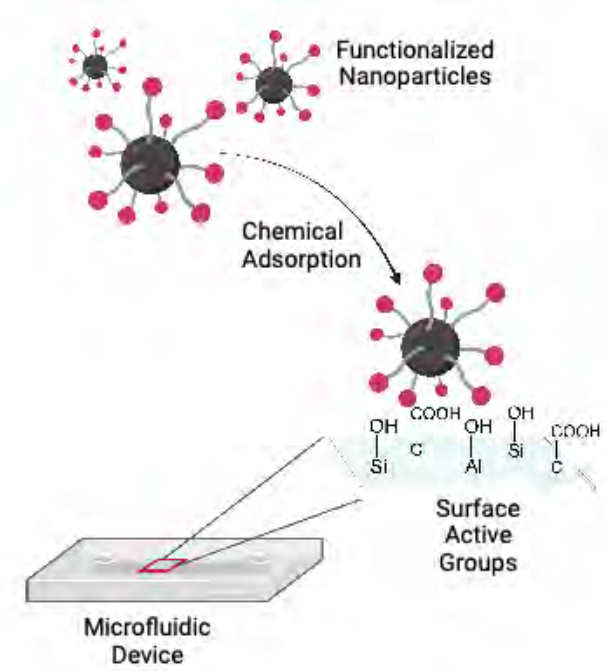
Oil layer

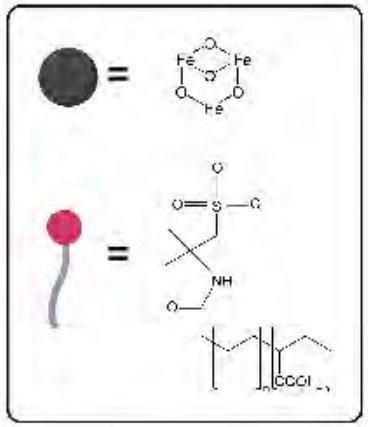
Treated water

(*Joohyung Lee *et al.*, ***Macromolecules***, 2017, 50, 7699-7711)

Polymer-Coated Nanoparticles

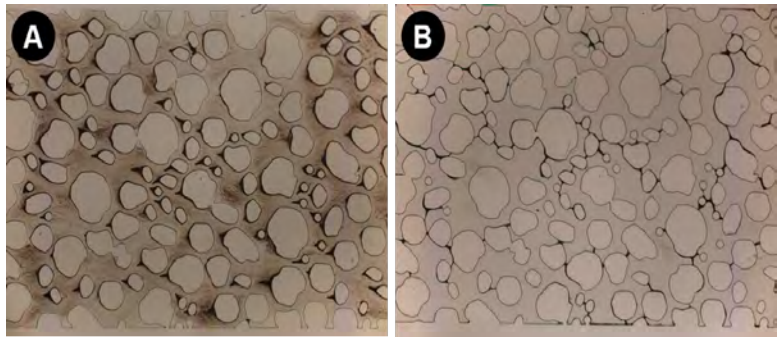
Nanoparticles are stable in high salinity brines at reservoir conditions.





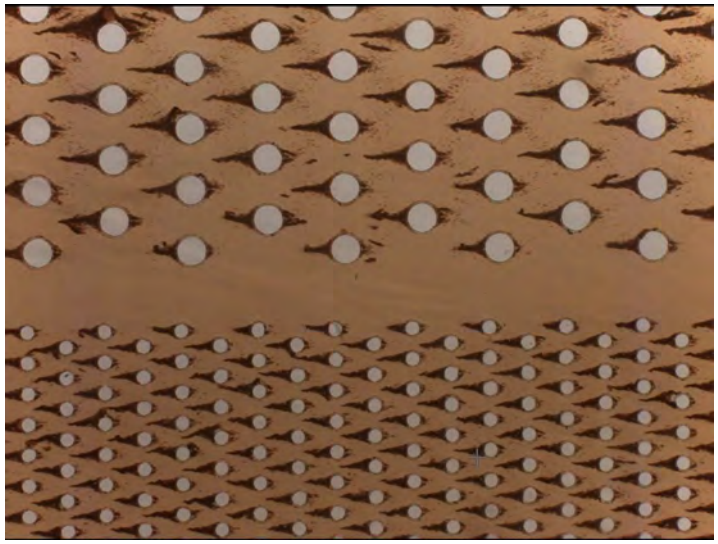
Synthetic Brine

Component	Concentration, g/L
NaCl	182.31
$CaCl_2$-$2H_2O$	77.25
$MgCl_2$-$6H_2O$	25.62



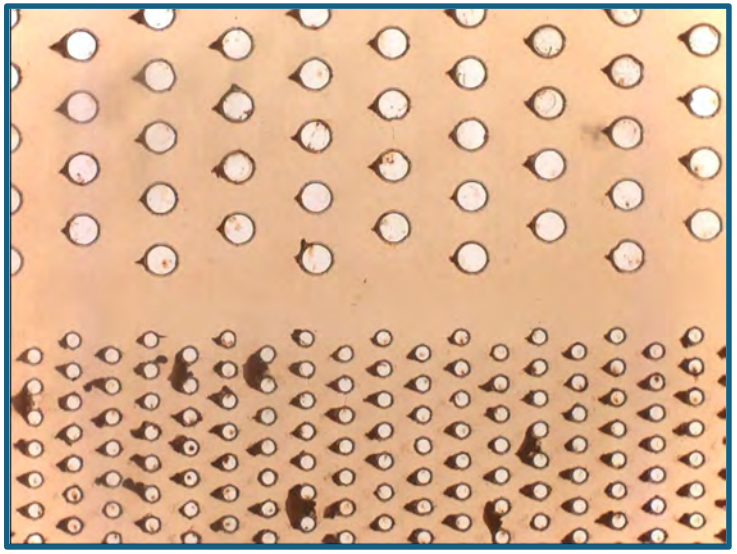
Nanoparticle performance

Without hairy nanoparticle coating



55 Vol% Heptane - 45 Vol% Crude Oil
@60uL/min 60 mins

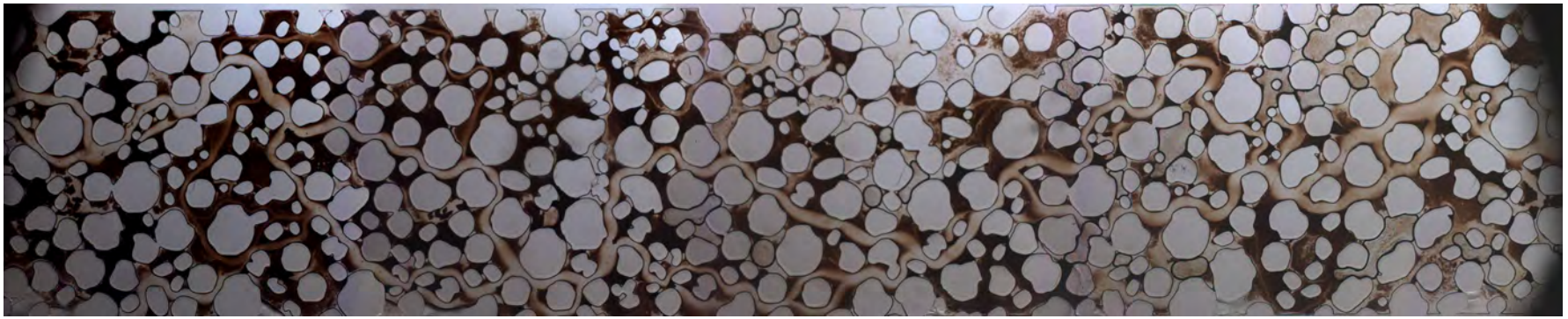
With hairy nanoparticle coating



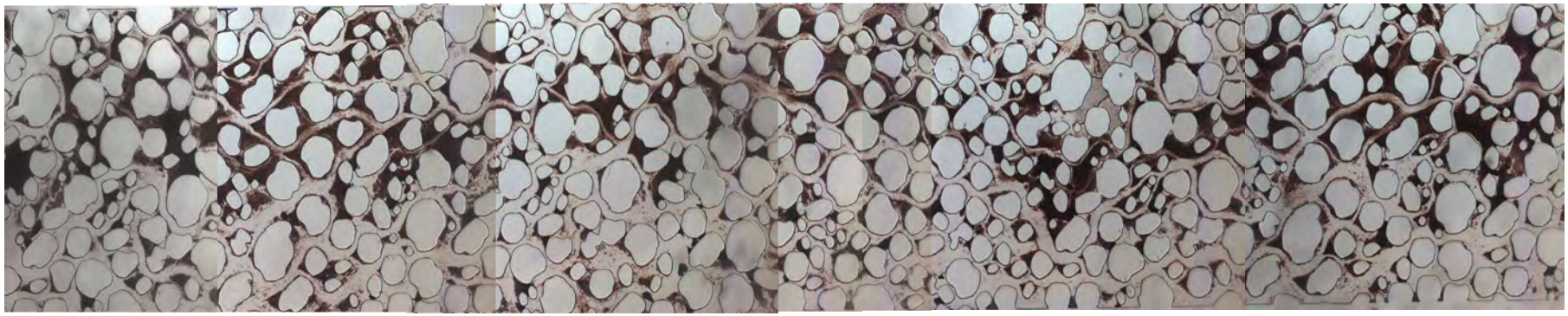
55 Vol% Heptane - 45 Vol% Crude Oil
@60uL/min 60 mins

Asphaltene Deposition Reduced

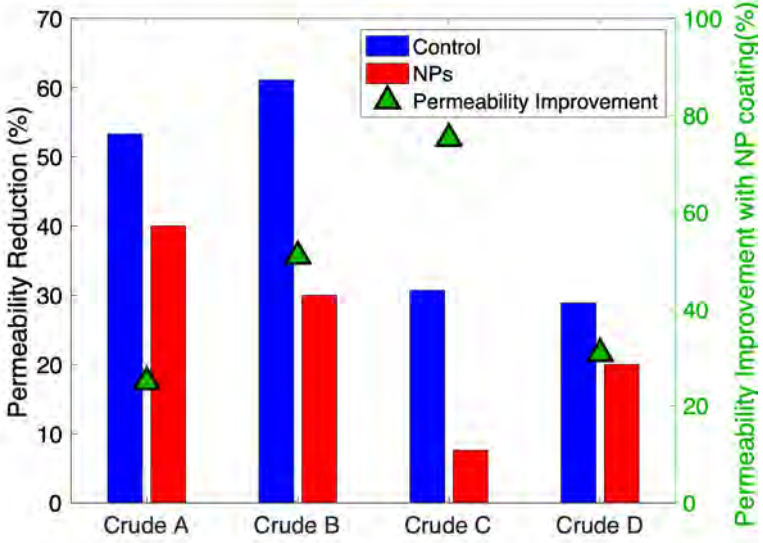
Blank Microchannel

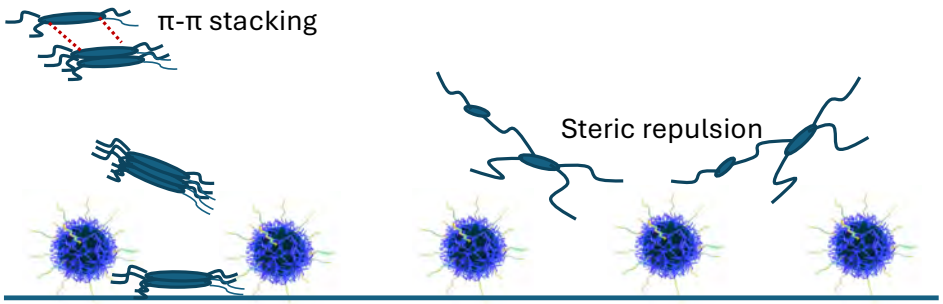


AA-AMPS-MNPs Coated Microchannel 500ppm

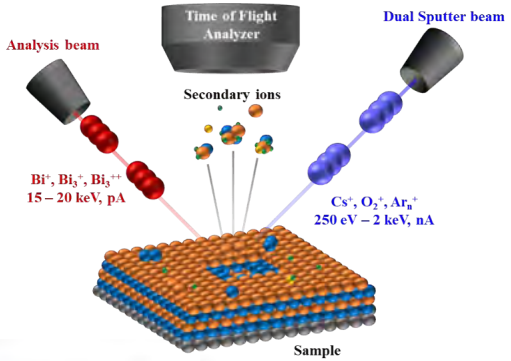


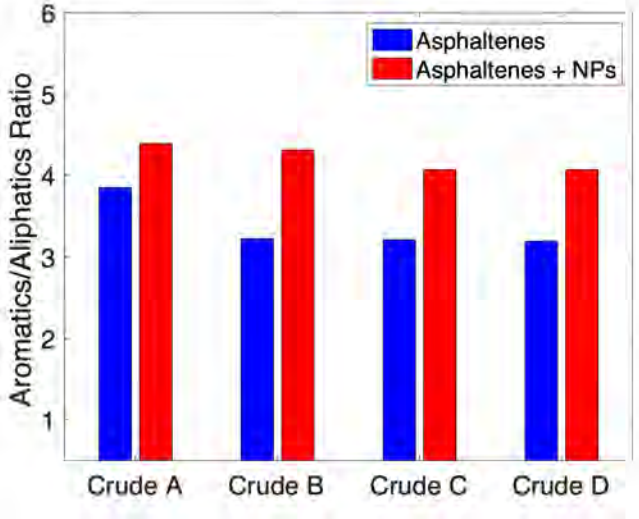
Effectiveness of Nanoparticles by TOF-SIMS





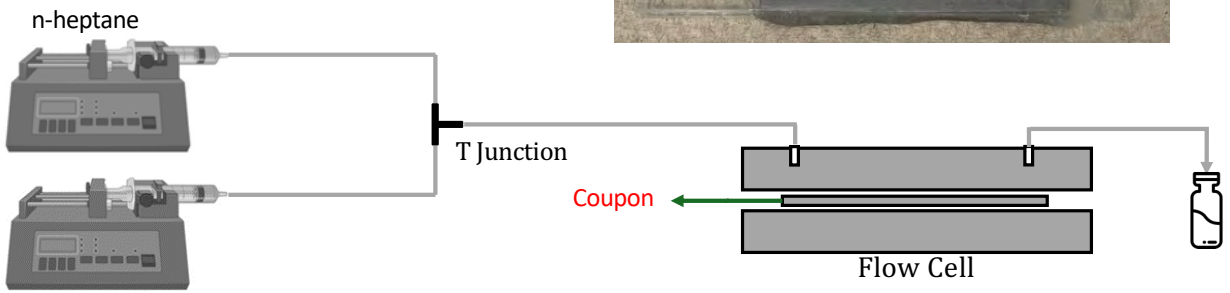
- Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a surface sensitive technique able to obtain both elemental composition and molecular information on the surface and in-depth.





Nguyen et al., Energy Fuels, 2023.

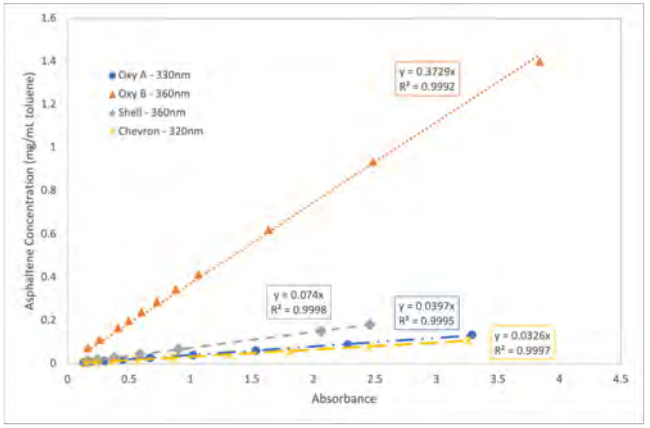
Asphaltene Deposition on Stainless Steel



10 mL Toluene

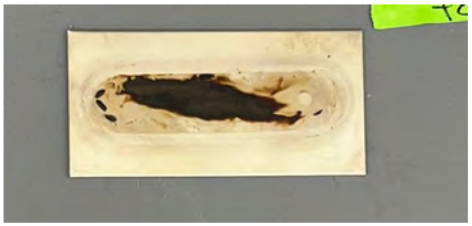
Coupon with asphaltenes deposits

UV-VIS



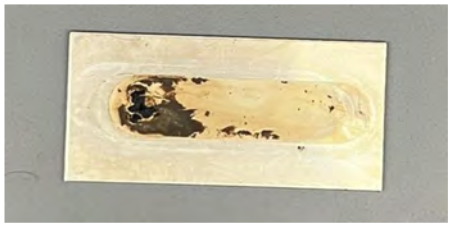
Images of steel

Control



Case # 1

Case # 2



Case # 3

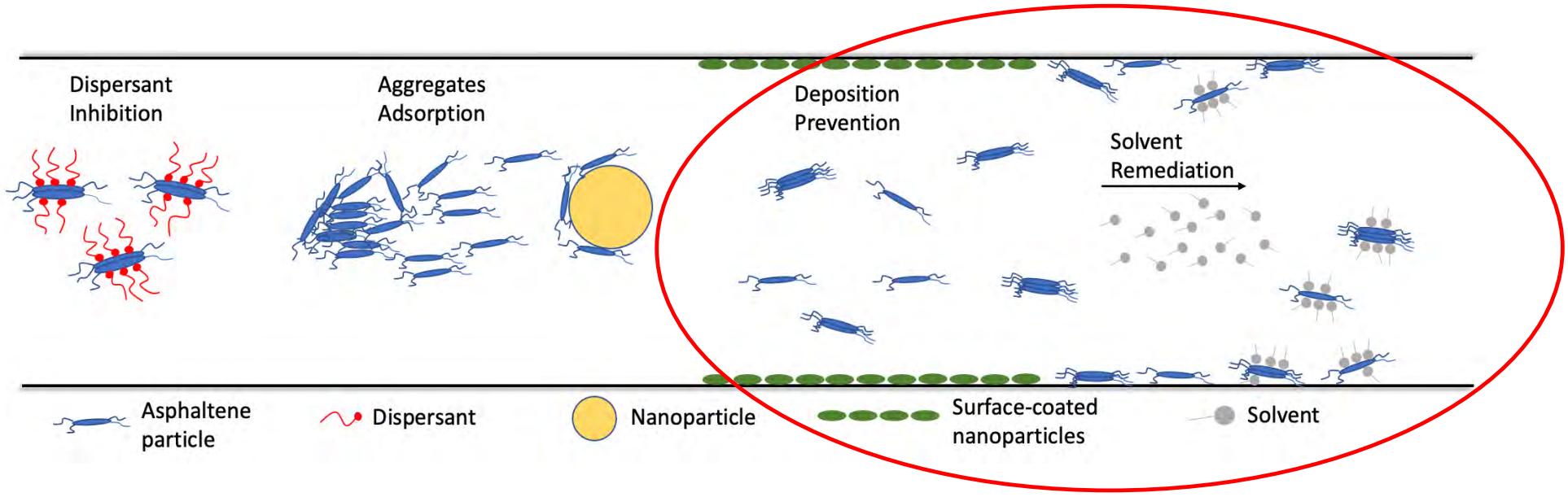
MNPs coated

Case # 1

Case # 2

Case # 3

Asphaltene Solutions

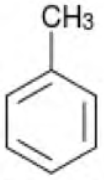


Remediation Methods

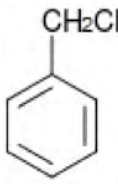
BTEX

BTE

benzene

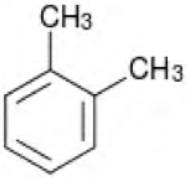


toluene

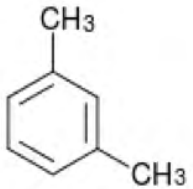


ethylbenzene

X's



ortho-xylene

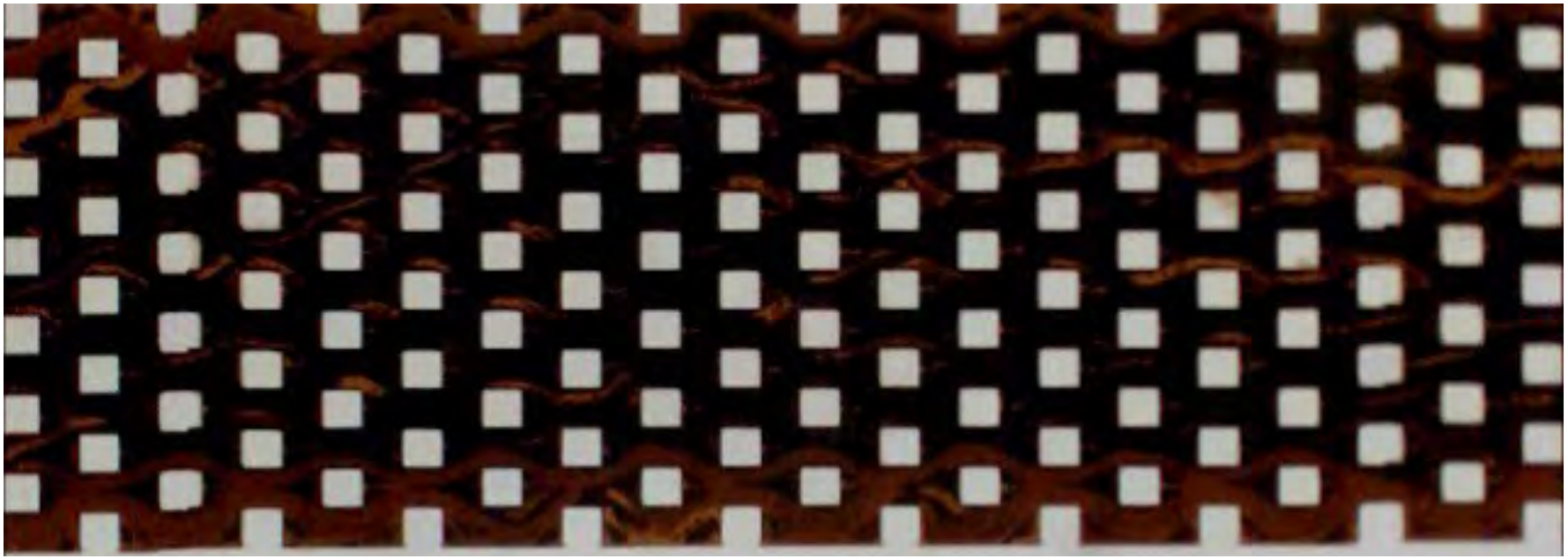


meta-xylene

para-xylene

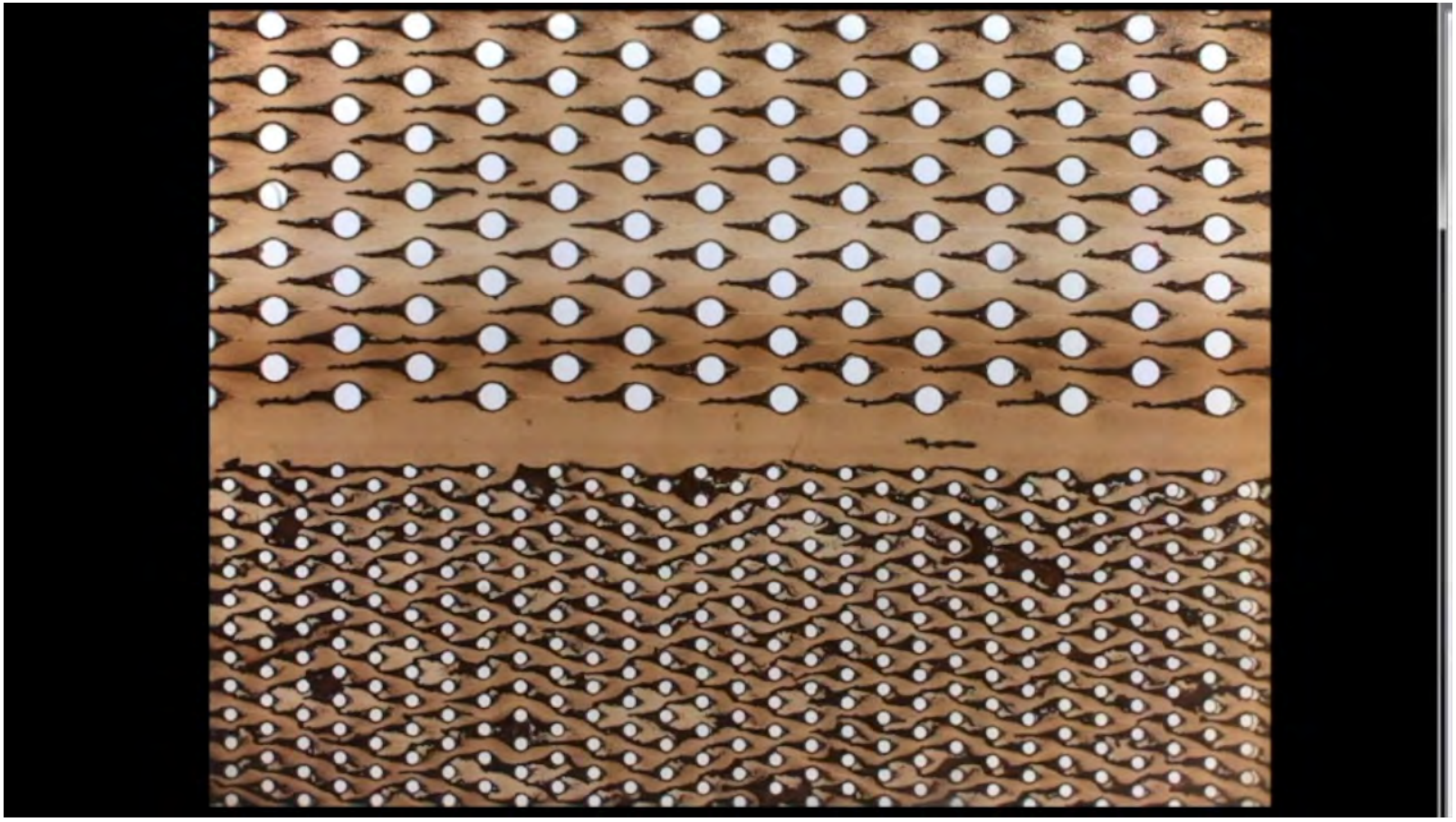
Gulf Coast Environmental **Systems**

Washing Asphaltene Deposits with Solvents



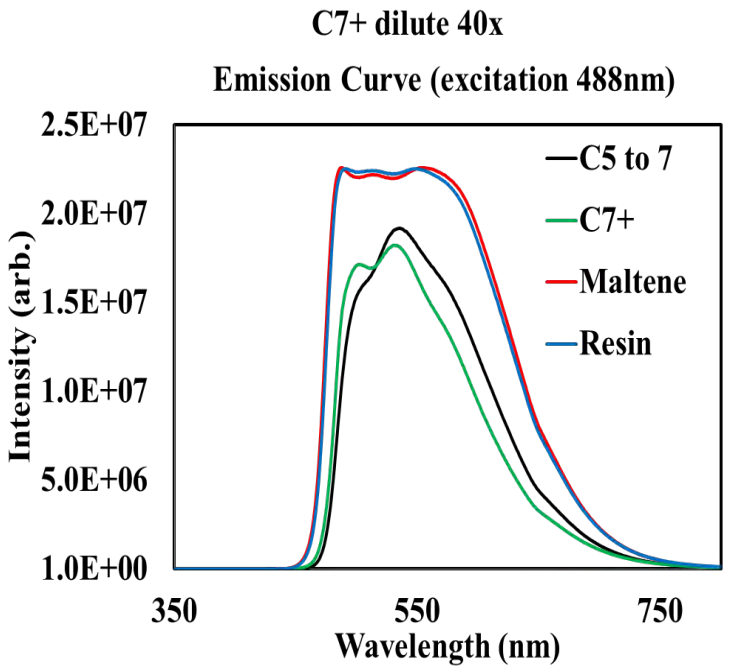
Xylene – good solvent for asphaltenes

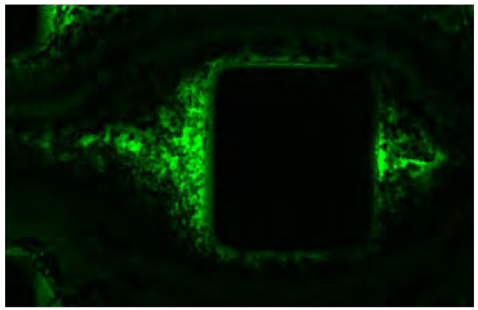
Washing Asphaltene Deposits with Microemulsions

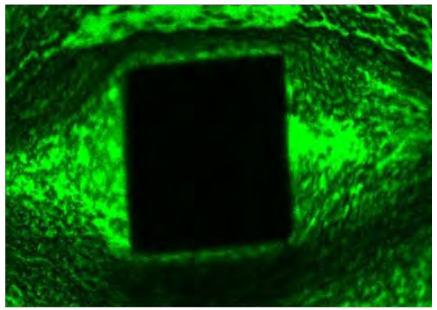


What is being removed?

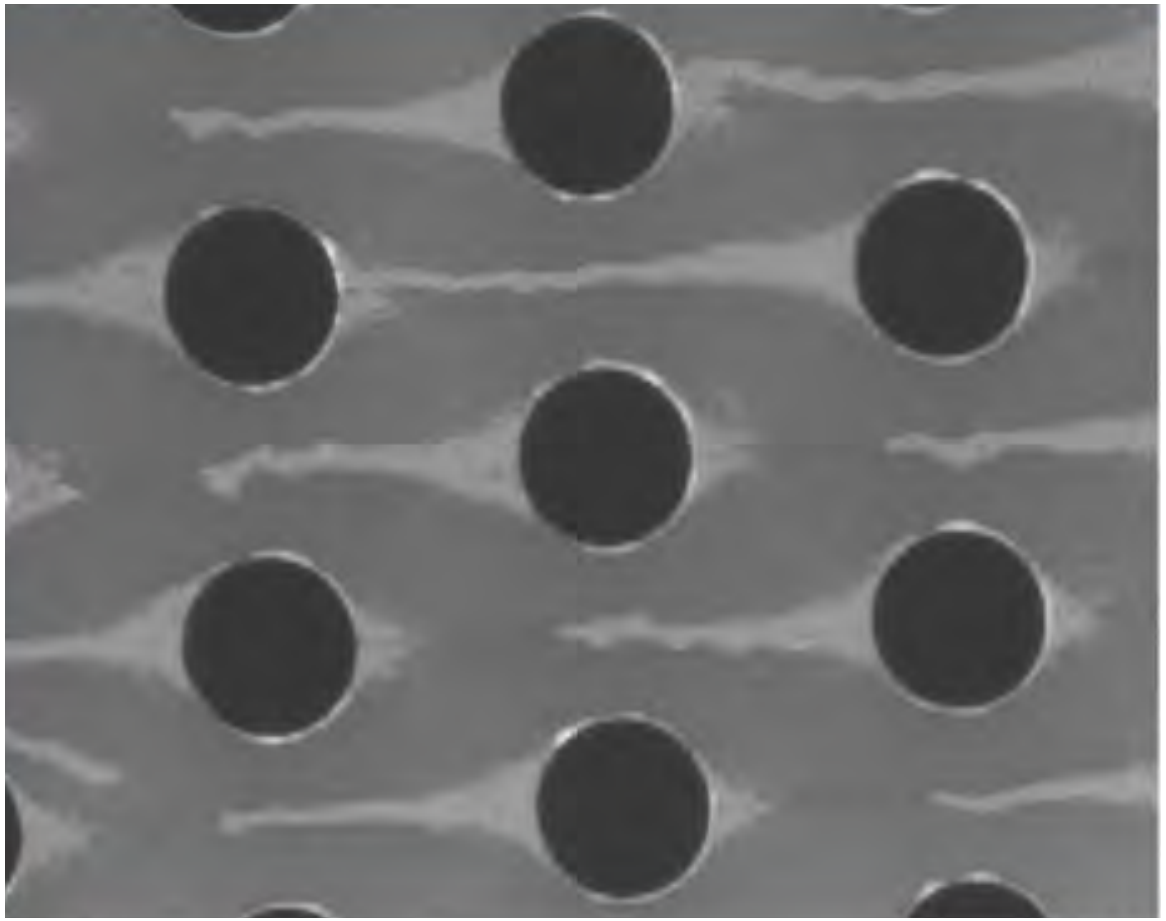
Fluorescence Microscopy Images allow Visualization of Resins (fluoresce) and Asphaltenes (non-fluorescent)



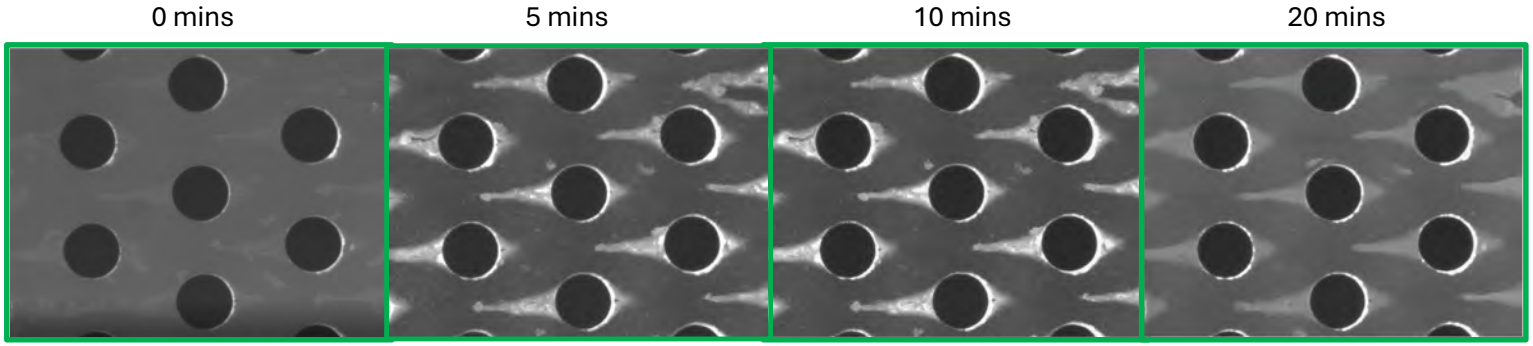


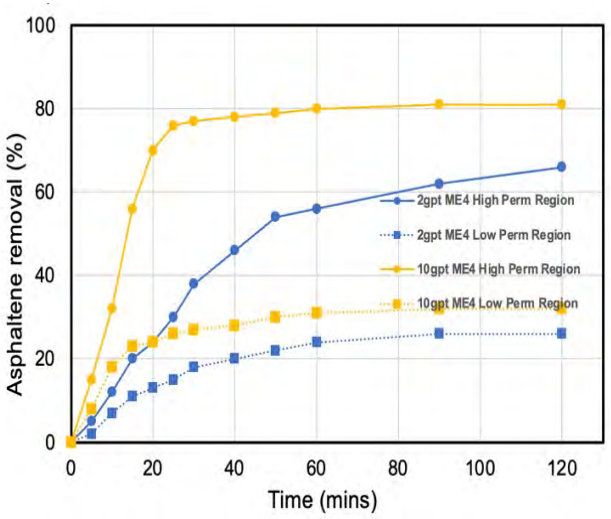


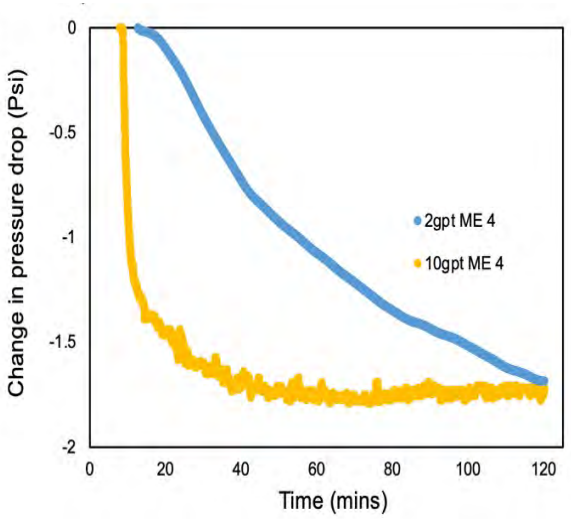
What is being removed?



Dynamics of asphaltene removal



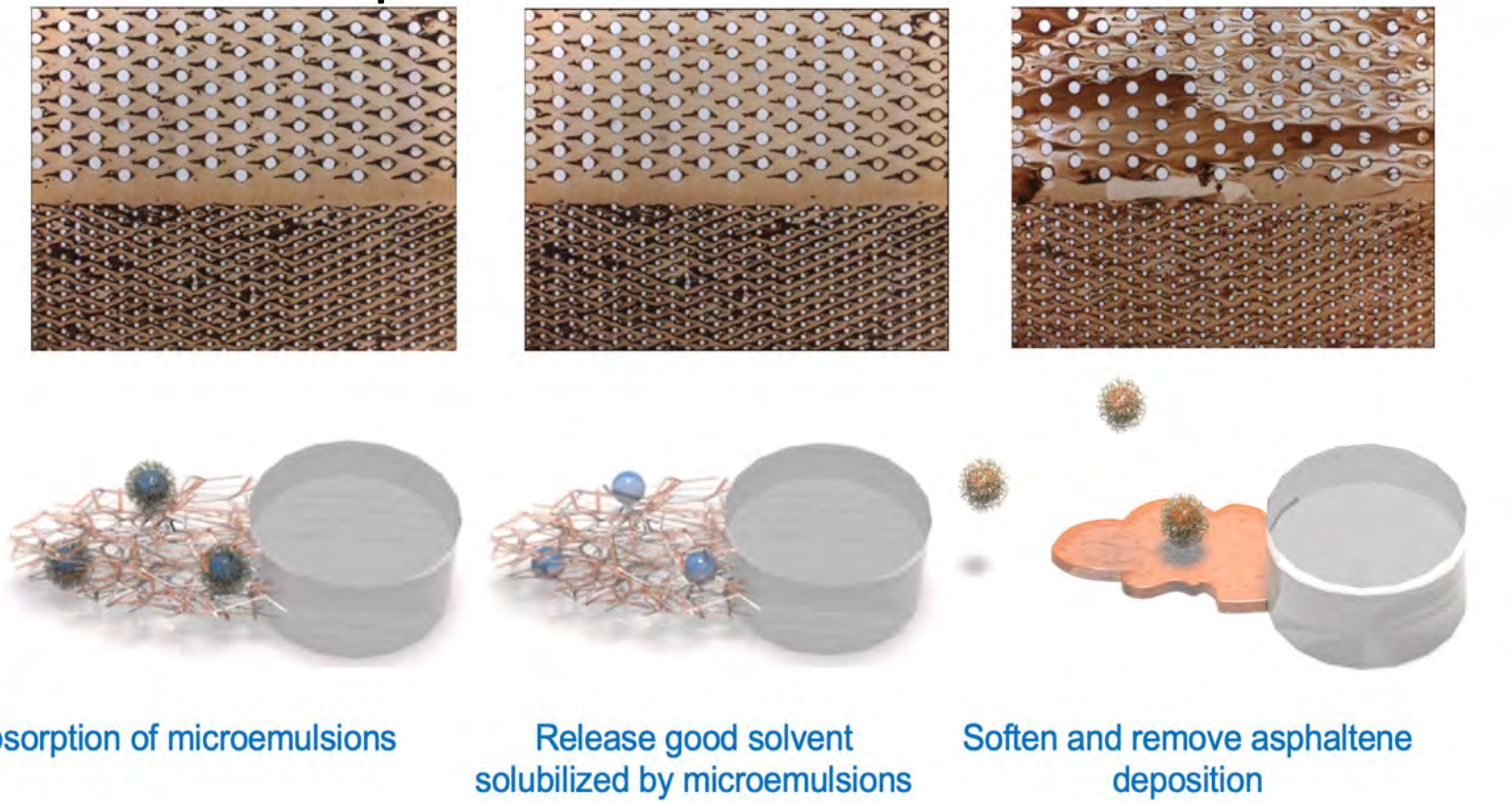




pseudo-second-order desorption kinetic model

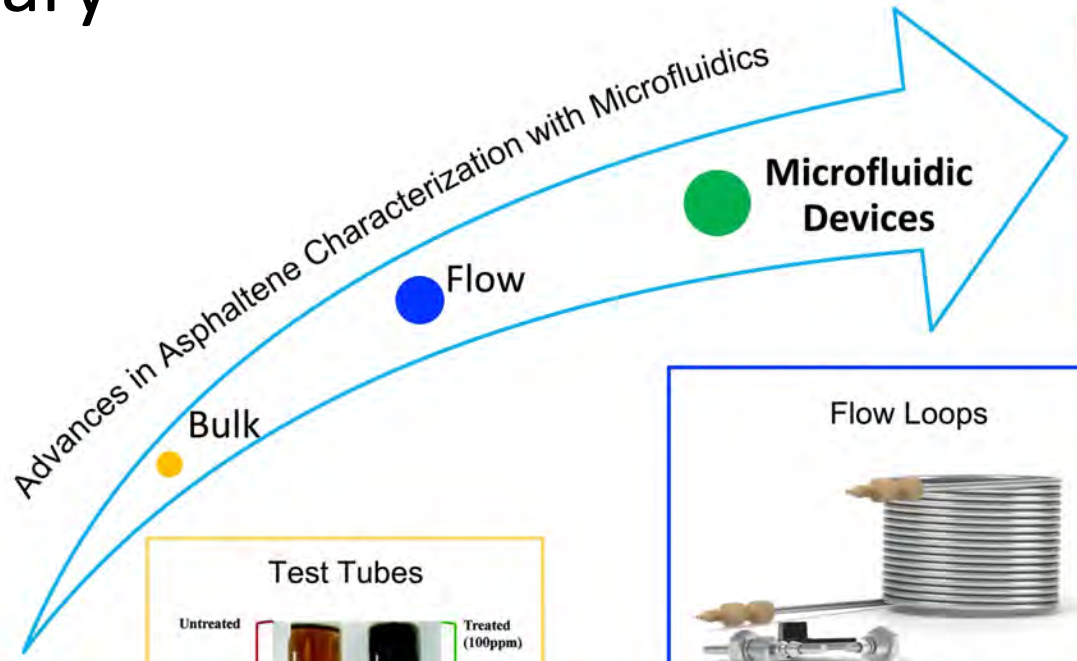
$$\frac{t}{q_t} = \frac{1}{kq_e{}^2} + \frac{t}{q_e}$$

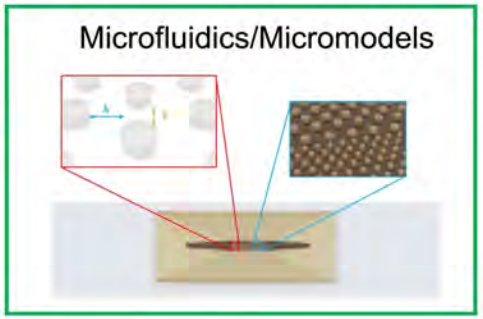
Mechanism for asphaltene removal



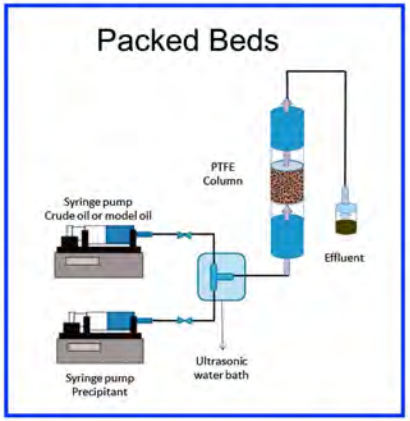
Zhang, Z., Perrard, A., Trabelsi, S., and Biswal, S.L., 2021. Evaluation of Asphaltene Remediation Using Microemulsion Formulations in a Porous Media Microfluidic Device. *Energy and Fuels*, *35* (14), 11162-11170

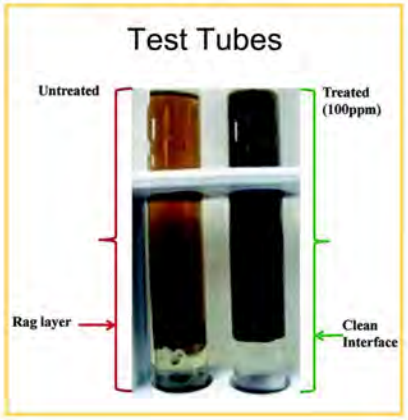
Summary


Advances in Asphaltene Characterization with Microfluidics
Bulk
Flow
Microfluidic Devices


Microfluidics/Micromodels

Flow Loops


Packed Beds
PTFE Column
Syringe pump Crude oil or model oil
Effluent
Ultrasonic water bath
Syringe pump Precipitant


Test Tubes
Untreated
Treated (100ppm)
Rag layer
Clean Interface

Acknowledgements

Yousif Alhouli
Omran Taqi
Maura Puerto
Jianxin Wang (Chevron)
Aparna Sagi (Shell)
Yogesh Kapoor (Oxy)

Vy Nguyen
Zhuqing Zhang
Qing Wang
Nate Lin
Siwar Trabelsi (Flotek)

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