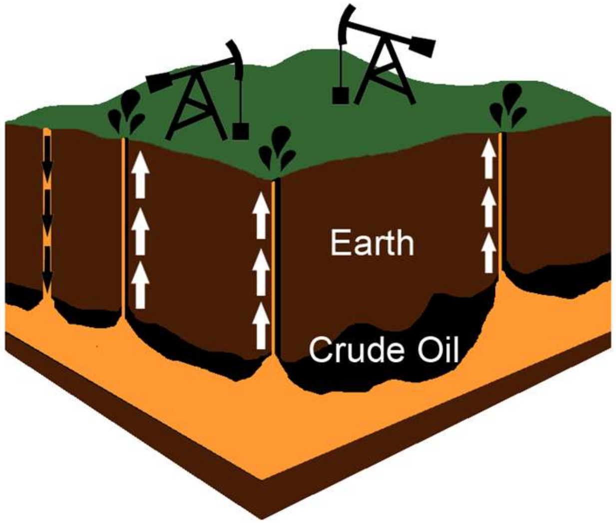
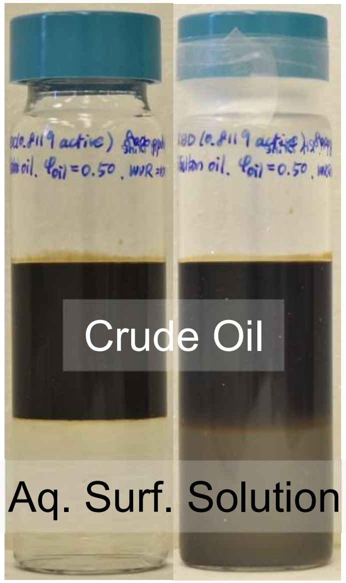
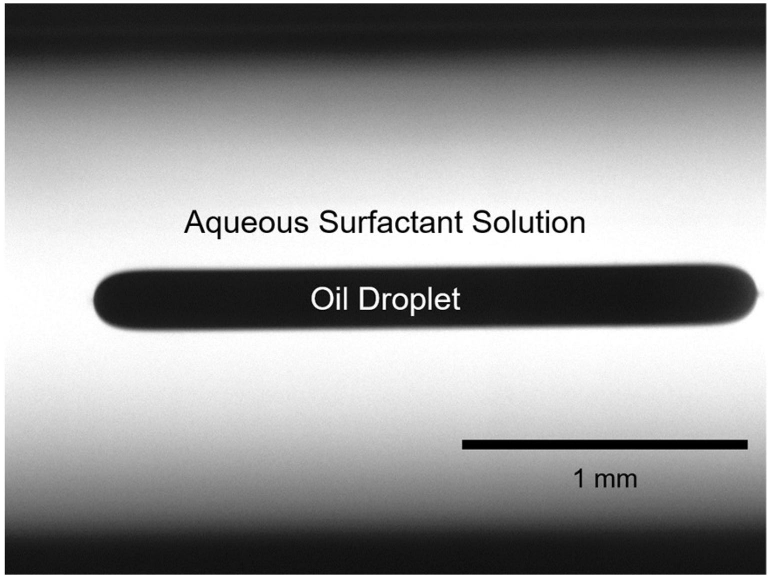
Phase Behavior and Interfacial Tension of Pre-Equilibrated Mixtures of Aqueous Solutions of a Commercial Surfactant and Crude Oil







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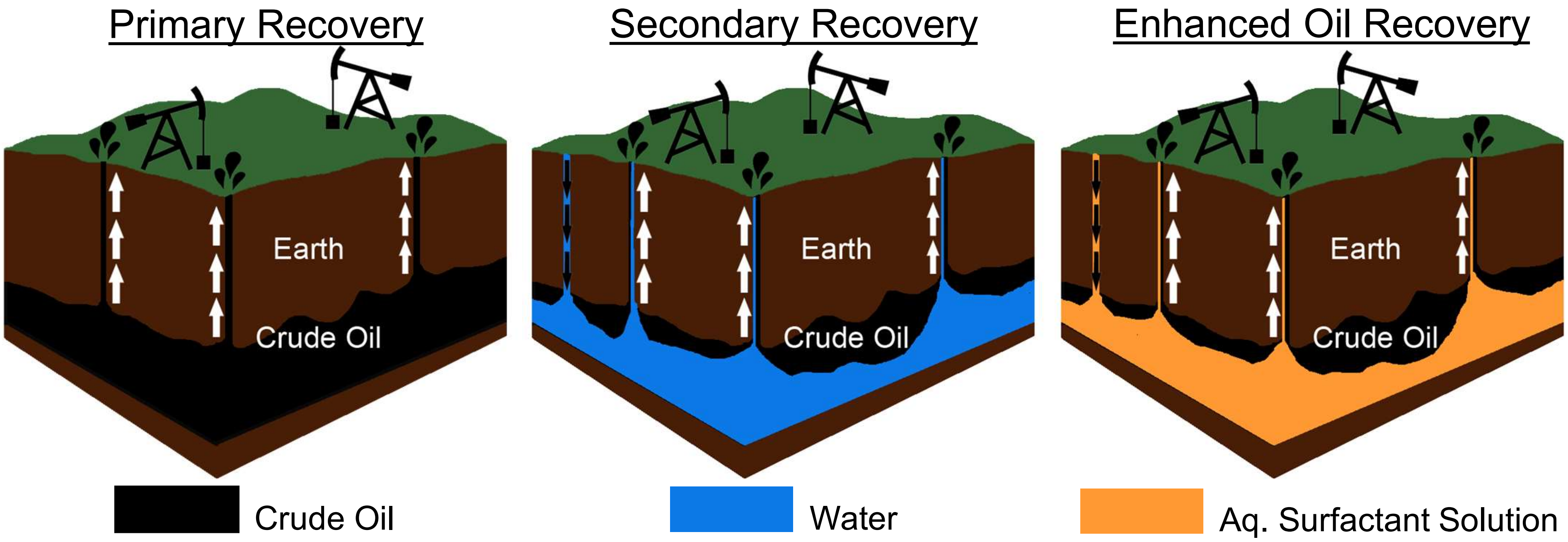
Thursday, May 9, 2019

Injection of Surfactant Solution Increases Oil Recovery



$$N_C = \frac{\mu U}{\gamma}$$

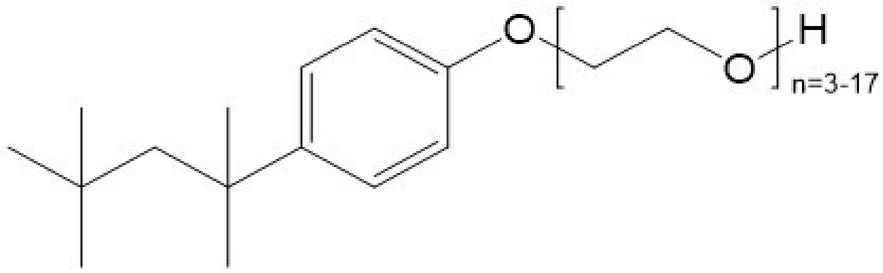
(μ: Fluid Viscosity; *U:* Fluid Velocity; γ: Interfacial Tension)

Injection of aqueous surfactant solutions, usually with polymer in brine, can dramatically improve the oil recovery.

Uren, L.C.; Fahmy, E.H. *Trans. AIME* **1927**, *77*, 318–335.
Sheng, J.J. *Modern Chemical Enhanced Oil Recovery: Theory and Practice;* Gulf Professional Publishing **2010**.
Hirasaki, G.J.; Miller, C.A.; Puerto, M.C. *Soc. Pet. Eng. J.* **2011**, *16*, 889–907.

Model Surfactant and Surfactant of Interest

Triton[TM] X-100 (TX100)



- Nonionic surfactant
- CMC = 0.24 mM (150 ppm)
- For procedural calibration

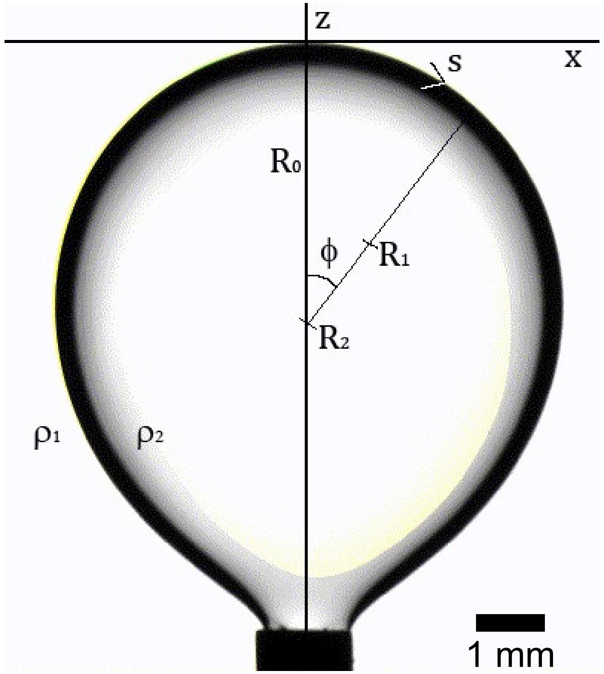
S-13D-HA

$C_nH_{2n+1} – (PO)_m – SO_3^-Na^+$

- Anionic surfactant
- 80 wt% active
- n, m = 13 (on average)
- PO = propylene oxide

Methods for Measuring ST and IFT

<u>Emerging Bubble/Drop Methods (EBM/EDM)</u>

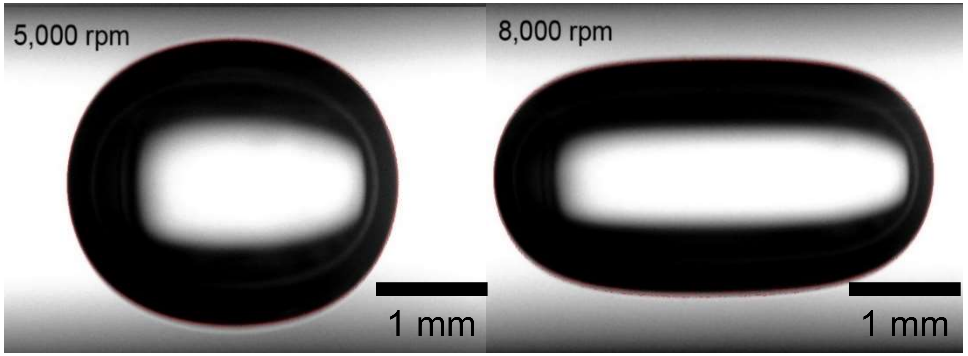


$$2\mathrm{H}\gamma = (\Delta\rho)\mathrm{gz}$$

H: Curvature, γ : ST or IFT, $\Delta\rho$: Density Difference

- Used for DST and DIFT (≥ 1 mN m^{-1})
- Area can be perturbed quickly by drop volume change to follow ST or IFT relaxation.

<u>Spinning Bubble/Drop Methods (SBM/SDM)</u>



$$\gamma \cong \frac{(\rho_1 - \rho_2)\omega^2 R^3}{4} \quad (L \geq 8R)$$

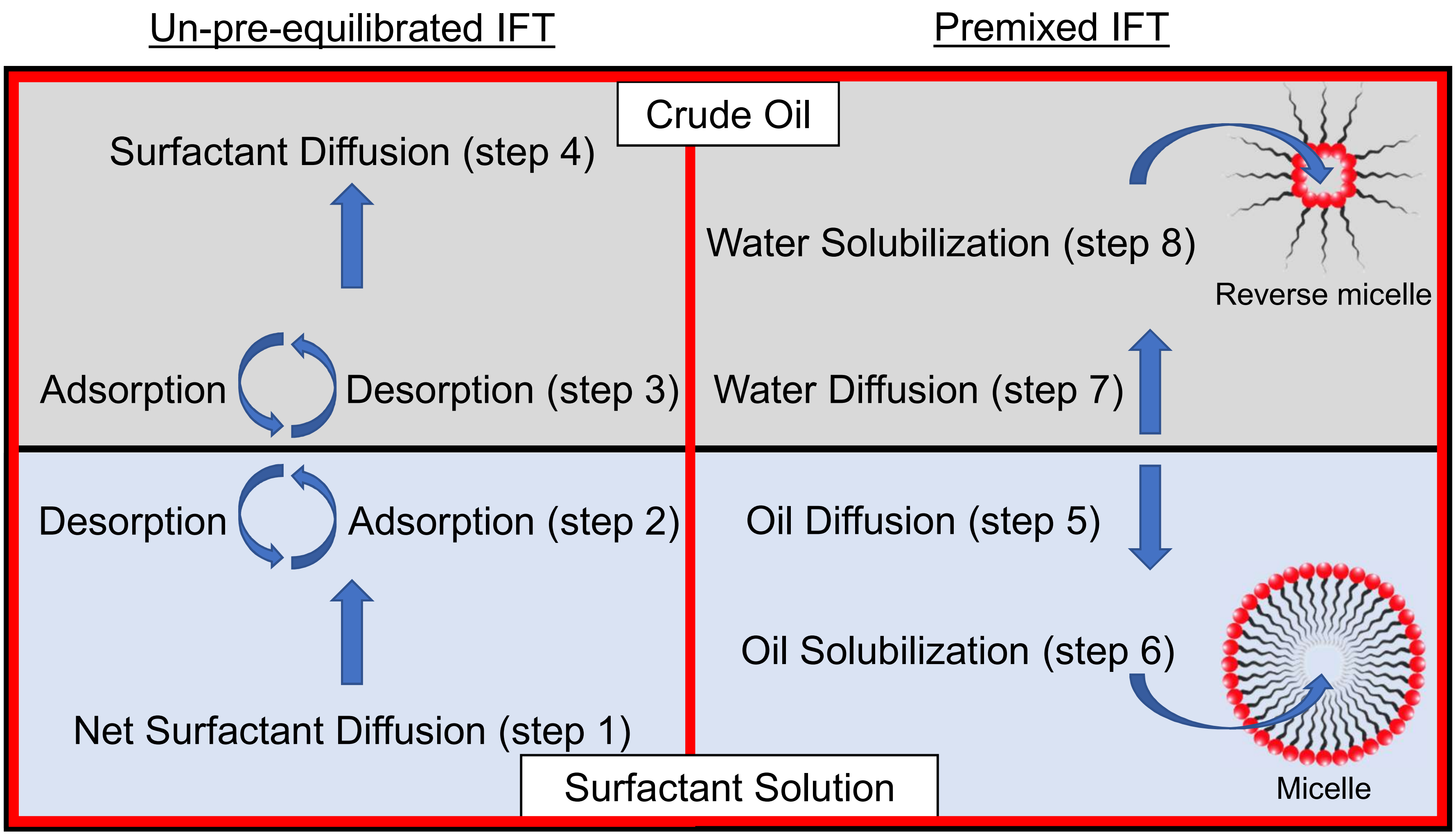
L: length of the drop, R: maximum radius of the drop

ω: Rotation Frequency, ρ: Density

- Used for both DST and DIFT (≤ 1 mN m^{-1})
- Area can be perturbed abruptly by changing rotation frequency to follow tension relaxation.

Rotenberg, Y.; Boruvka, L.; Neumann, A.W. *Journal of Colloid and Interface Science* **1983**, *93*, 169-183.
Vonnegut, B. *Review of Scientific Instruments* **1942**, *13*, 6-9.

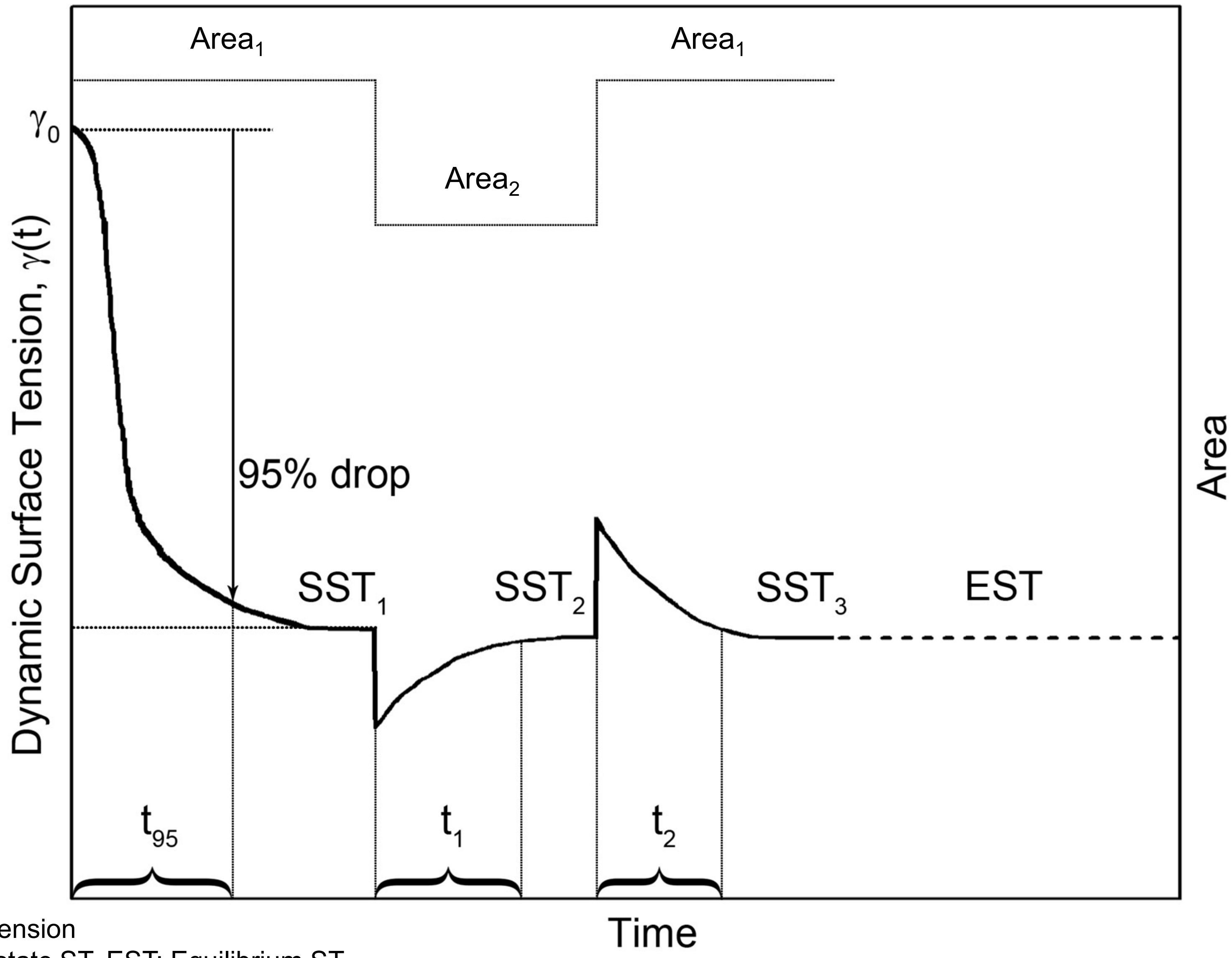
Possible Mechanisms of IFT Equilibration



IFT: Interfacial Tension

Chung, J.; Boudouris, B.W.; and Franses E.I. *Colloids Surfaces A* **2018**, *537*, 163-172.

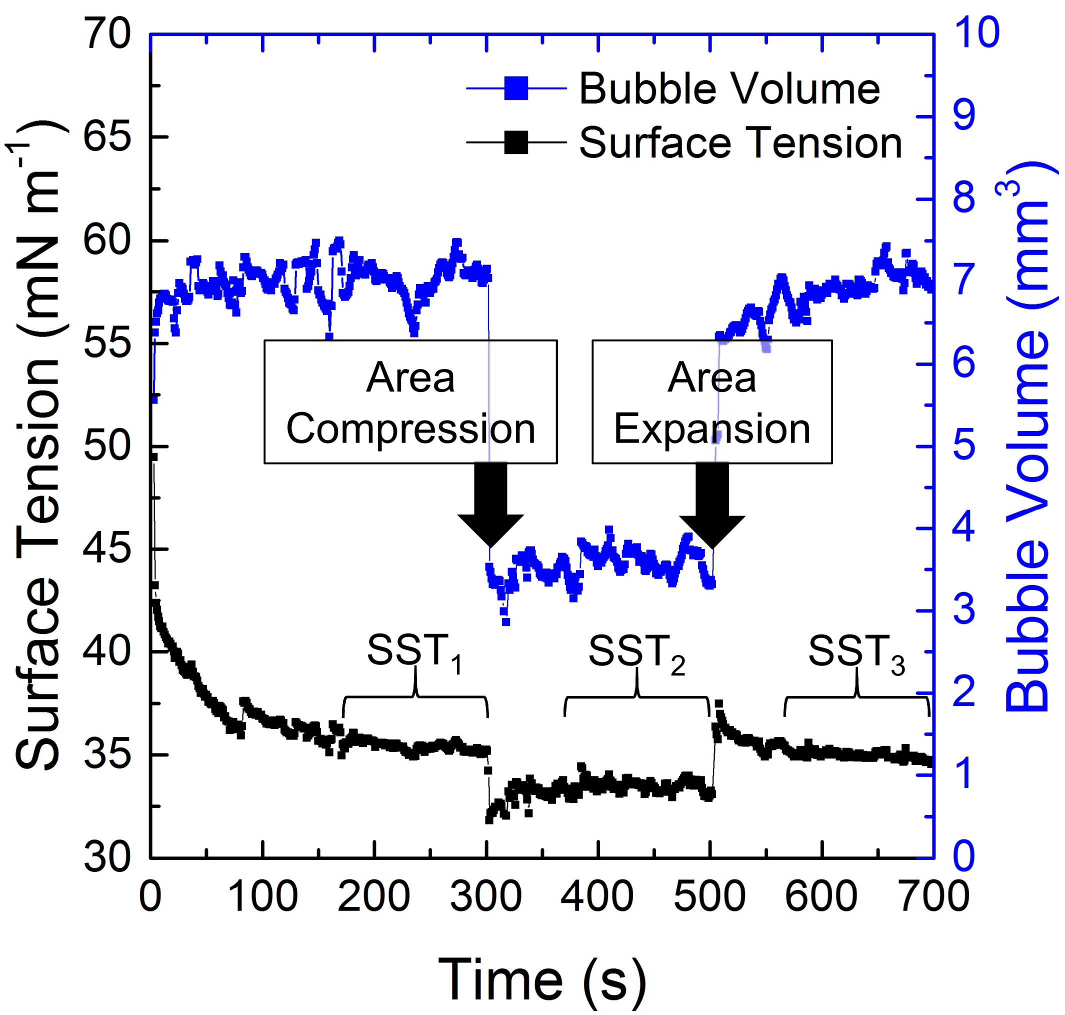
Area Perturbations Test The Stability of Steady-state Tension Values

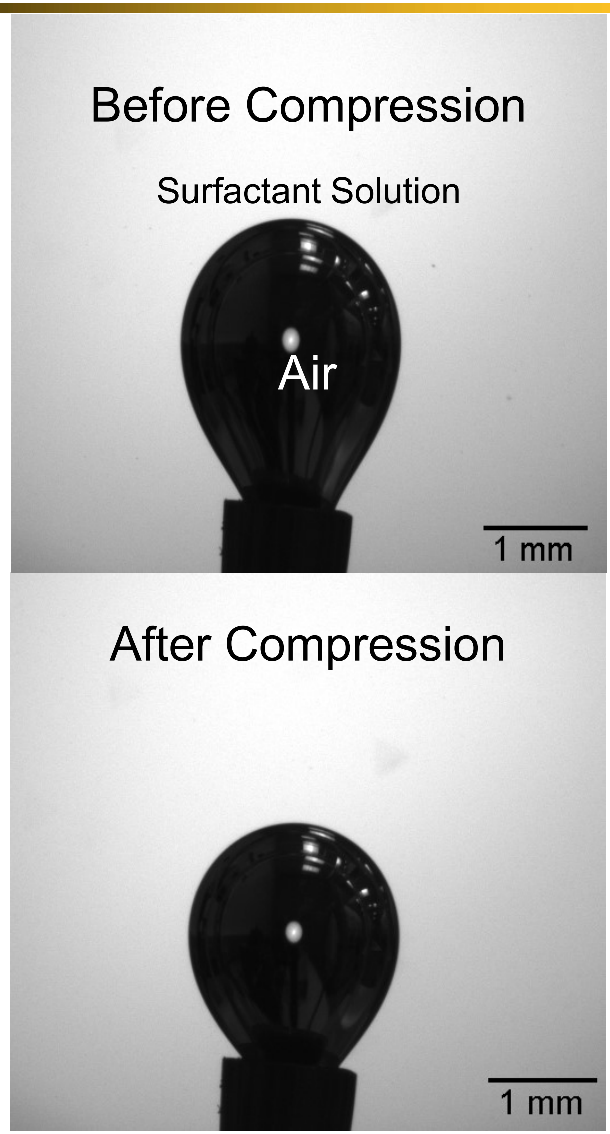


ST: Surface Tension
SST: Steady-state ST, EST: Equilibrium ST

Chung, J.; Boudouris, B.W.; and Franses E.I. *Colloids Surfaces A* **2018**, *537*, 163-172.

DST Data After Area Perturbations



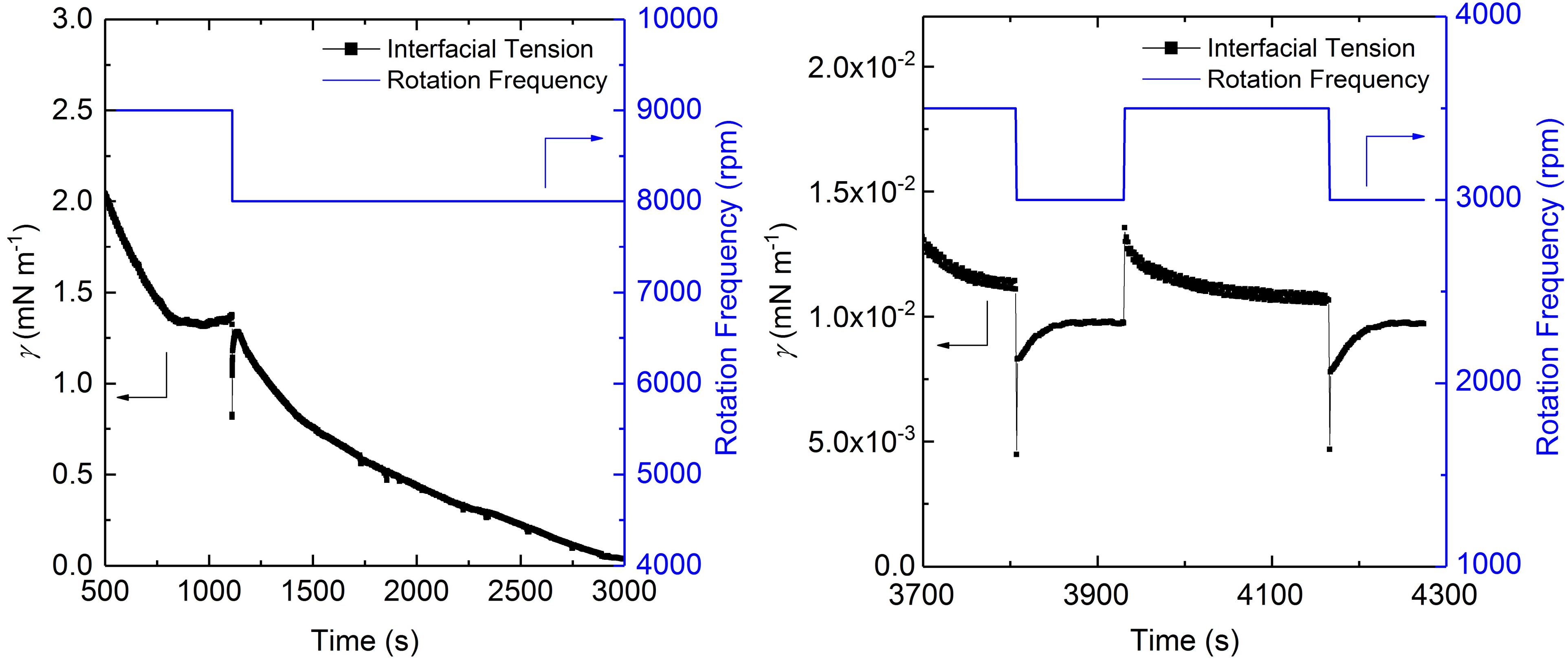


- $SST_1 \approx SST_2 \approx SST_3$ = Equilibrium Surface Tension (EST) = 35 $mN \cdot m^{-1}$

Chung, J.; Boudouris, B.W.; and Franses E.I. *Colloids Surfaces A* **2018**, *537*, 163-172.

IFT Relaxation After Area Perturbations

S13D 20 ppm in Brine Against Crude Oil (SDM)

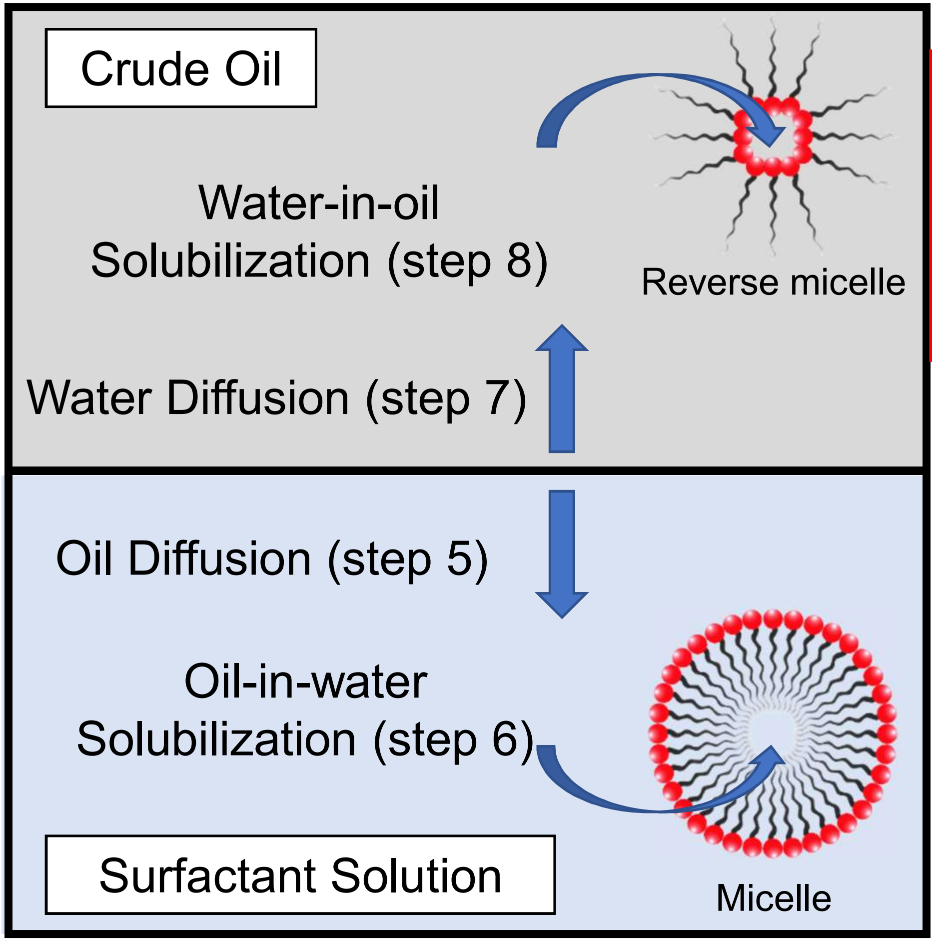


- Area perturbation tests are important for testing the stability of the steady-state IFTs.
- Adsorbed surfactant layer on the interfaces are inferred to be monolayer.

Chung, J.; Boudouris, B.W.; and Franses E.I. *Colloids Surfaces A* **2018**, *537*, 163-172.

Examination of Premixed Systems

<u>Pre-equilibrated IFT</u>

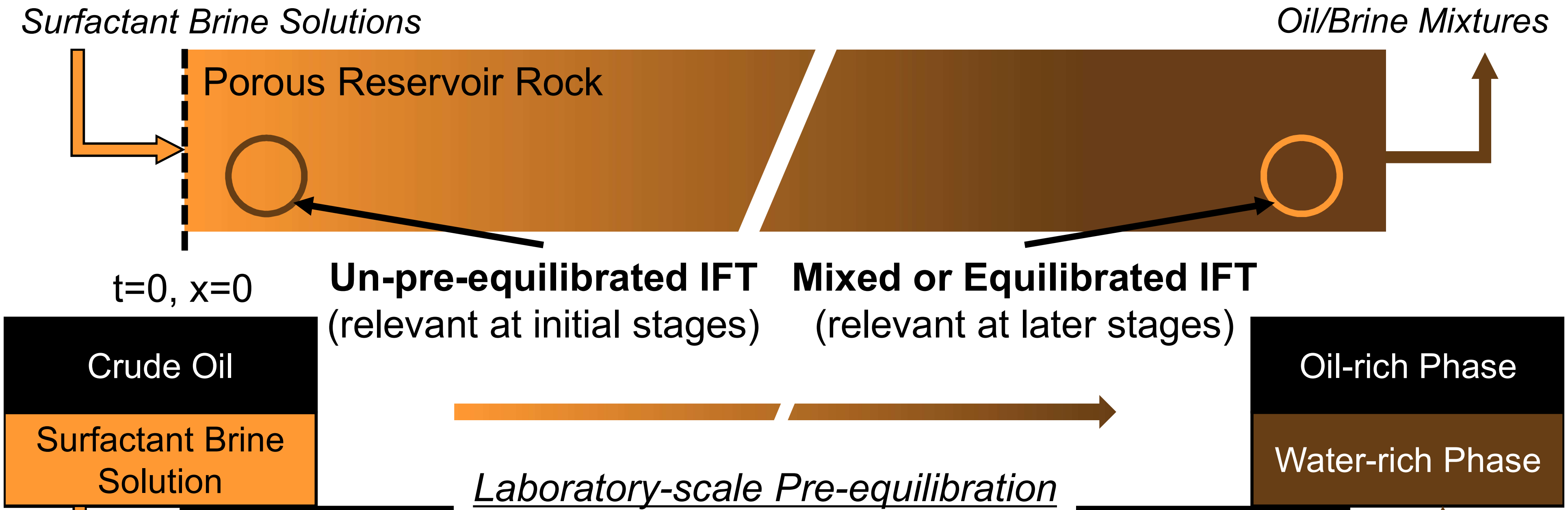


<u>Additional Issues for the Premixed Systems</u>

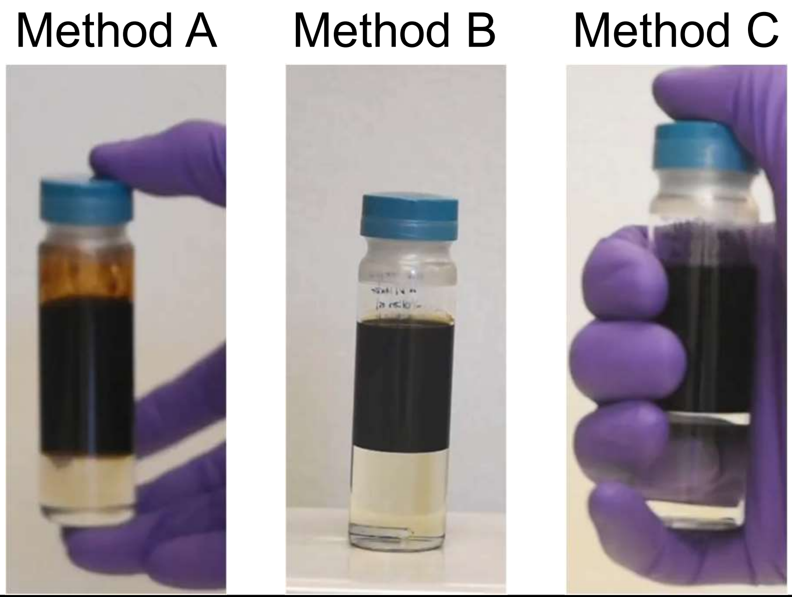
1. Partitioning of components in each phase
   - Quantification of surfactant
   - Volume ratio of each phase
2. Solubilization of components into micelles
   - Distinguish solubilization/dissolution from emulsification
3. Effect of surfactant components
4. Effect of surfactant structures

IFT: Interfacial Tension

Laboratory-scale Pre-equilibration



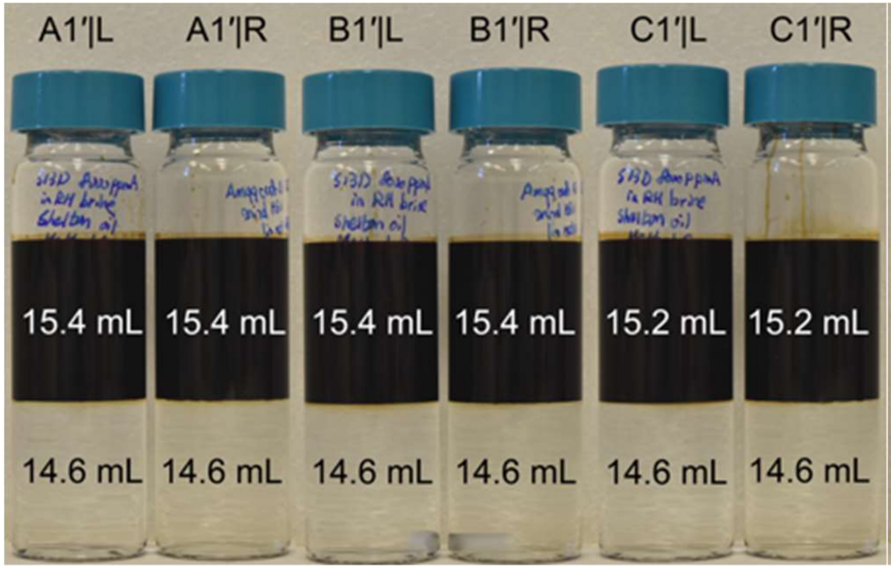
- Surfactant partitioning
- Oil solubilization
- Water solubilization



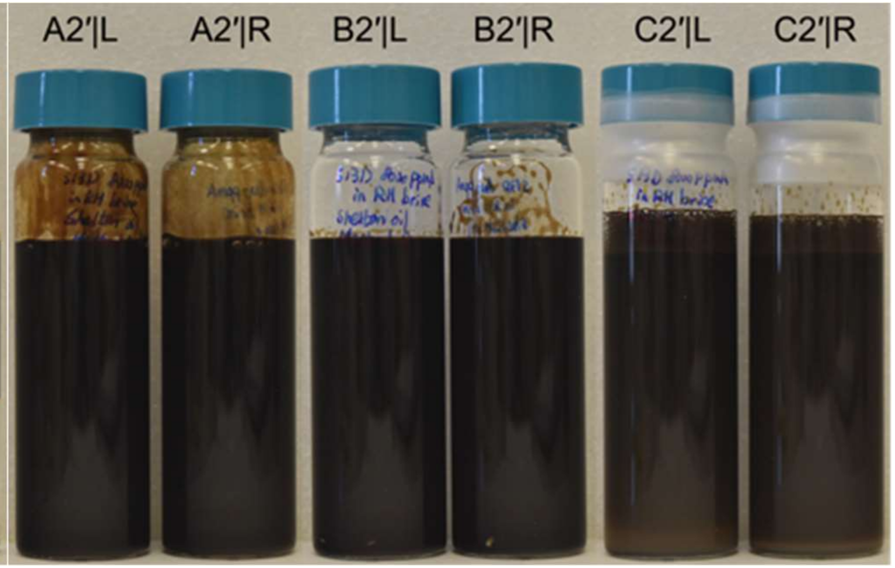
Chung, J.; Boudouris, B.W.; and Franses E.I. *Colloids Surfaces A* **2019**, *571*, 55-63.

Pre-equilibration Results for Brine Systems

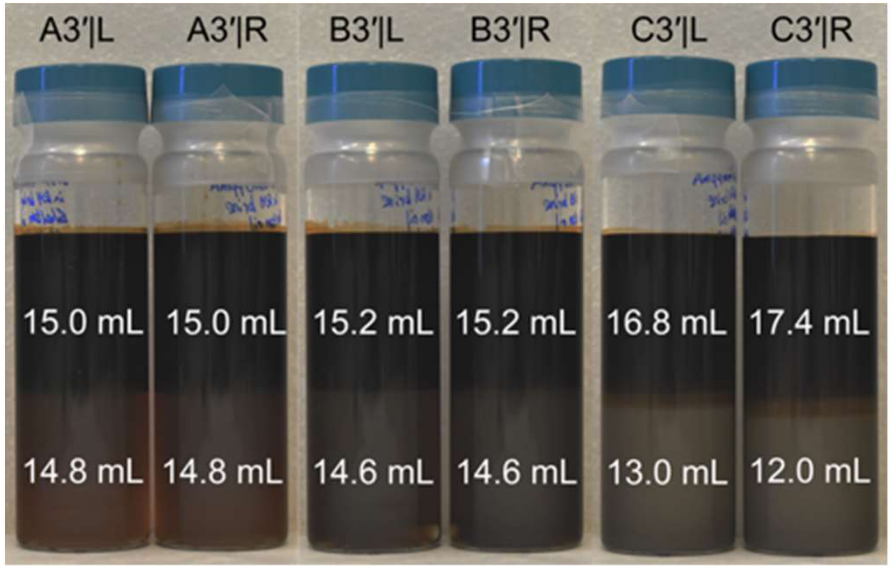
Just Layered



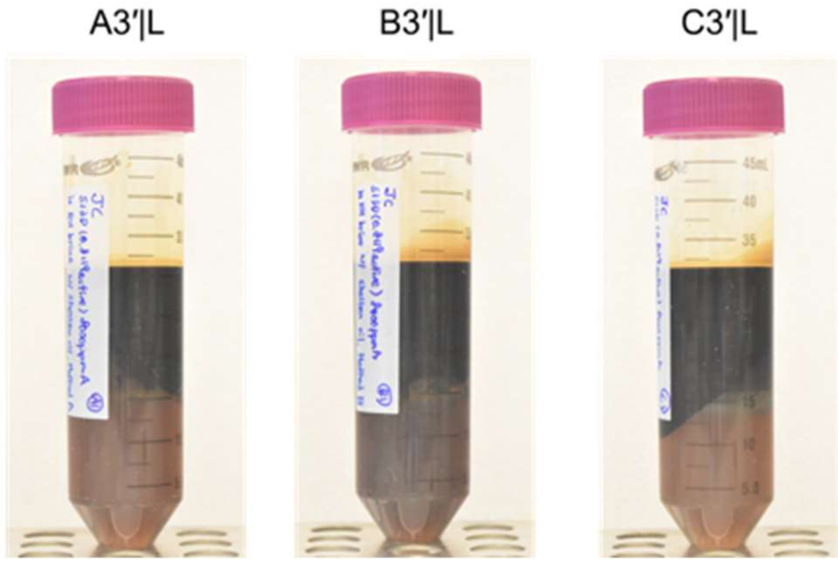
10 s after mixing



200 h after mixing



After centrifugation



Chung, J.; Boudouris, B.W.; and Franses E.I. *Colloids Surfaces A* **2019**, *571*, 55-63.

Shaking by Hand Provides Mixtures Closer to the Equilibrium

Mixing Method	Surfactant Concentration In the Bottom Layer (ppm)	$\frac{C_{T,o}}{C_{T,w}}$	EIFT Before Mixing ($\times 10^{-3}$ $mN \cdot m^{-1}$)	EIFT After Mixing ($\times 10^{-3}$ $mN \cdot m^{-1}$)
(A) Mild Mixing	8,000 ± 100	(< 0.009)	14 ± 1	16 ± 1
(B) Magnetic Stirring	7,900 ± 100	(< 0.021)	14 ± 1	37 ± 2
(C) Shaking by Hand	4,300 ± 100	1.07	14 ± 1	387 ± 7

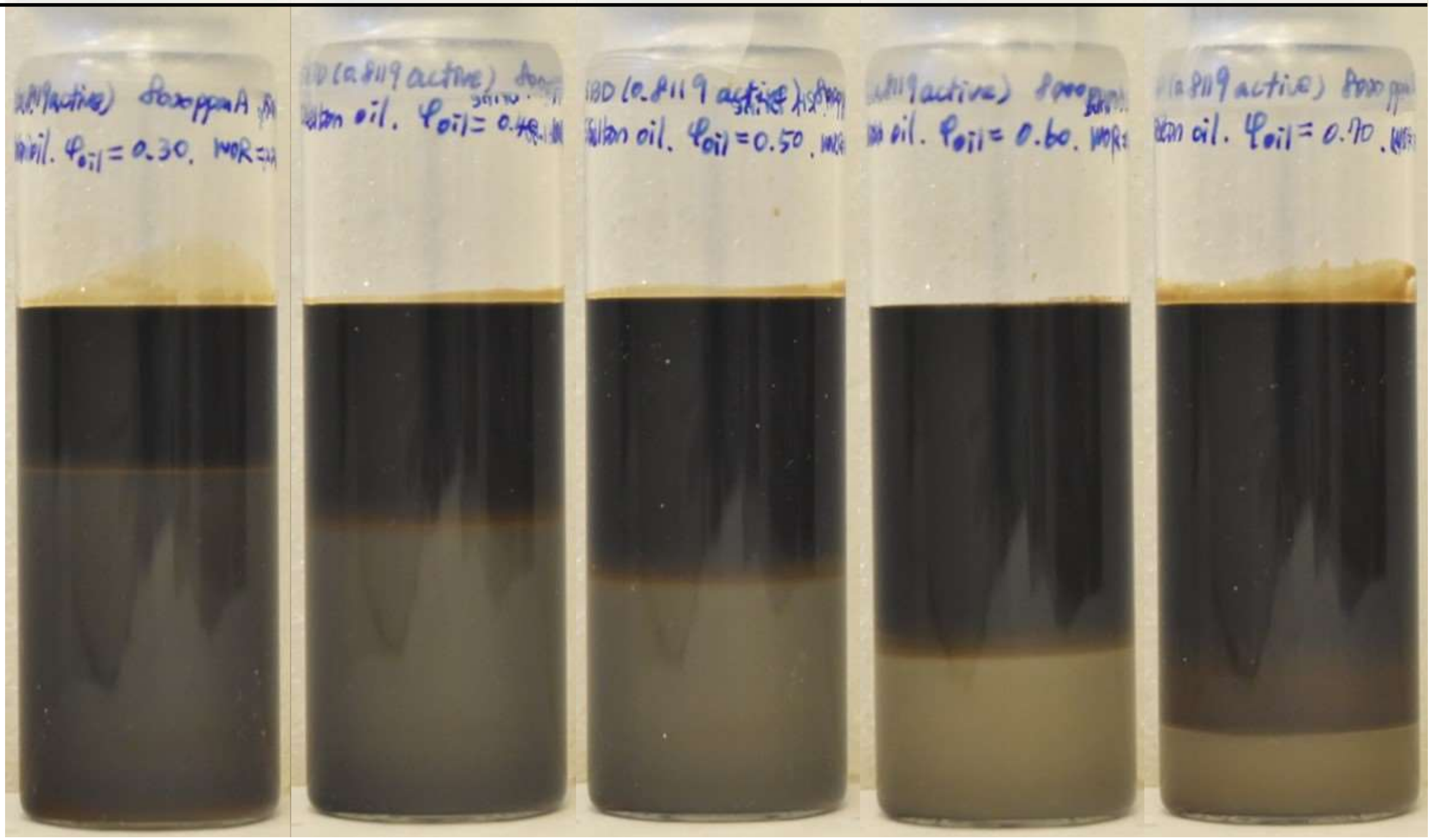
- Only two phases were observed for all mixtures.
- Method C produced mixtures closest to the phase equilibrium.
- EIFT varies significantly among three mixing methods. EIFT was higher for Method B than for Method A, and much higher for Method C.

Chung, J.; Boudouris, B.W.; and Franses E.I. *Colloids Surfaces A* **2019**, *571*, 55-63.

Effect of the WOR or Oil Volume Fraction (φ) To Phase Behavior

S13D 1 % in brine with crude oil

WOR	2.33	1.50	1.00	0.67	0.43
φ_{oil}	0.30	0.40	0.50	0.60	0.70

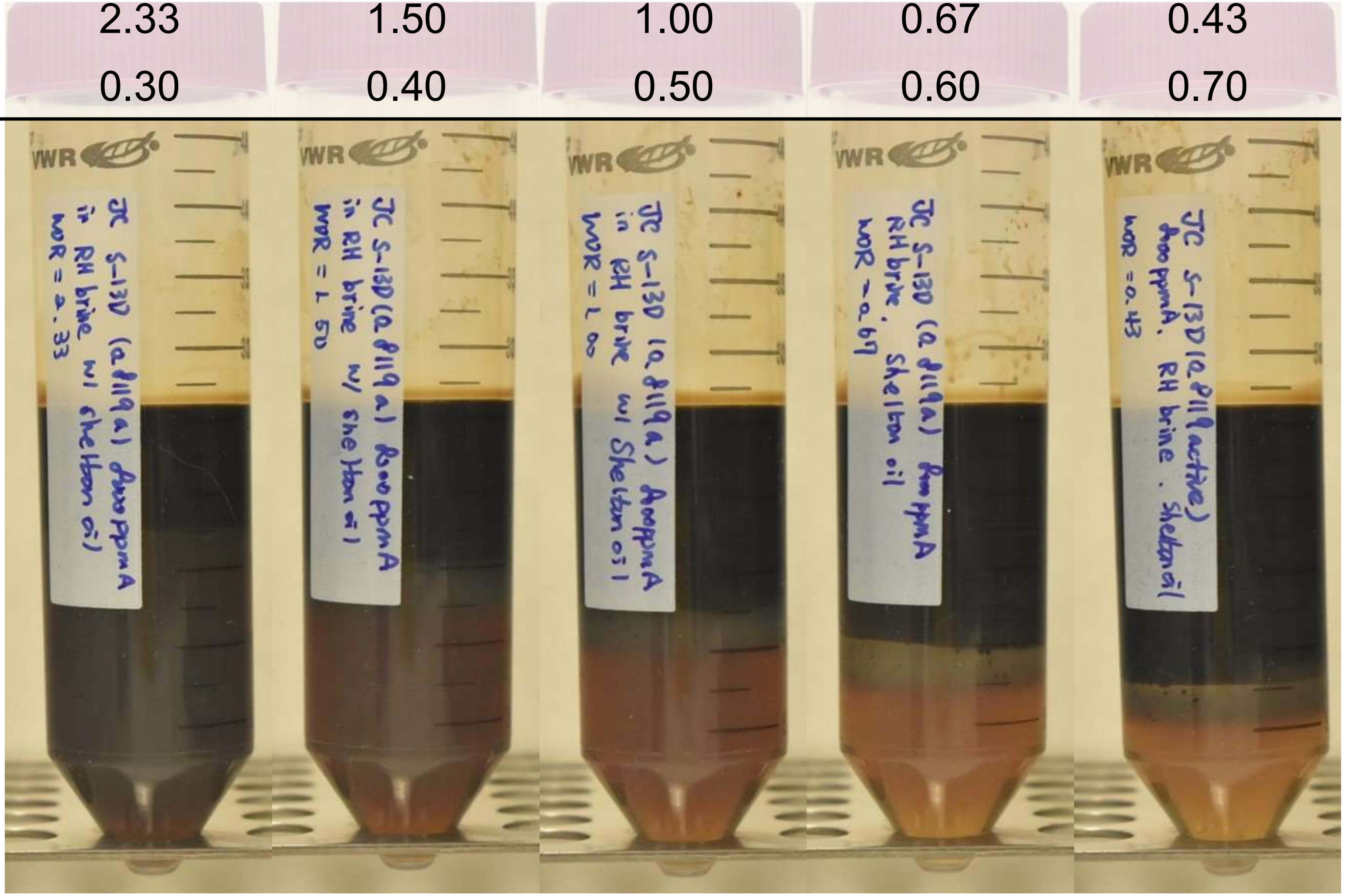


Chung, J.; Boudouris, B.W.; and Franses E.I. *Colloids Surfaces A* **2019**, *571*, 55-63.

Effect of the WOR or Oil Volume Fraction (φ) on Phase Behavior After Centrifugation

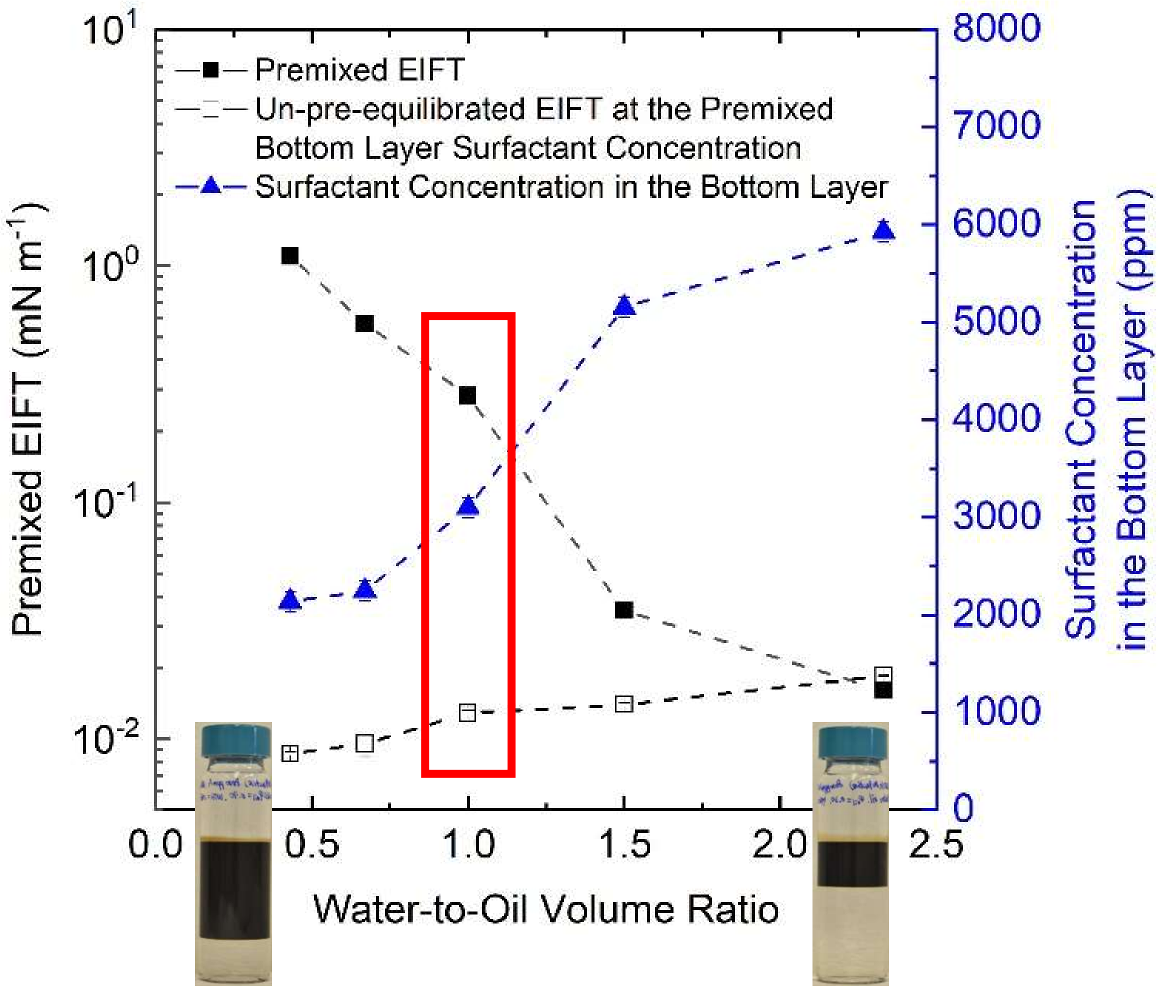
S13D 1 % in brine with crude oil

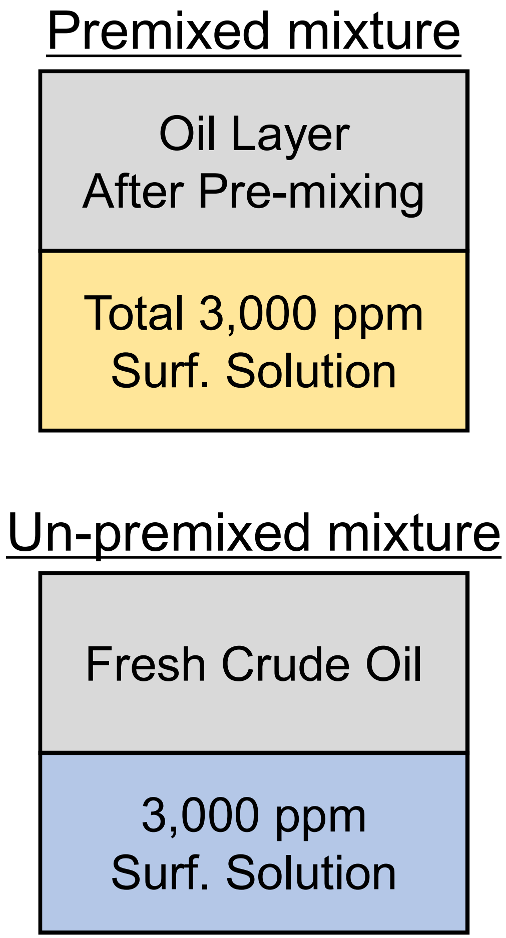
WOR	2.33	1.50	1.00	0.67	0.43
φ_{oil}	0.30	0.40	0.50	0.60	0.70



Chung, J.; Boudouris, B.W.; and Franses E.I. *Colloids Surfaces A* **2019**, *571*, 55-63.

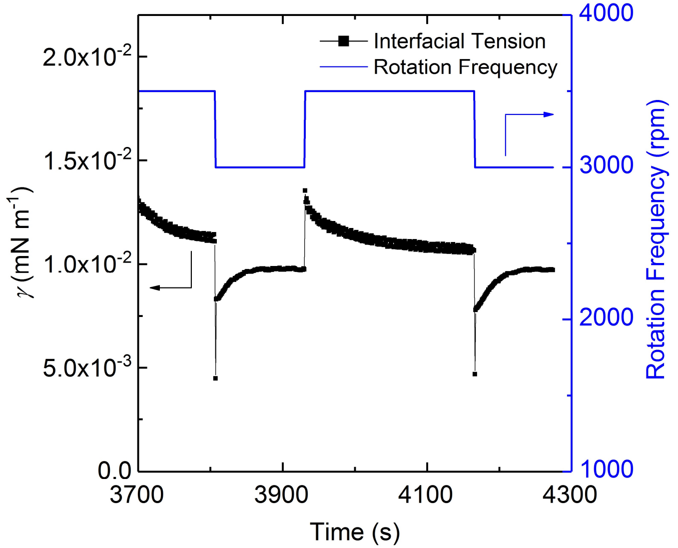
Effect of WOR on Phase Behavior and EIFT

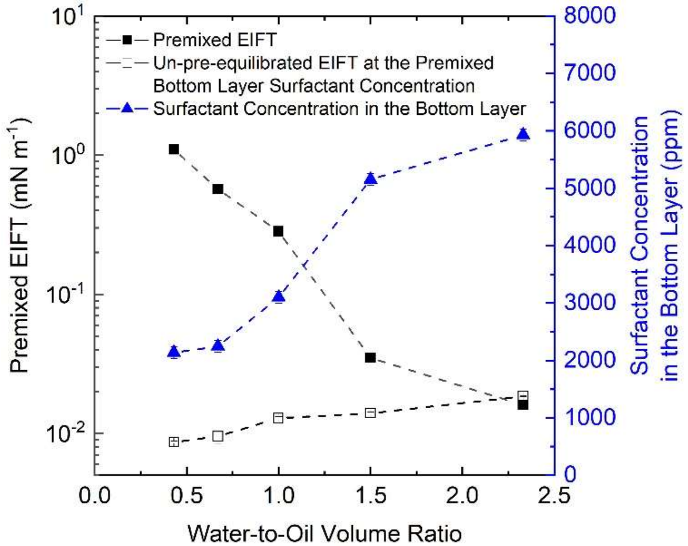




- As the WOR decrease, or as φ increase, more surfactant partitions into the oil phase.
- Partitioning of various surfactant components is inferred to be preferential.

Conclusions





- Area perturbation tests stability of the steady-state tension values so that reliable equilibrium tension values can be established.

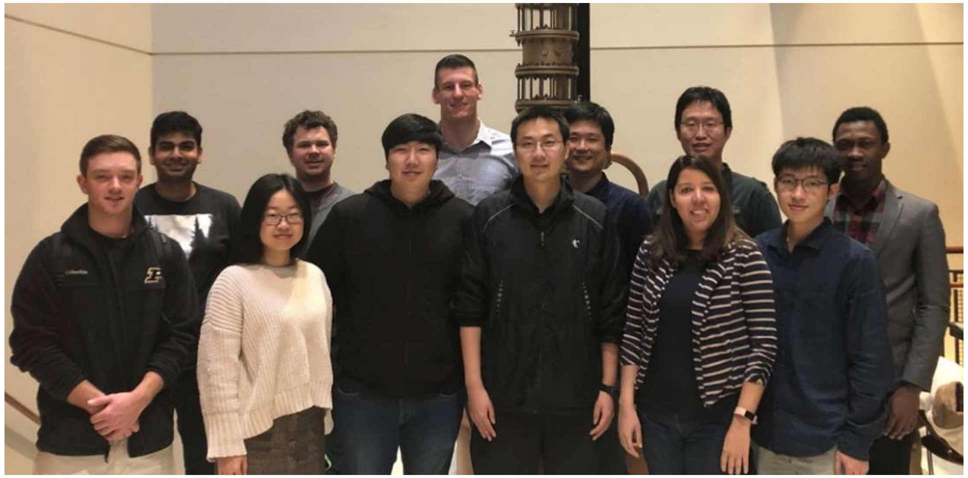
- Adsorbed surfactant layer on the interfaces are inferred to be monolayer based on the tension relaxation behavior after each area perturbation.

- Premixed EIFTs can be different from un-pre-equilibrated EIFTs. Such differences are due to preferential surfactant component partitioning in oil for multicomponent surfactants.

- No single EIFT value can fully characterize the performance of a surfactant formulation for surfactant water flooding. Therefore, One should determine how EIFT may vary with the WOR in order to infer or predict the performance of a surfactant formulation in a surfactant water flooding applications.

Acknowledgements

Boudouris Research Group



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