Visualization of Asphaltene Deposition and Removal Using Microfluidic Porous Media

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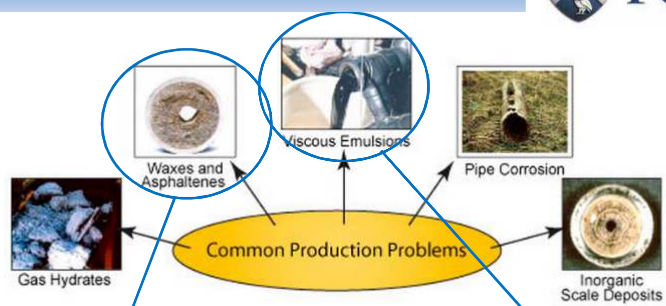
Flow Assurance Problems

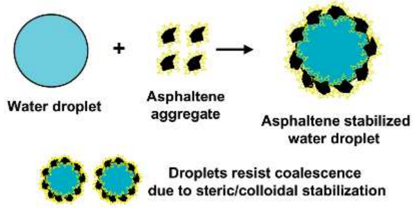


- The ability to produce multiphase fluids from reservoirs to processing plants in an economically and technically feasible way.

Plugging

(*Oilfield review*, Summer 2007)

W/O Emulsion



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

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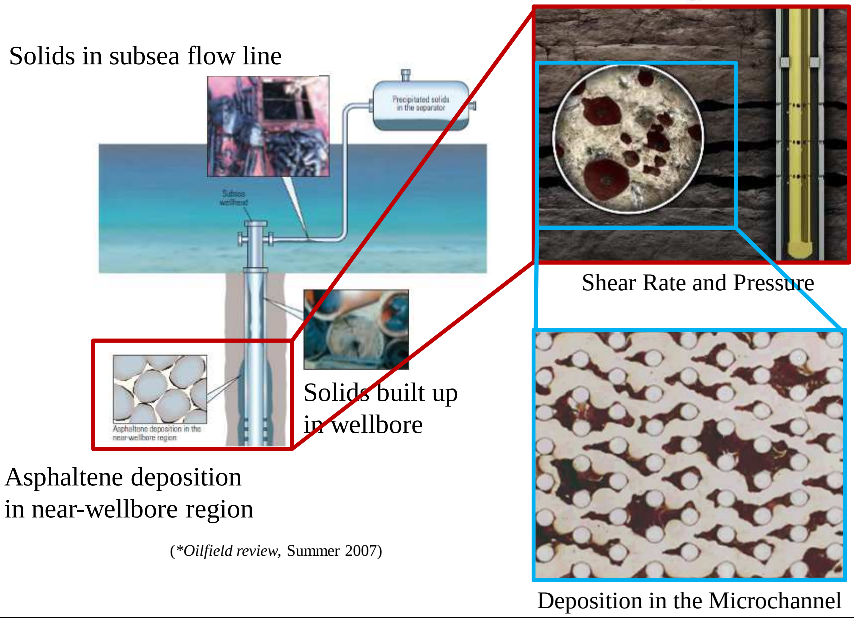
Asphaltene Problems

RICE



(*Oilfield review*, Summer 2007)

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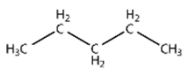
Crude Oil Components : SARA

RICE

Crude oil

dilute with n-alkane



solution → Maltenes

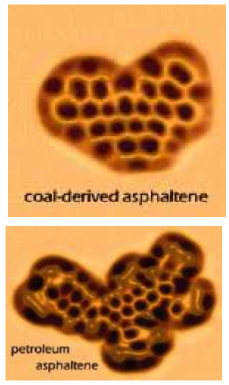
adsorb on chromatographic column elute with:

(1) alkane → Saturates

(2) aromatic → Aromatics

(3) polar solvent → Resins

precipitate → Asphaltenes



(*B. Schuler *et al.*, *JACS, 2015*)

S A R A

Nonpolar → Molecular weight, Aromaticity & Polarity

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

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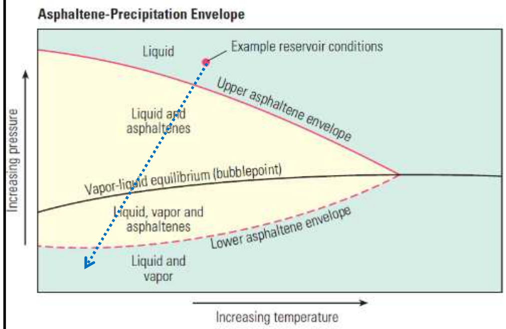
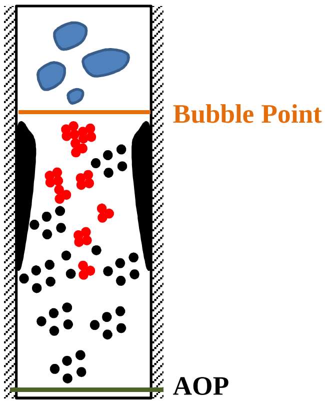
What are Asphaltenes?

- Polydisperse distribution, a global asphaltene molecule does NOT exist
- Precipitate due to pressure, temperature, and composition change
- Composition alteration:
  - Gas injection
  - Incompatible chemicals
  - Mixing with crude streams
- Insoluble: *n*-alkane (*n*-heptane and *n*-pentane)
  Soluble: aromatics (toluene and xylene)





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

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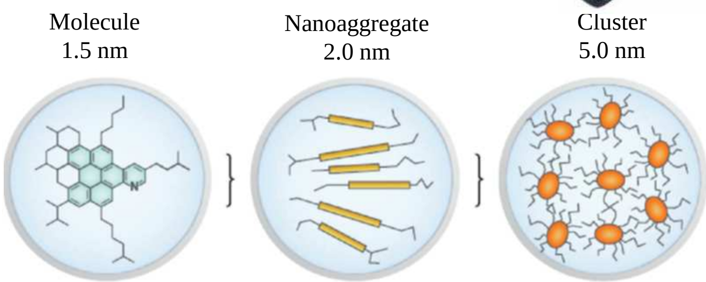
(*Jill Buckley's Lab, New Mexico Tech) (**Oilfield review*, Summer (*F. M. Vargas et al, **Fuel**, 2013)

Structures of Asphaltenes



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

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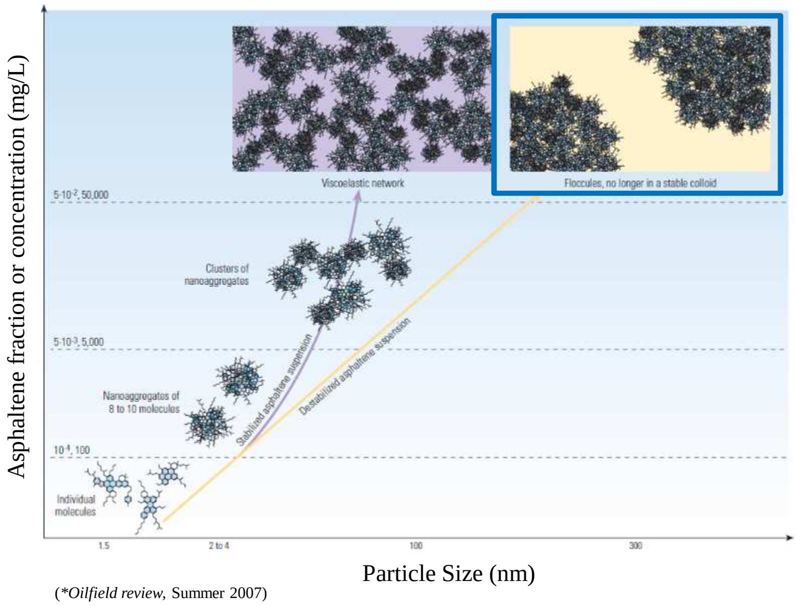
(*Vargas *et al.*, **OTC** 2014)

Structures of Asphaltenes

RICE



(**Oilfield review*, Summer 2007)

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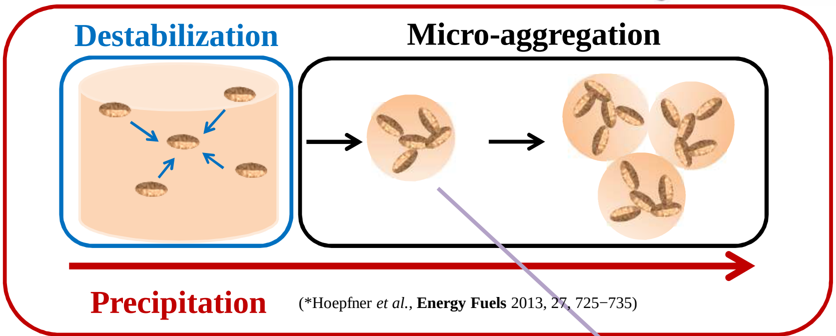
Precipitation and Deposition

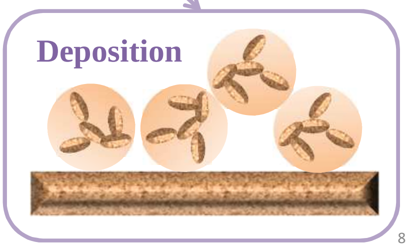
RICE



(*Hoepfner *et al.*, **Energy Fuels** 2013, 27, 725–735)

Asphaltene Nanoaggregate

Oil or Solvent



Changes in P, T, and Composition:

- Solubility parameter of the solvent ↓
- van der Waals attraction ↑

(*Wang *et al.*, **Langmuir** 2010, 26, 183–190)

(*Buckley *et al.*, **Petro. Sci. Tech.** 1998, 16, 251-285)

(*Vargas *et al.*, **Energy Fuels** 2010, 24, 2294–2299)

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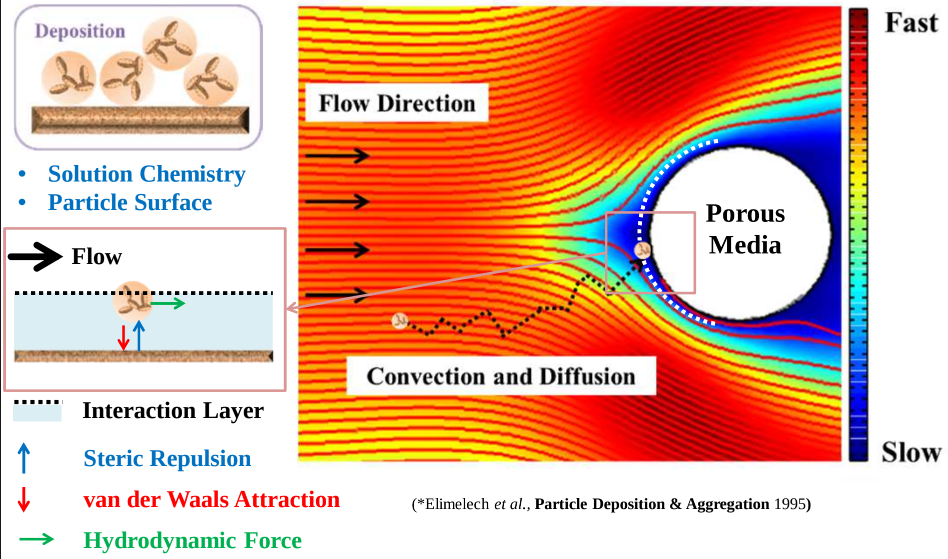
Transportation and Attachment



(*Elimelech *et al.*, **Particle Deposition & Aggregation** 1995)

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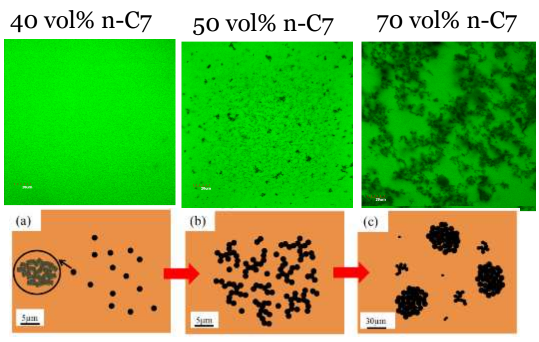
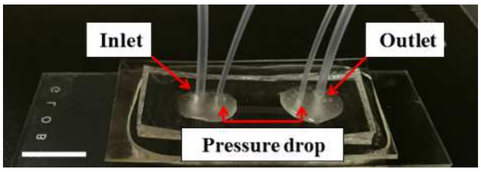
Asphaltenes form fractal aggregates

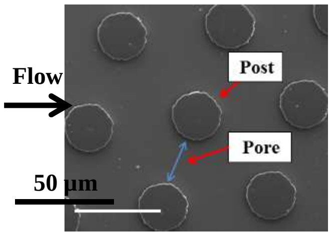
The solubility of asphaltenes can affect how fractal-like microstructure of the precipitate.

4.6wt% asphaltene in a model oil



Porous Micromodel





Post

5ºC)

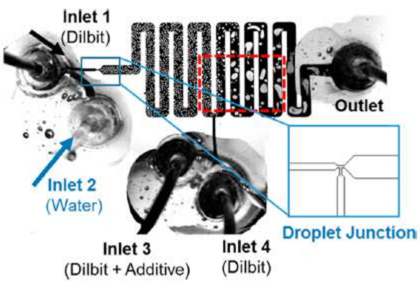
(*Yu-Jiun Lin *et al.*, **Langmuir**, 2016)

…oth 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***

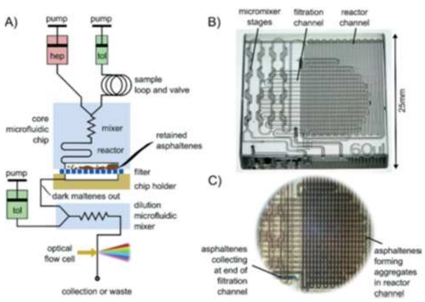
Industrial Applications

Microfluidic investigation of additives on the stability of emulsions



(*Nowbahar *et al.* **EnergyFuels**, 2017)
Dow Chemical, Midland, USA

Asphaltenes yield curve measurements on a microfluidic platform
(Maze SARA Analysis)



(*Sieben *et al.* **SPE**, 2013)
Schlumberger, Alberta, Canada

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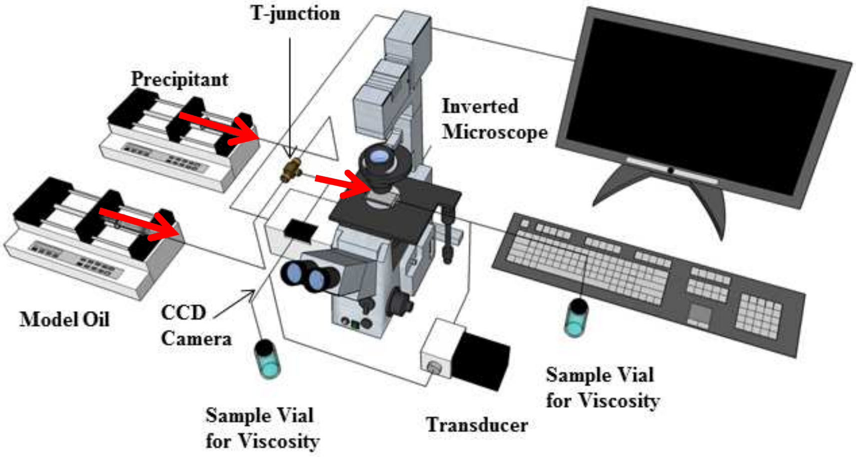
Experimental Setup



- Change composition
- T and P are constants

(*Yu-Jiun Lin *et al.*, **Langmuir**, 2016, 32, 8729−8734)

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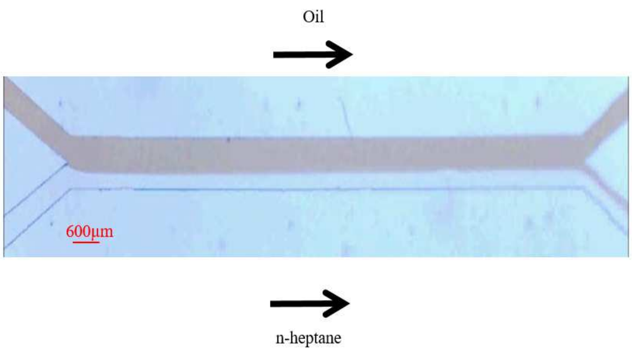
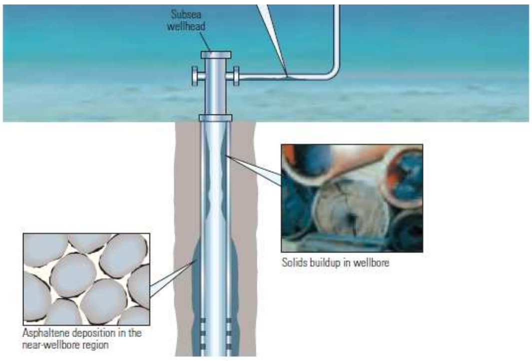
Asphaltene Deposition & Solubiliation



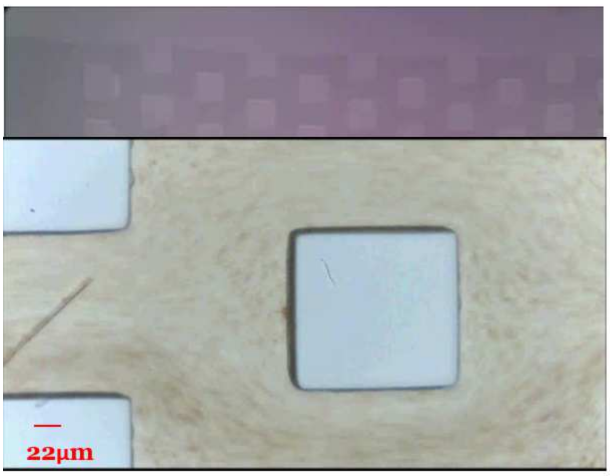
Asphaltene Deposition in Porous Media Microfluidic Devices

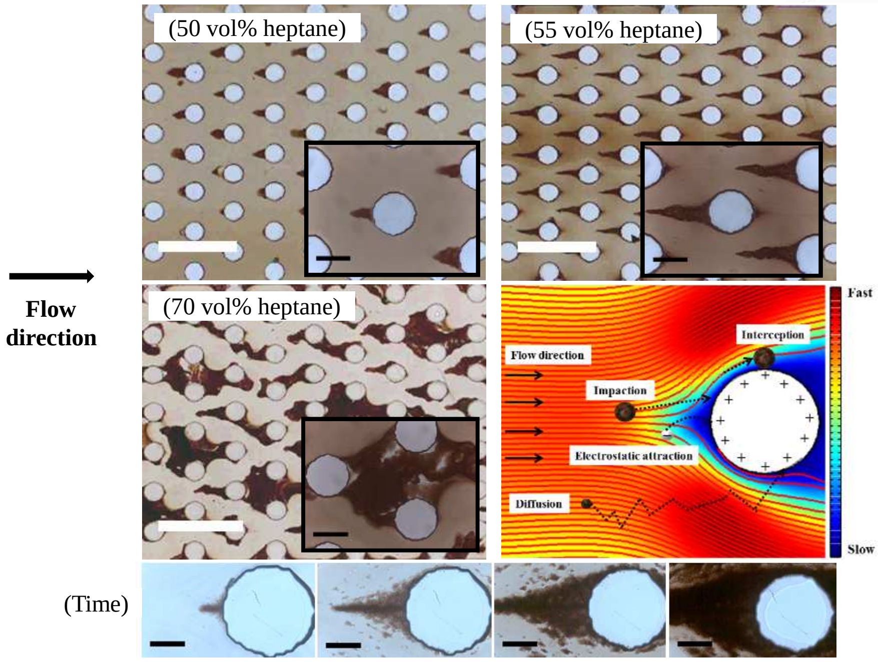


(**Oilfield review*, Summer 2007)

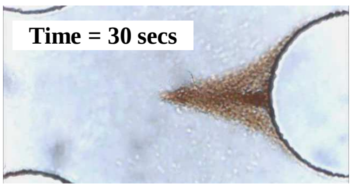
Asphaltene Deposition in Porous Media

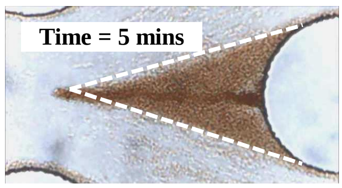
1. n-C7 70%, Oil 30%
2. Ambient Conditions

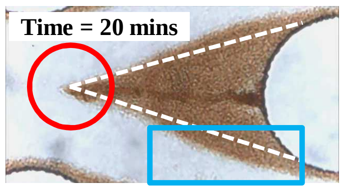




Pore-scale Profile







Flow direction

- **The front point of the deposition stops growing when the critical shear rate is reached.**
- **However, the side of the deposition keeps growing**

Solubility Parameter

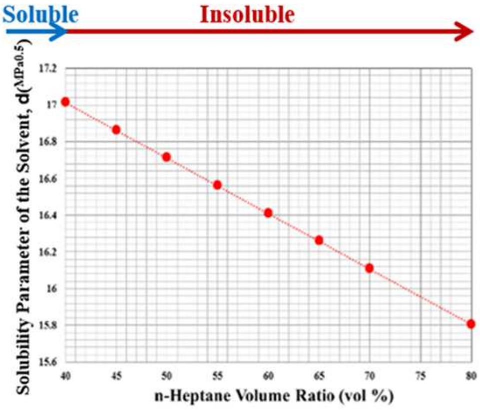
RICE

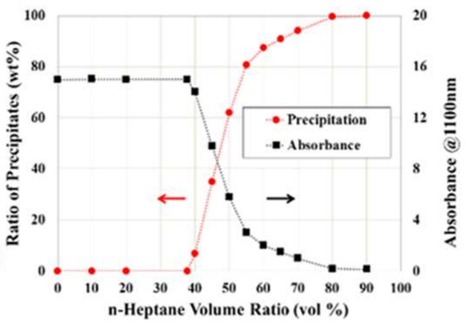
$\delta = \sqrt{Cohesive\ energy\ density}$

- Energy needed to completely remove unit volume of molecules from their neighbors to infinite separation

- Materials with similar values of δ are likely to be miscible

Asphaltene: 19 - 24 $MPa^{0.5}$
Toluene: 18.2 $MPa^{0.5}$ Solvent
n-Heptane: 15.2 $MPa^{0.5}$ Precipitant
n-Pentane: 14.4 $MPa^{0.5}$





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

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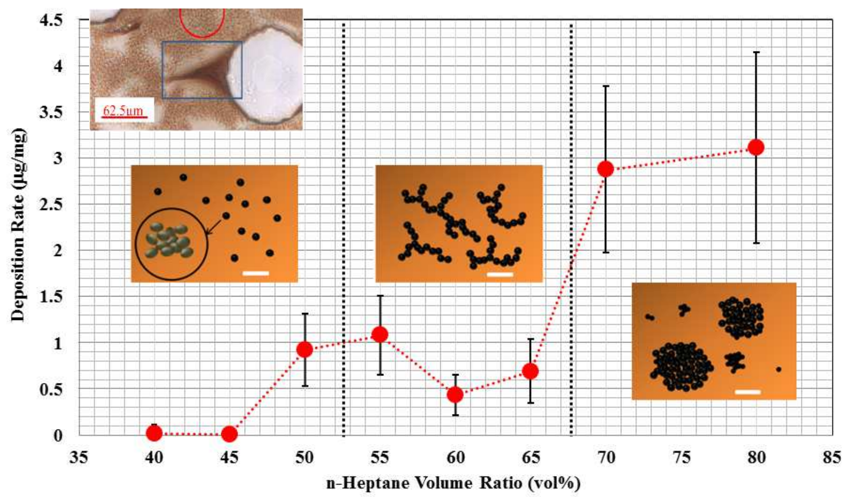
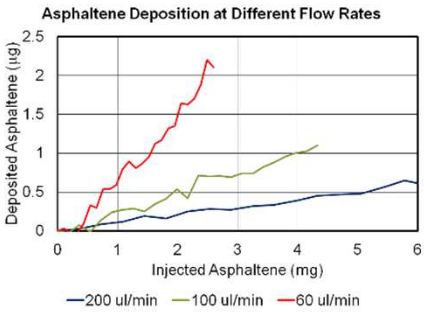
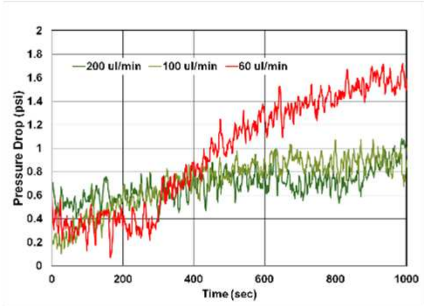
RICE

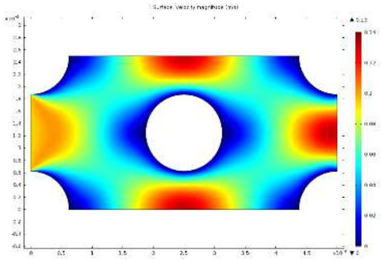
Deposition Rate and Capture Efficiency



Effects of Flowrates on Deposition



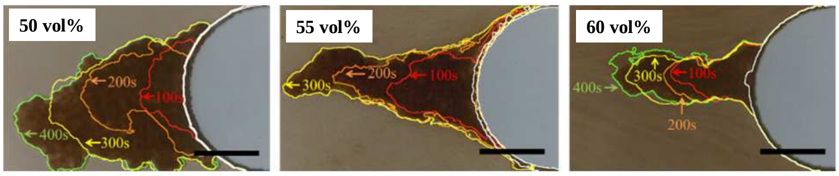




COMSOL Simulation indicates stagnation zone and high-shear region, which will affect asphaltene deposition shape and entrainment

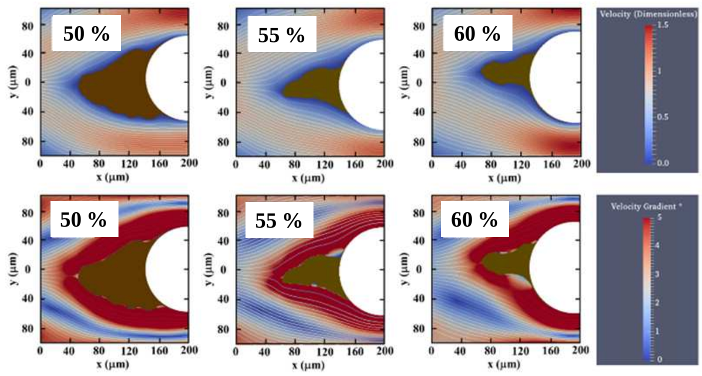
Pore-Scale Velocity and Shear Rate Profile

Increasing Pe



Velocity

Shear Rate

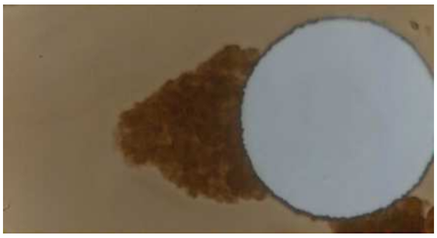


(Yu-Jiun Lin et al., Langmuir, 2016)

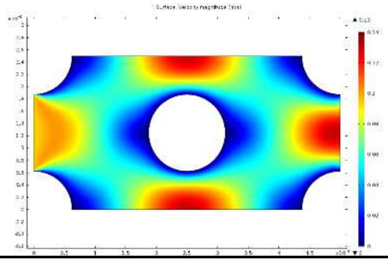
Competition Between Asphaltene Aggregate and Convection

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

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



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



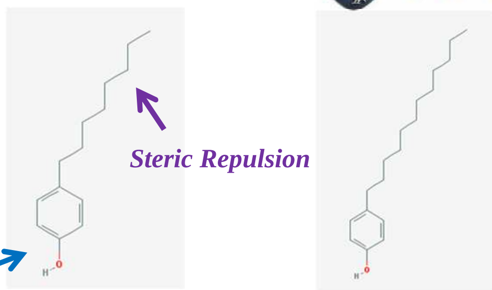
Deposition profile a function of Peclet number, which is a function of solubility

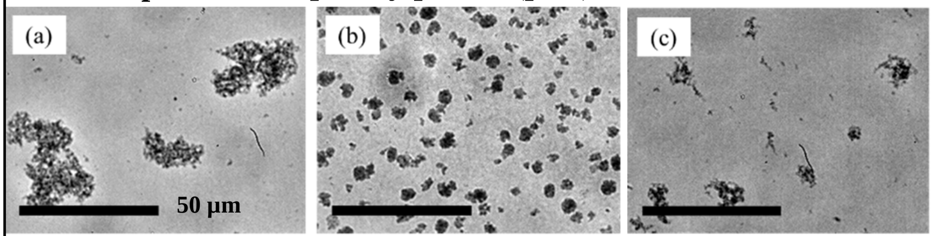
Chemical Dispersants Evaluated in Microfluidic Devices

(**Oilfield review*, Summer 2007)

Aggregation with 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)





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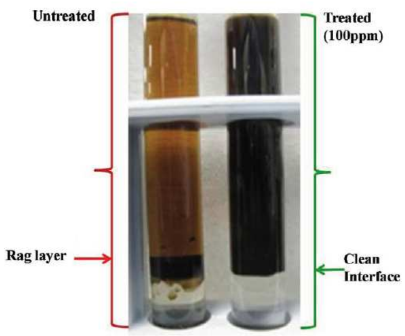
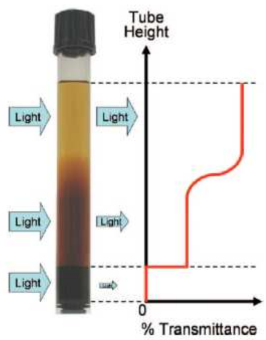
(*Yu-Jiun Lin *et al.*, **EnergyFuels**, 2017)

Dispersant Tests



(*Juyal *et al.*, **EnergyFuels**, 2012)



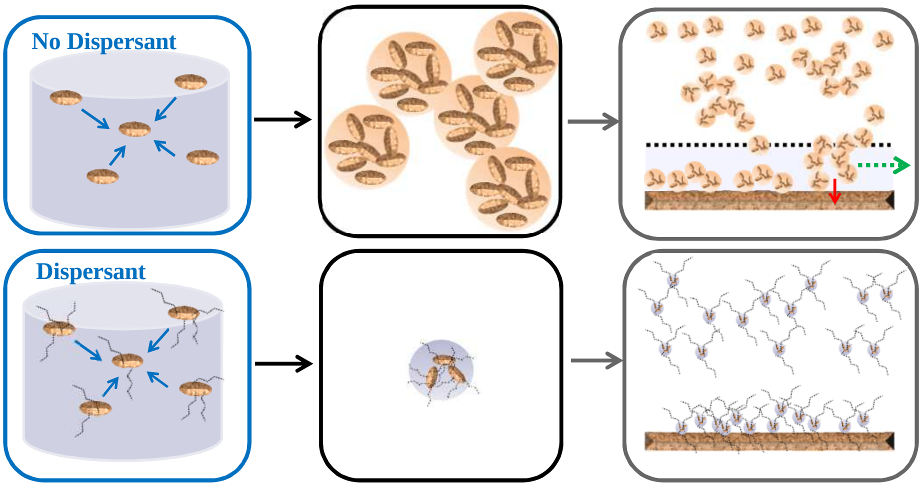
(*Kraiwattanawong *et al.*, **EnergyFuels**, 2009)

- (Static examination) Commonly, people study the performance of dispersant effect on asphaltene suspension and settling time.
- Dynamic test (with flow) is needed.

Dispersant Effect on Deposition

RICE

Destabilization **Micro-aggregation** **Deposition**



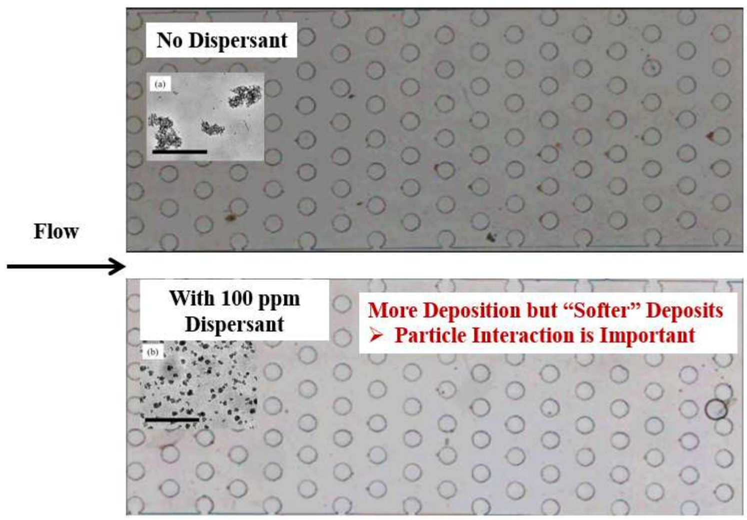
More deposition?

Dispersant effect:

- **Solubility parameter of the solvent remains constant**
- **Steric repulsion ↑**

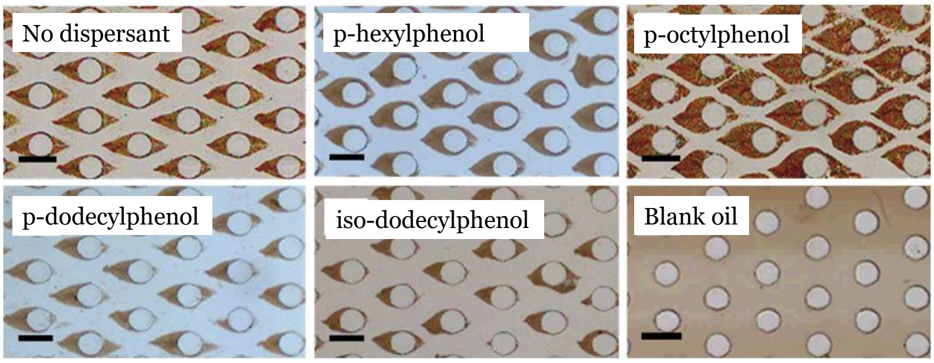
Dynamic Deposition Process

RICE

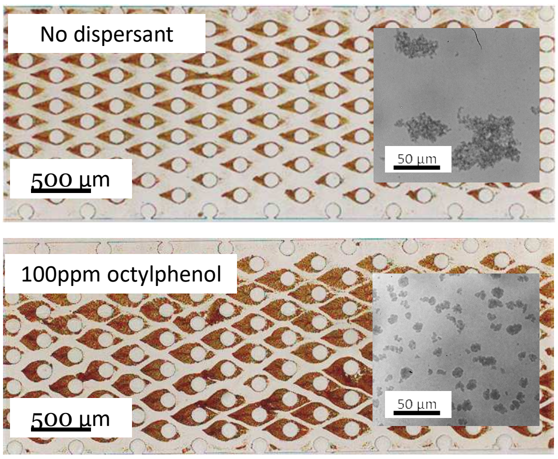


Dispersant + Model Oil

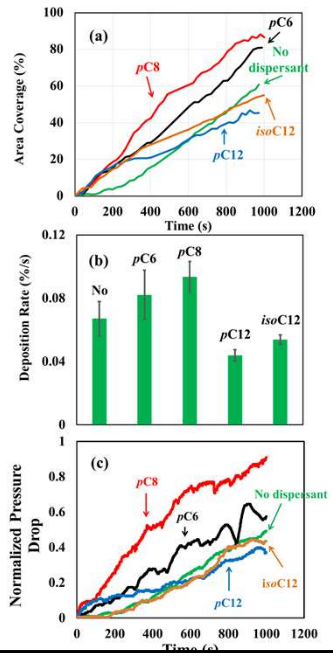
Dispersants alter asphaltene deposition in porous media



Dispersant + Model Oil



Flow direction



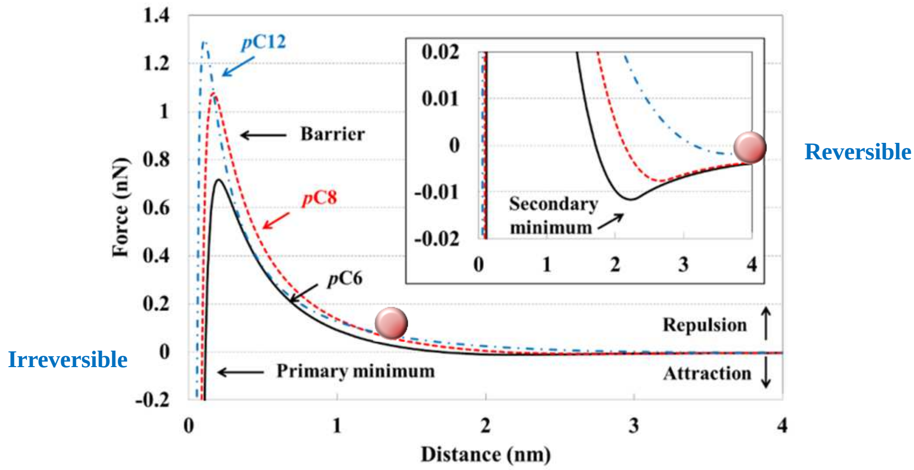
Forces between Asphaltenes

$$F_A = \frac{A_{ama} R_p}{6D^2}$$

van der Waals attraction

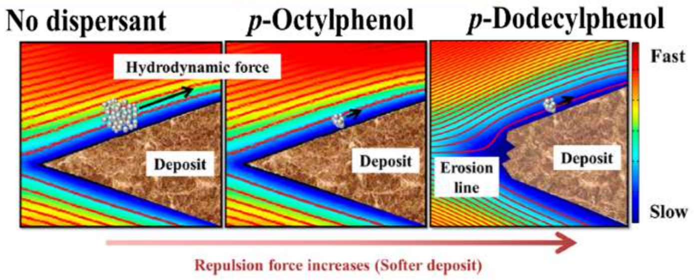
$$F_s(D) = 2\pi R_p \left(\frac{k_B T}{s^3}\right)\left\{\frac{8L}{5}\left[\left(\frac{2L}{D}\right)^{5/4} - 1\right] + \frac{8L}{7}\left[\left(\frac{D}{2L}\right)^{7/4} - 1\right]\right\} \quad \text{for } D < 2L$$

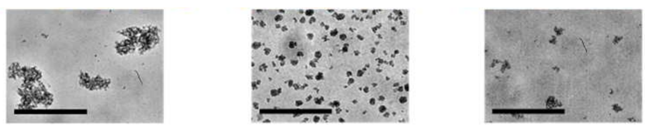
steric repulsion



(*Yu-Jiun Lin *et al.*, **Energy Fuels**,

Dispersant Mechanism

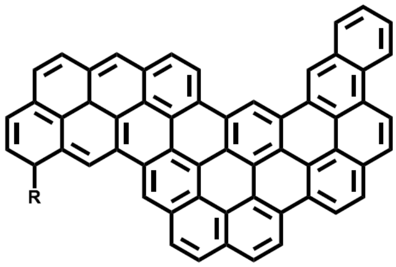




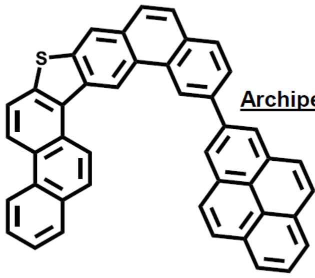
(*Yu-Jiun Lin *et al.*, **Energy Fuels**,

Island & Archipelago

Island *vs.* Archipelago Motifs

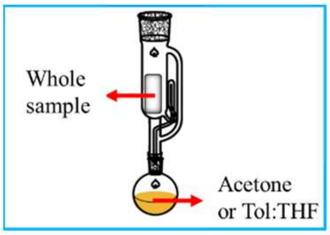


Island



Archipelago

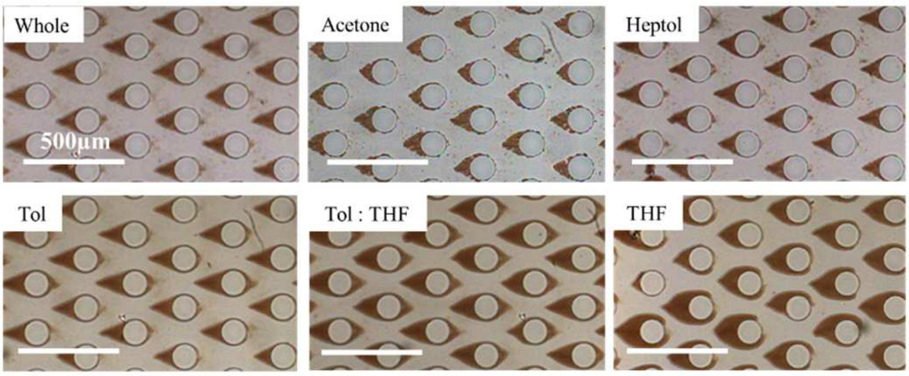
- ➢ Run the deposition tests with various fractions
- ➢ Asphaltene solids are from PetroPhase 2017 provided by Total



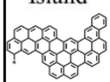
(*M. L. Chacon *et al.*, *Florida State University*)

Deposition for Various Fractions

More Island → More Archipelago



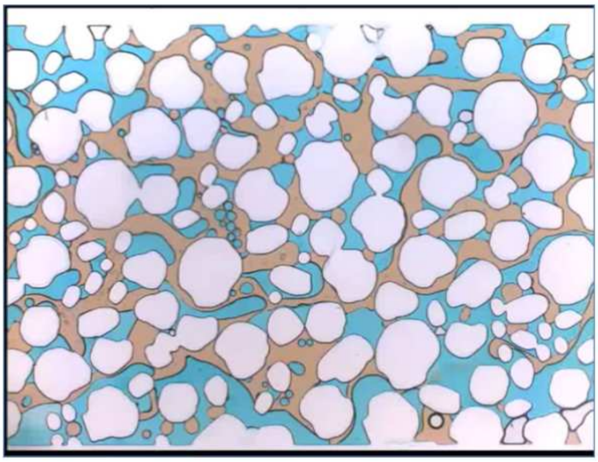
More Island → More Archipelago



- ➢ Archipelago type seems easier to be destabilized by precipitants and deposit onto solid surfaces

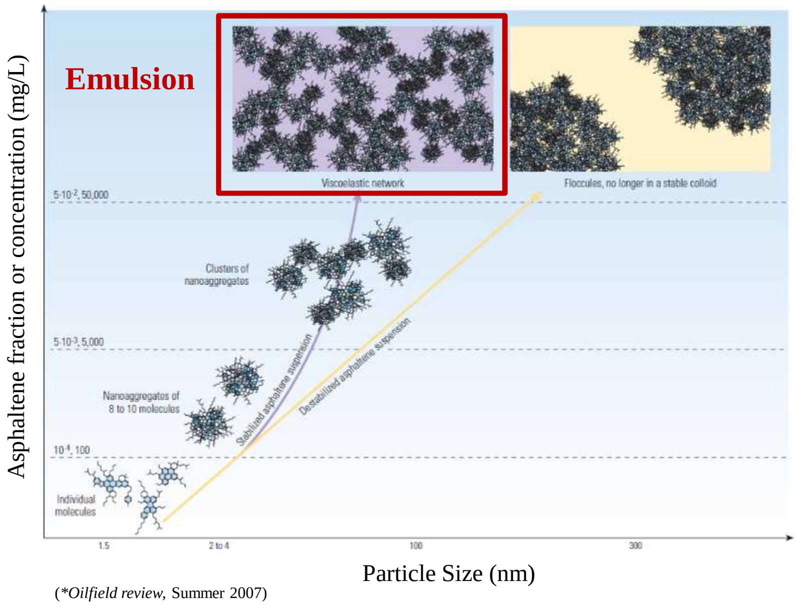
Two-Phase Saturated Porous Media

Heterogeneous porous media designs that can be saturated with two-phases.



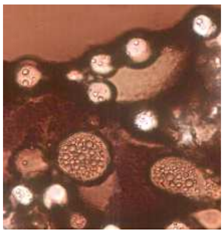
Asphaltene-Stabilized Emulsions in Microfluidic Devices

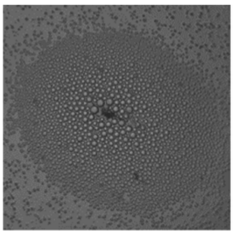
Structures of Asphaltenes



(**Oilfield review*, Summer 2007)

Asphaltene-Stabilized Emulsions





(*Simone *et al.*, **Langmuir**, 2017)

Goal:
Investigate the interfacial properties of asphaltenes to understand and predict the coalescence phenomena

Objective:
Understand dispersant effect on the cross-linked adsorbed asphaltenes at interfaces

Stability of Emulsions (Liquid-Liquid Interface)

Interfacial Shear Rheology (Dispersant effect) → **Dilatational Rheology and Demulsifiers** → **Deposition of Emulsions and the Effect of Brine Ions**

Rheology

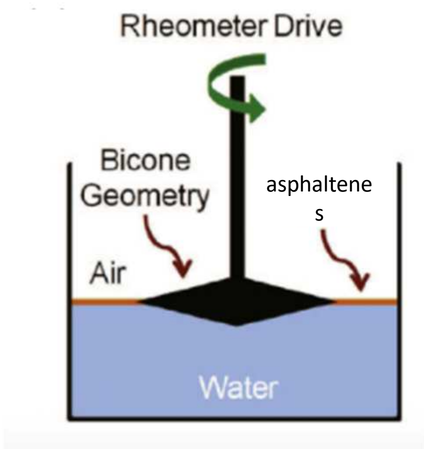
- Rheology:
  The science of the flow and deformation of matters under stress (It applies to substances which have a complex structure.)
- Viscoelasticity:
  Property of materials that exhibit both viscous and elastic characteristics when undergoing deformation

Viscoelasticity
- Viscosity → Energy dissipation (G′′: viscous modulus)
- Elasticity → Energy storage (G′: elastic modulus)

Interfacial Rheology

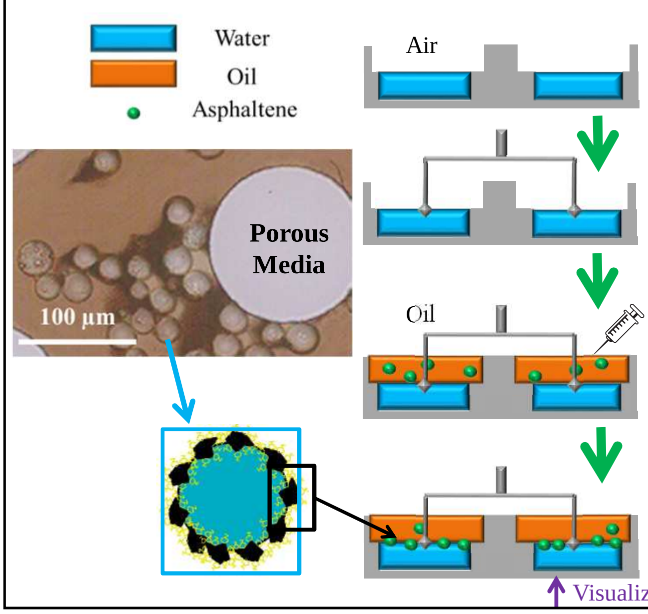
- Double wall ring rheometer:
- Rheology combined with interfacial imaging

(*G. Fuller et al., *Rheol Acta*, 2010)

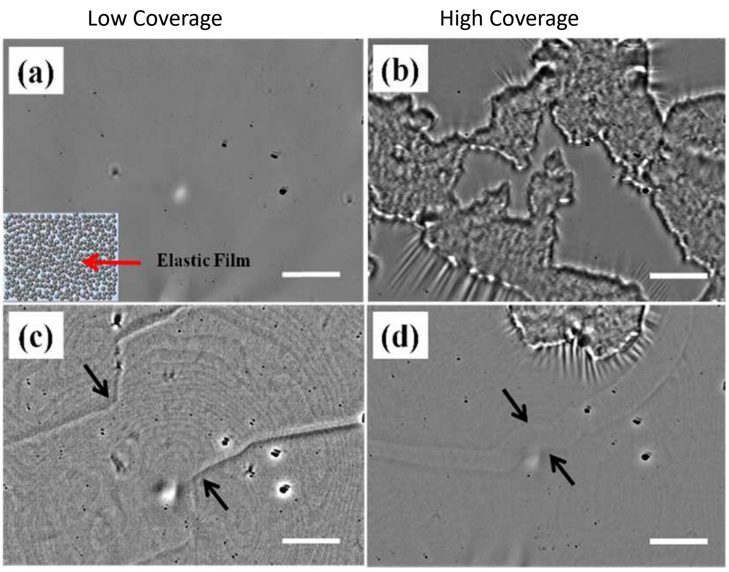


Preparation of the Interface

1. Water in the container
2. Ring on water
3. Sample on water
4. Adsorption to equilibrium



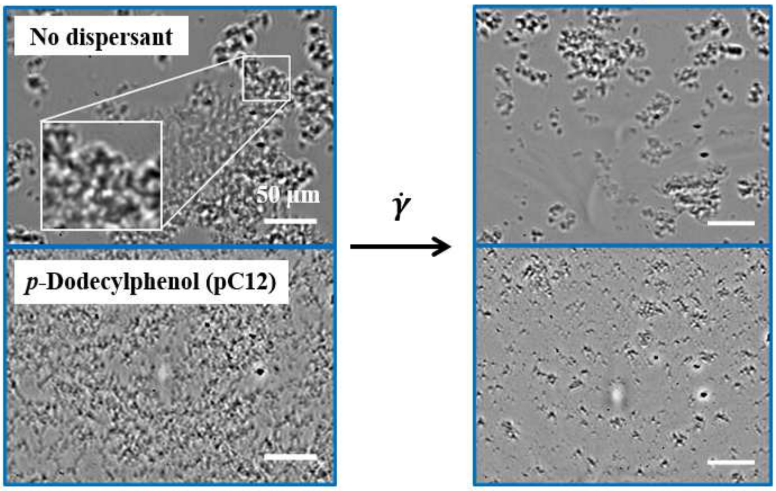
Shearing the Asphaltene Interface



(*Yu-Jiun Lin *et al.*, **J. Rheology**, 2017

Rheological Properties

RICE

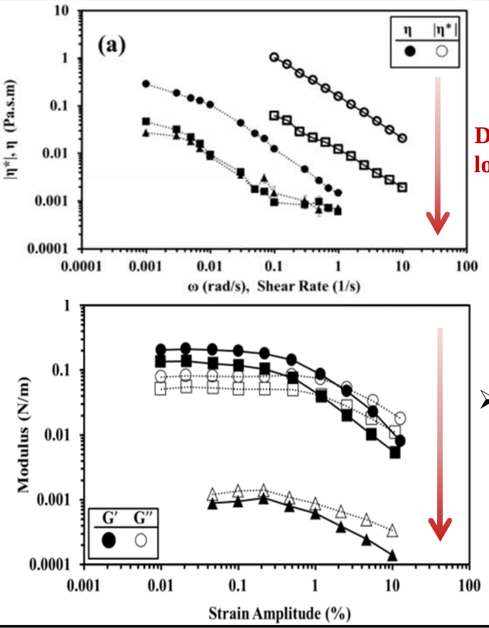


$G' \sim \phi^{\nu} \sim \phi^{\frac{d-\boxed{D_{bb}}}{d-D_f}}$ → Fractal dimension of the backbone of the aggregate: More connecting points, higher elastic modulus

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

Rheological Properties

RICE



Decrease with a longer alkyl tail

● **No Dispersant**

■ ***p*-Octylphenol**

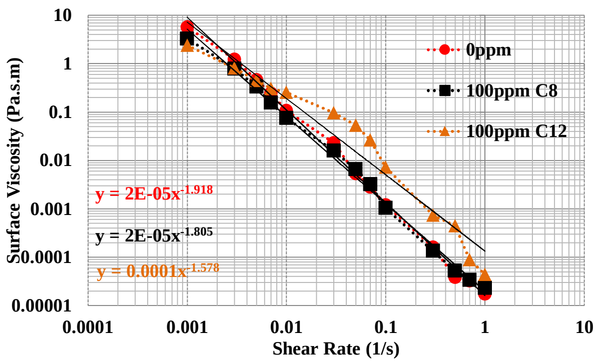
▲ ***p*-Dodecylphenol**

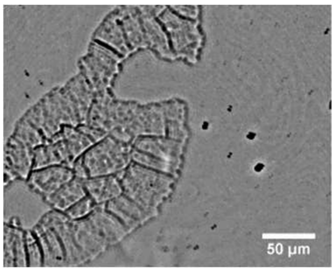
➢ Rheological measurements show that injection of dispersants decreases viscous and elastic moduli: softer asphaltenes

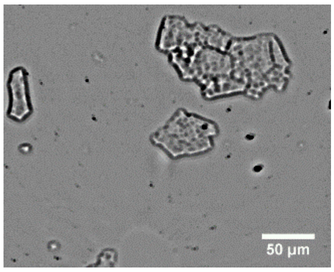
(*Yu-Jiun Lin *et al.*, **J. Rheology**, 2017)

High Surface Coverage

4µg/cm²





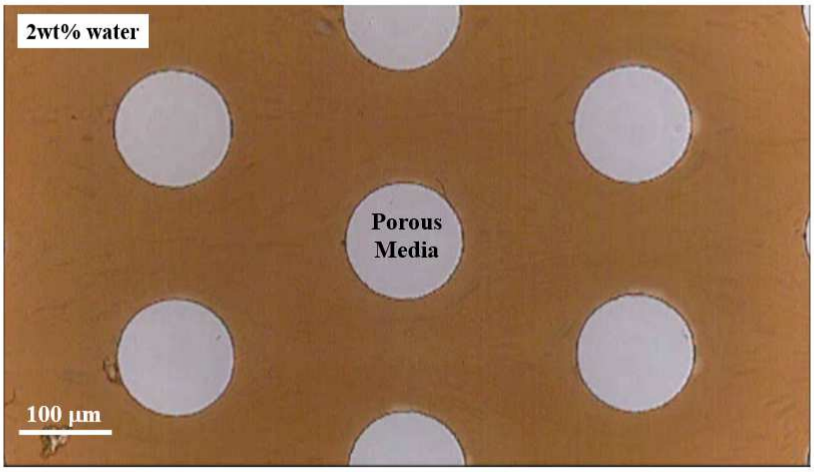


Emulsion Deposition

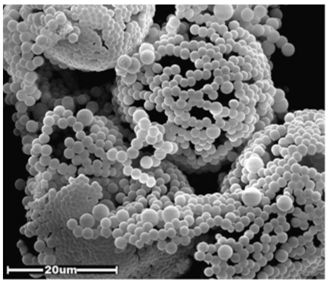
RICE

→ Flow direction

2wt% water



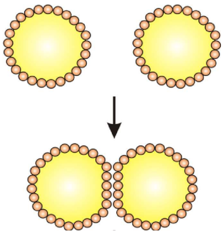
Pickering Emulsions



- 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)

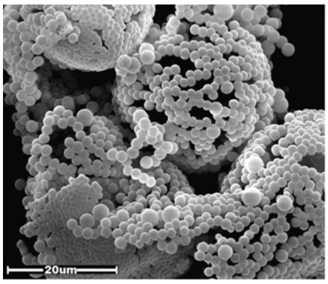
Pickering Emulsion Resist Coalescence



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

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

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

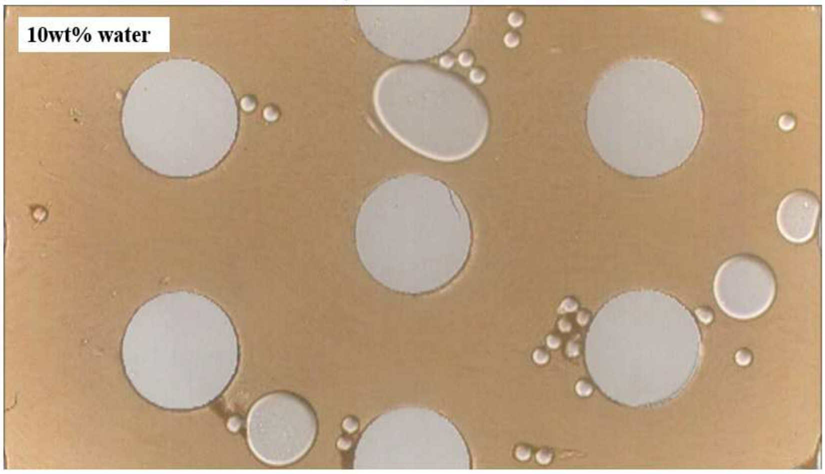
(*Oldroyd, J.G. *Proc. Royal Soc. London A* 1955)

Emulsion Deposition-10wt%

RICE

Flow direction

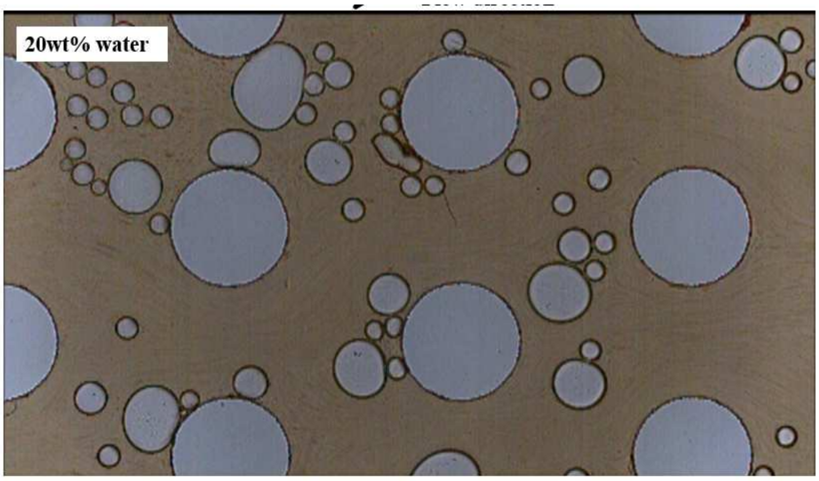
10wt% water



Emulsion Deposition-20wt%

RICE

Flow direction



Multiphase Composition

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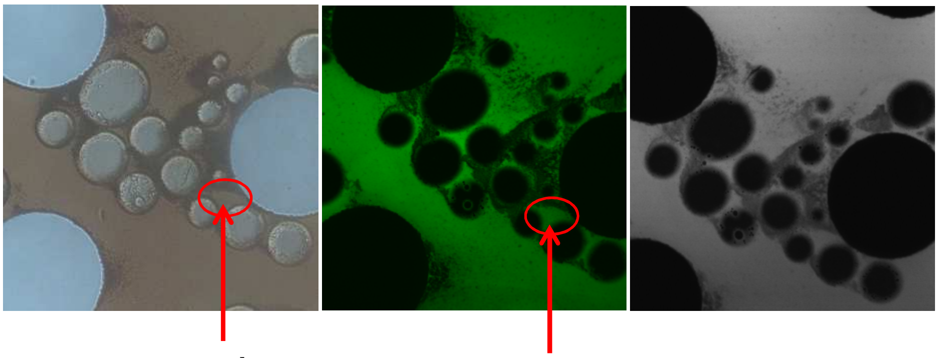
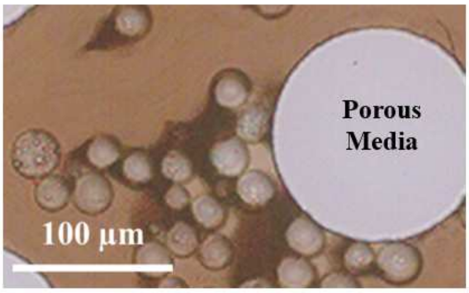
Bright field | **Confocal 488nm** | **Confocal 635nm**

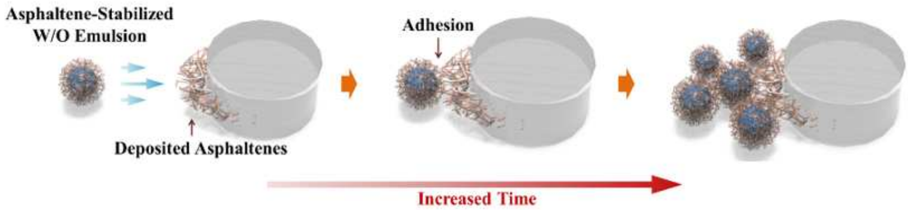


Adhesive

RICE

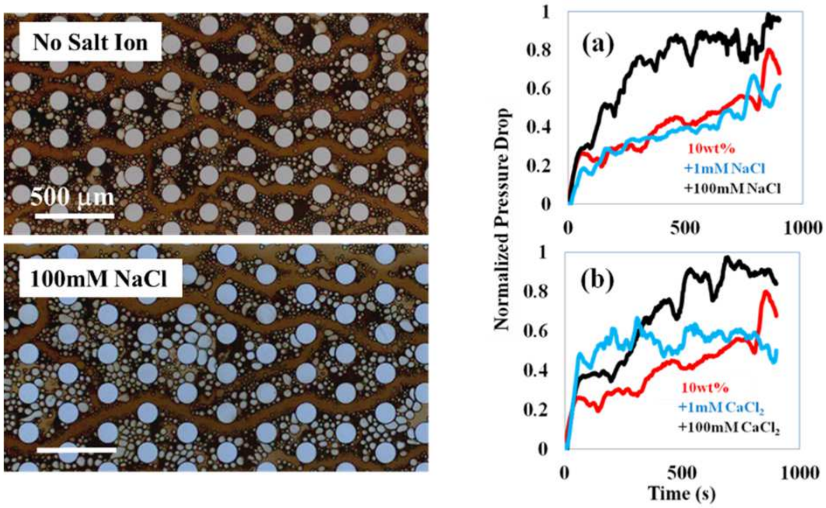


- Hamaker constant representing the van der Waals attraction:
  $A_{ama} > A_{wmn}$
  Asphaltene-medium-asphaltene (ama):
  A_{ama} is $4.3 \times 10^{-22} J$
  Water-medium-NOA81 (wmn):
  A_{wmn} is $5.3 \times 10^{-23} J$



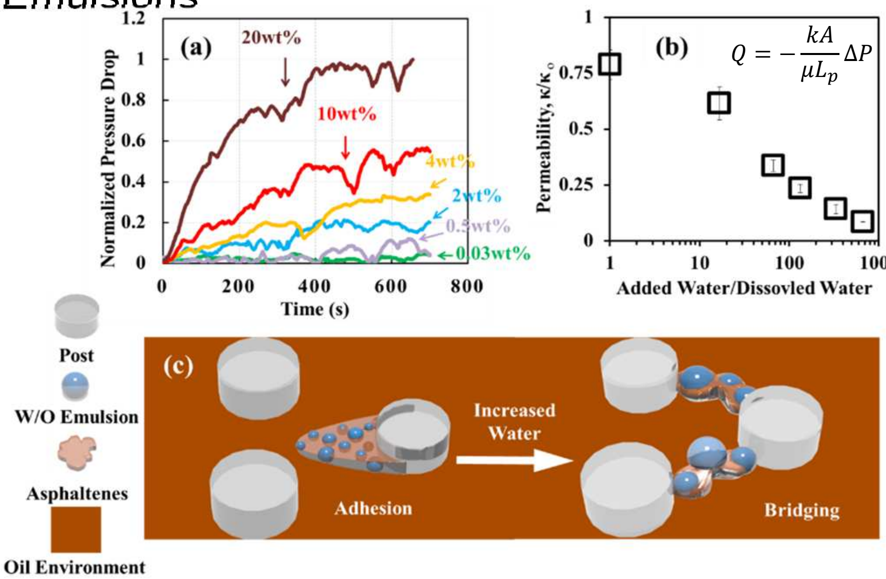
- Asphaltenes enable both the stabilization of water-in-oil emulsions *and* assist the adhesion of these emulsions to surfaces.

Brine Ions

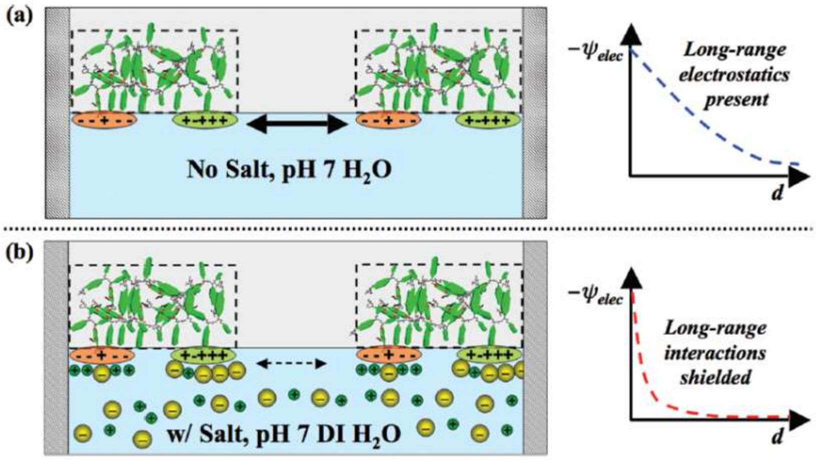


- Pressure drop was higher for high salt concentration due to a larger number of emulsions causing hydrodynamic bridging.

Plugging/Jamming of Asphaltene-Stabilized Emulsions



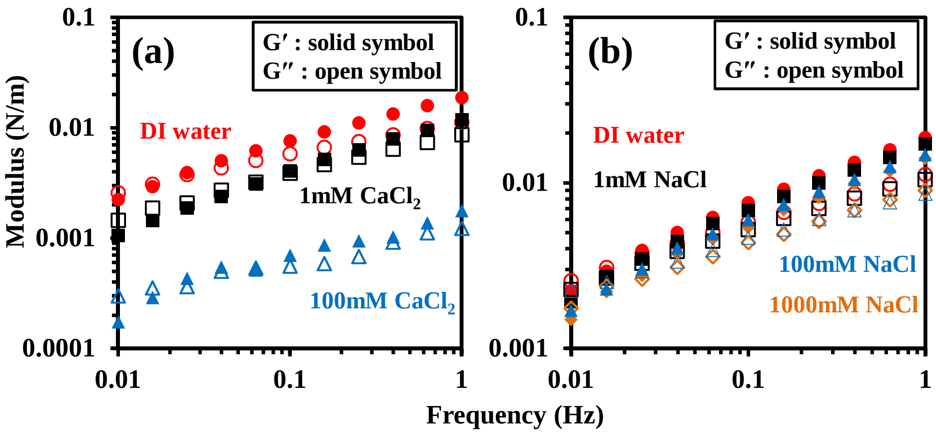
Shielding Effect by Ions



- Salts provide the long-range shielding for the asphatlene interactions.

(*V. J. Verruto *et al.*, **J. Phys. Chem. B**, 2009)

Rheological Properties from Frequency



- Frequency-sweep results indicated that the network behaved like viscoelastic liquid. Dissipated energy under low frequency and stored energy under high frequency.

Zeta Potential

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	DI Water	NaCl			$CaCl_2$	
		1mM	100mM	1000mM	1mM	100mM
Avg (mV)	-93.85	-94.83	-48.13	-14.5	-45.36	-8.38
stdev	2.47	3.36	0.60	2.03	0.75	2.23

- Zeta potential also showed $CaCl_2$ alters the surface charge more significantly.

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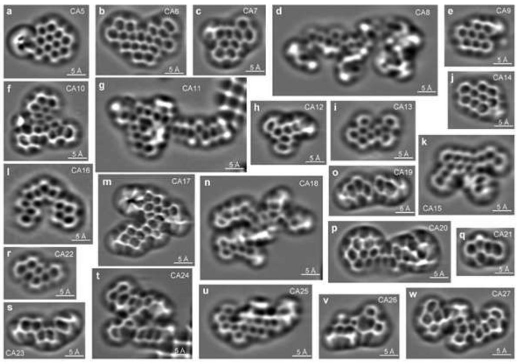
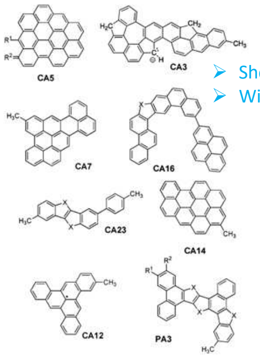
Coalescence of Model Asphaltene-Stabilized Water-in-Oil Emulsions in Microfluidic Devices

Introduction

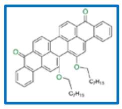
Asphaltene Characterization Using AFM





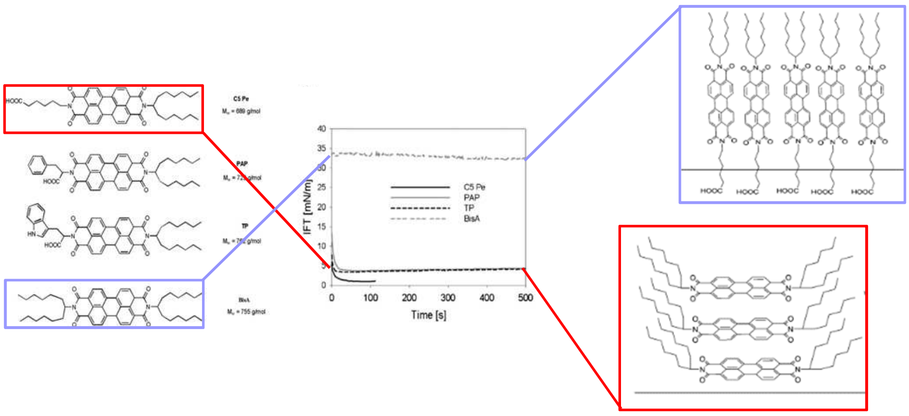
- Sheet like Structure
- With side chains

Coronene

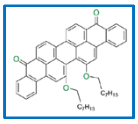


VO-79

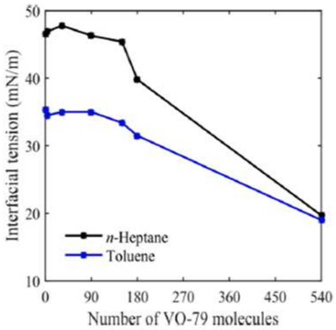
Model Asphaltene Molecules

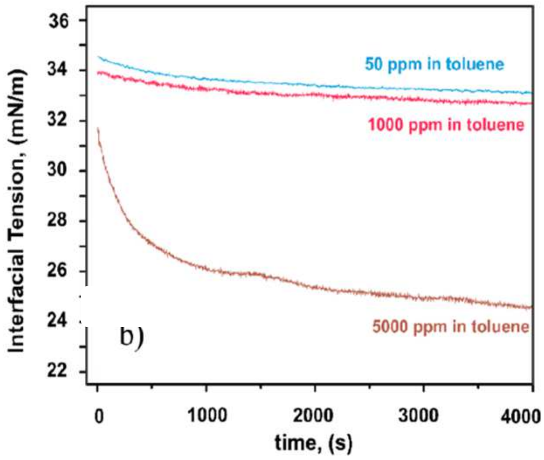


Nordgård et al Langmuir 2008 24(16) : 8742–51



Vo-79

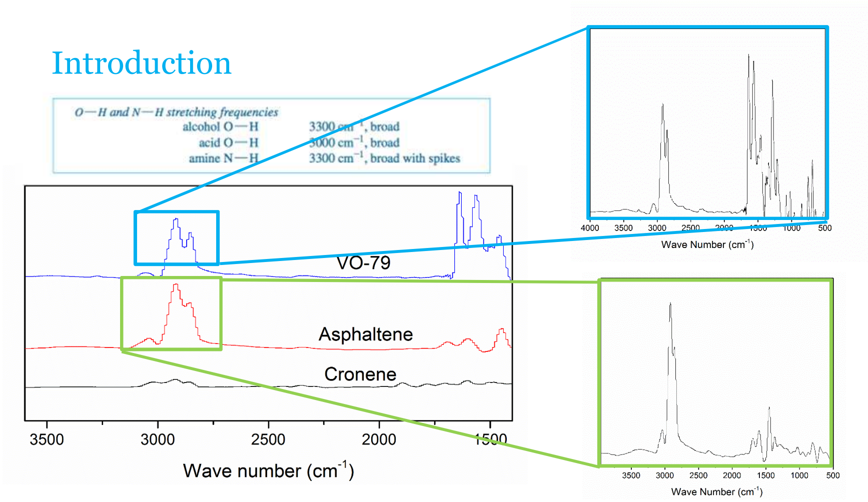




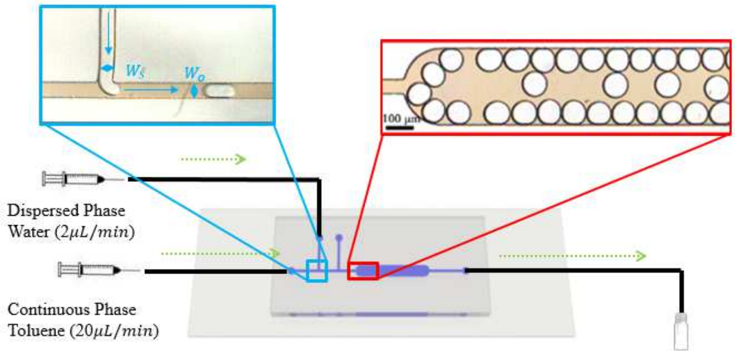
Introduction

O—H and N—H stretching frequencies

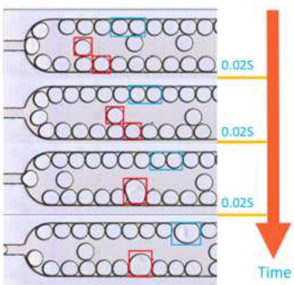
alcohol O—H	3300 cm^{-1}, broad
acid O—H	3000 cm^{-1}, broad
amine N—H	3300 cm^{-1}, broad with spikes

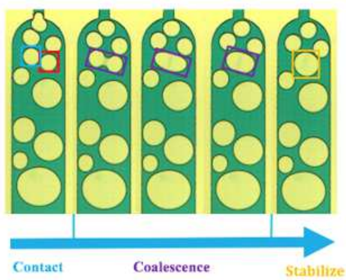


Probing Emulsion Stability Using Microfluidic Devices



Coalescence Phenomenon Inside Micromodel





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

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

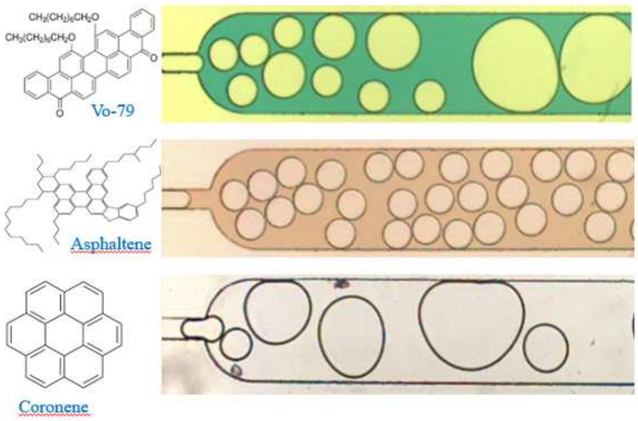
R_c - Coalescence rate $(m^{-2} \cdot s^{-1})$

A_c- Monitored area (m^2)

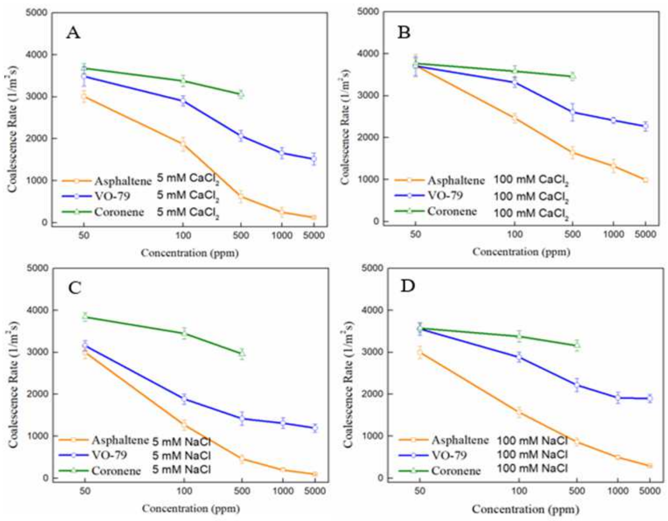
n_c -number of coalescence events

n_T – total number of initial emulsions

Coalescence Behavior Inside Collision Chamber



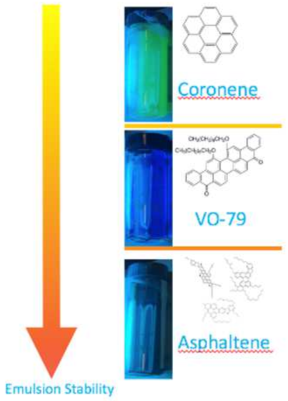
Effect of salt relate to emulsion stability

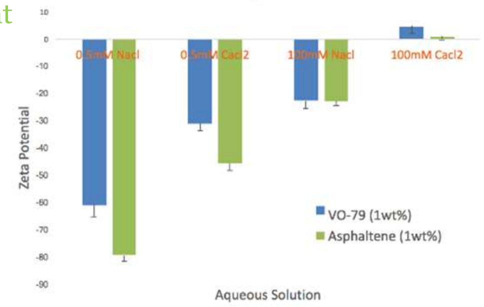


- Coronene stabilized emulsions are not affected by salt concentration
- Asphaltene stabilized emulsions are more sensitive to salt concentration
- Asphaltene stabilized emulsions are more stable than that of VO-79 in both high and low salt concentration

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

Take Away …

- Asphaltene deposition is directly correlated to asphaltene solubility and hydrodynamic factors
- Dispersants can worsen deposition in porous media by decreasing the effective particle size
- Asphaltenes stabilize emulsions based on their interfacial rheological characteristics that can be tuned by altering the physiochemical interactions.
- Model asphaltene molecules can be used to elucidate the role of interfacial stability.

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Soft Matter (2013)
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Langmuir (2017)
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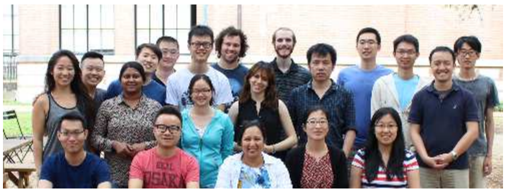

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- -Keith Johnston
- -Francisco Vargas
- -Gordon Christopher

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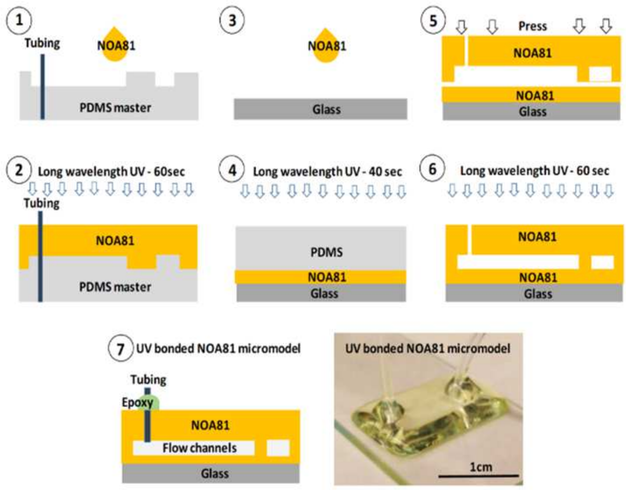
Fabrication of NOA-81 micromodel



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Material and Method

Surface wettability alteration of NOA-81