# Crude Oil Emulsions. Occurrence and Chemical Destabilization

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# Outline

- Water production in oil and gas industry.
- Emulsions. Fundamentals.
- Occurrence of crude oil emulsions.
- Natural emulsifiers/surfactants in crude oil.
- Demulsification: steps and methods.
- Physicochemical formulation of surfactant-oil-water (SOW) systems
- Hydrophilic-Lipophilic-Deviation (HLD).
- HLD application in crude oil demulsification.
- Final considerations.
- Acknowledgments.
- References.

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# Water production in oil & gas industry

**More than 300 MM bbls/day of production water worldwide***

**Production water can be mainly found as:**

- **Free water:** separated within 3 -10 mins
- **W/O emulsions:** complex treatment is required to break them up

*Ahmadun et al. 2009. J. Hazardous Materials, 170: 530-551

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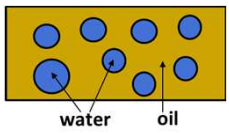
# What is an emulsion?

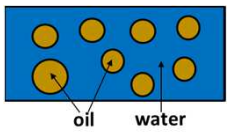
## Dispersion of a liquid in another in which it is not miscible

-Thermodynamically unstable, but kinetically stable

-Main types: Water-in-oil (W/O) or oil-in-water (O/W)




W/O (most common in oil production)




O/W

-Typical droplet size: 0.1 – 100 µm

-Variable water content (W/O emulsions): a few % up to 90% (in some cases)

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# Some examples of emulsions in oil industry

| Undesirable emulsions | |
|---|---|
| Well-head emulsions (oil field) | W/O |
| Oil spill mousse emulsions | W/O |
| Oil sand flotation process | W/O or O/W |
| Fuel oil emulsions | (W/O) |

| Desirable emulsions | |
|---|---|
| Heavy oil pipeline emulsion | O/W |
| Emulsion drilling fluid | W/O or O/W |
| Asphalt emulsions | O/W |
| EOR in situ emulsions | O/W |

Schramm. 1992. Emulsions: Fundamentals and applications in the petroleum industry

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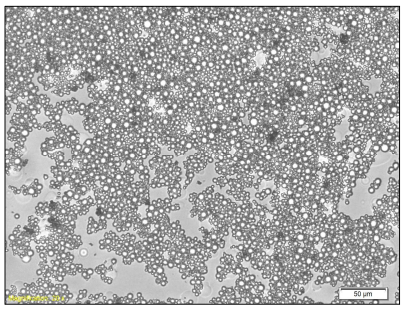
# Where do crude oil emulsions occur?

**Emulsion formation:** Oil + Water + Energy + Emulsifiers (natural surfactants)

**Water:** Naturally occurred in the reservoir or injected in recovery processes.

**Emulsifiers:** Asphaltenes, resins, acids, solids, injected chemicals.

**Energy:** Shear provided by chokes, fittings, T's, elbows, reductions/expansions, pumping, etc.



Emulsions occur at well head, pipeline, drilling operations, EOR, separators and other equipment

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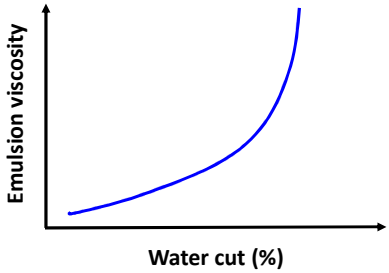
# Problems generated by crude oil emulsions

- Increase oil viscosity:




- Overloading surface equipment.
- Increase vessel heating costs.
- Corrosion risk due to salt presence (max. 25 lb salt/1000 barrels).
- Risk of catalyst poisoning at refineries.
- Reduce value of crude oil (max. water content 0.5 – 3 %).
- Formation of sludge in stock tanks.

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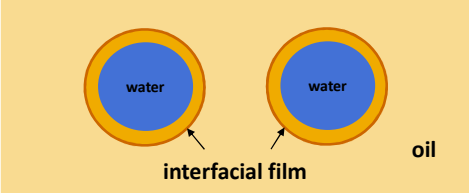
# Natural surfactants: lipophilic emulsifiers

Create an interfacial film that avoids coalescence of water droplets




***Emulsion stabilizers:***
-Natural surfactants: **asphaltenes**, resins, acids, added chemicals.
-Inorganic solids, waxes.

**To be considered:**

- Asphaltenes may associate and form aggregates with variable interfacial activity.
- Interfacial film is a mixture of different crude oil species.
- Interfacial re-organization (aging) plays a major role in emulsion stability.

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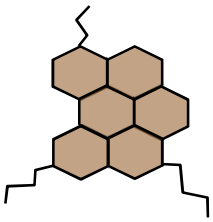
# Asphaltenes: main emulsion stabilizers

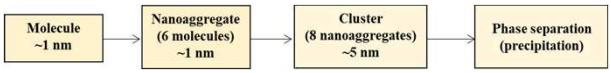
Soluble in aromatics and insoluble in paraffins



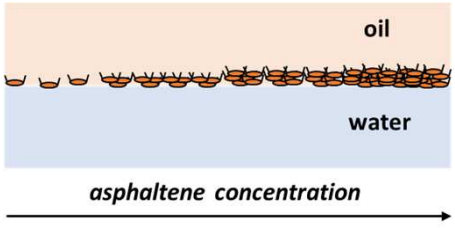
- Aromatic core.
- Aliphatic branches.
- Polar groups.

MW ~ 750 Da
Heteroatoms: O, N, S, Ni and V.

Bulk association with concentration (Yen-Mullins model)




Association at water-oil interfaces with concentration




Chen et al. 2020. Energy & Fuels, 11: 14074-14093
Mullins. 2010. Energy & Fuels, 24: 2179-2207
Alvarez et al. 2009. Energy & Fuels, 23: 294-299

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## Asphaltenes: main emulsion stabilizers

- Only a small fraction of asphaltenes (~2%) are in the interfacial film.
- Emulsion stability increases with asphaltene concentration.
- Asphaltenes near precipitation point have their highest interfacial activity.
- Role the asphaltenes as emulsion stabilizer are influenced by cross-interactions with other fractions, such as resins and acids.

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## Other factors affecting emulsion stability

- Difference in density between crude oil and water.
- Water droplet size.
- Crude oil viscosity.
- Water salinity.
- Agitation.
- Emulsion aging.

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## Steps involved in emulsion breaking (demulsification)

1. **Approaching of water droplets (sedimentation)**: inter-droplet distance ~ 1µm. Improved by *thermal and mechanical methods*.
   *Governed mainly by Stokes' law*

$$\text{Velocity of water sedimentation} = \frac{2(\rho_{water}-\rho_{oil})gr^2}{9\mu_{oil}}$$

2. **Drainage of liquid inter-droplet film**: depends on the adsorbed surfactants (natural surfactants and commercial demulsifiers). Improved by the *addition of demulsifiers*.

3. **Coalescence of water droplets**: very rapid process.

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## Demulsification methods

- **Thermal: T ~ 50 - 65°C.**

Reduce oil viscosity, increase droplet collisions, melt waxes and destabilize interfacial film.

- **Electrical: 10,000 – 35,000 V AC.**

Polarization of water droplets increases collisions and destabilizes interfacial film.

- **Chemical:**
  - Addition of demulsifiers (*surfactants*).
    *Change the physicochemical formulation to destabilize the water-oil interface and induce water coalescence.*
  - New demulsifiers: nano-particles and ionic liquids.

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# Chemical demulsification: the most common method

## Blends of surfactants and solvents

| Year | Dose (ppm) | Demulsifiers (active components) |
|---|---|---|
| **1920-1930** | 1,000 | Soap, naphthenic acid salts and alkylarylsulphonate, sulphated castor oil |
| **1930-1940** | 1000 | Petroleum sulphonates, derivatives of sulpho-acid oxidized castor oil and sulphosucinic acid ester |
| **1940-1950** | 500-100 | Fatty acids, fatty alcohols, alkylphenols |
| **1950-1960** | 100 | Ethylene oxide, propylene oxide copolymers, alkoxylated cyclic p-alkylphenol formaldehyde resins |
| **1960-1970** | 50-30 | Amine alkoxylate |
| **1970-1980** | 30-10 | Alkoxylated cyclic p-alkylphenol formaldehyde resins |
| **1980-1990** | 20-5 | Polyesteramines and blends |

**Solvents and other chemicals (> 50% of demulsifier formula):** Aromatic cuts and short alcohols.

Staiss et al. 1991. SPE Prod. Eng., 6: 334-338
Al-Sabagh et al. 2011. Sep. Sci. Technol., 46: 1144-1163
Schramm. 1992. Emulsions: Fundamentals and applications in the petroleum industry

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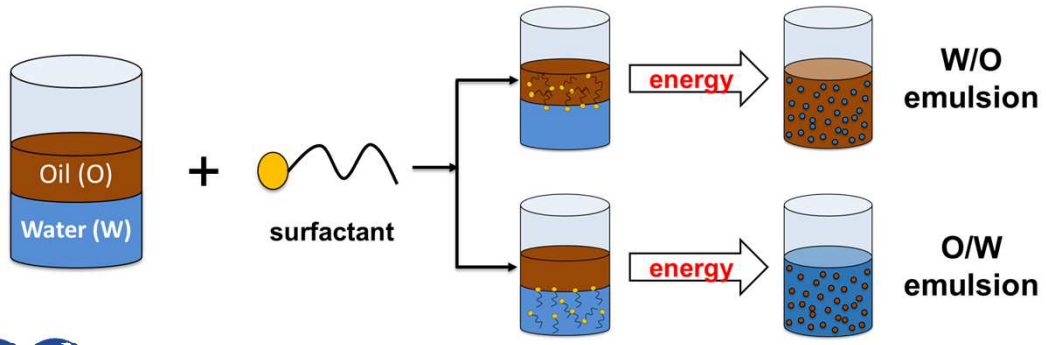
# Physicochemical formulation of surfactant-oil-water (SOW) systems: from the "black art" to a systematic demulsifier selection. Some basic concepts

**Bancroft's rule:** *"The phase in which an emulsifier is more soluble constitutes the continuous phase"*




Tip: **Natural surfactants in crude oils are generally lipophilic (oil soluble)**

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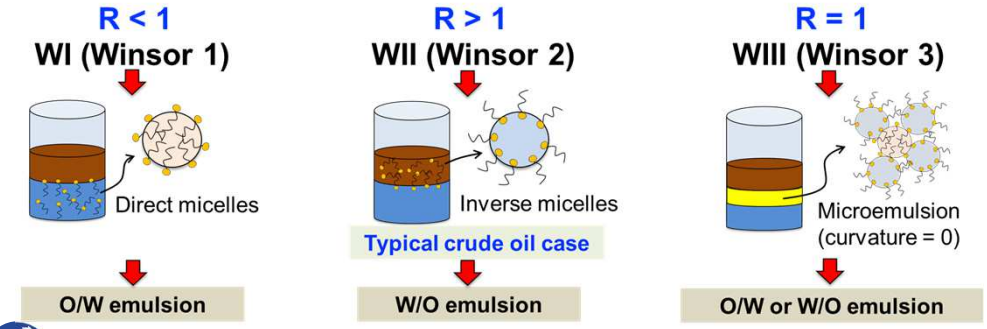
# Winsor's R ratio: a pedagogical approach

*It considers the interactions between surfactant molecules (at interface) and oil and water molecules*

$$R = \frac{net\ "surfactant-oil"\ interaction}{net\ "surfactant-water"\ interaction}$$




**Drawback: Impossible to quantify the interactions**

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# Hydrophilic-Lipophilic-Deviation (HLD)-Salager's model

$$\mathbf{HLD} = \frac{\mu_w^o - \mu_o^o}{RT}$$ ⇒ Difference between the standard chemical potential of the surfactant in each phase (oil and water)

$$\mathbf{HLD} = \sum \mathbf{contributions} = \sum (\mathbf{water} + \mathbf{oil} + \mathbf{surf.} + \mathbf{alcohol} + \mathbf{temp.})$$

**ionic surfactants :**

$$\mathrm{HLD} = \ln S - \mathrm{kACN} + \mathrm{f(A)} + \alpha - a_T \Delta T$$

salinity, oil, alcohol, Surfactant (**SCP**), temperature

**nonionic surfactants :**

$$\mathrm{HLD} = bS - \mathrm{kACN} + \emptyset(A) + \beta + c_T \Delta T$$

**α,β** = surfactant contribution parameter (**SCP**)

Salager et al. 1979. SPE J., 19: 107–115
Bourrel et al. 1980. J. Colloid Interface Sci., 75: 451–461
Salager et al. 2000. Langmuir, 16, 5534-5539

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## HLD versus Winsor's R ratio

| R | HLD | Surfactant is in: | Emulsion type |
|---|---|---|---|
| < 1 | < 0 | water | Oil-in-Water (O/W) |
| > 1 | > 0 | Oil | Water-in-Oil (W/O) |
| =1 | = 0 | Microemulsion | O/W or W/O |

Typical condition in oil production

Desired condition for oil dehydration

- ✓ The sign indicates the "side".
- ✓ The value represents the "deviation" from the optimum formulation (HLD=0).
- ✓ HLD is single variable taking into account the most important interfacial. interactions of equilibrated systems.

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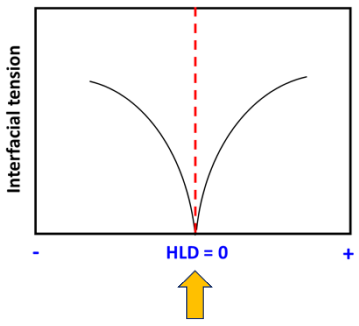
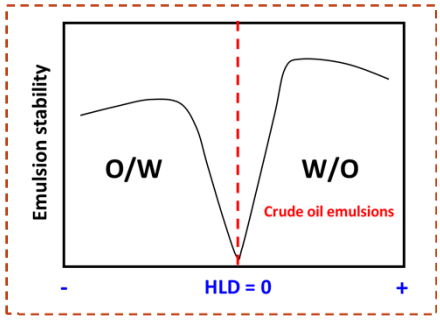
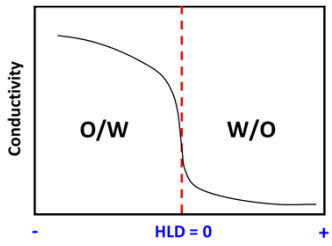
## Behavior of SOW systems and emulsions as a function of HLD. Unstable emulsions are obtained at HLD = 0

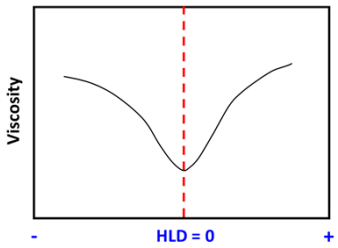



Ultralow interfacial tension is ideal for EOR

**"Optimum formulation"**




Salager and Forgiarini. 2012. Energy & Fuels, 26: 4027-4033
Salager et al. 2022. Energy & Fuels, 36: 711-730

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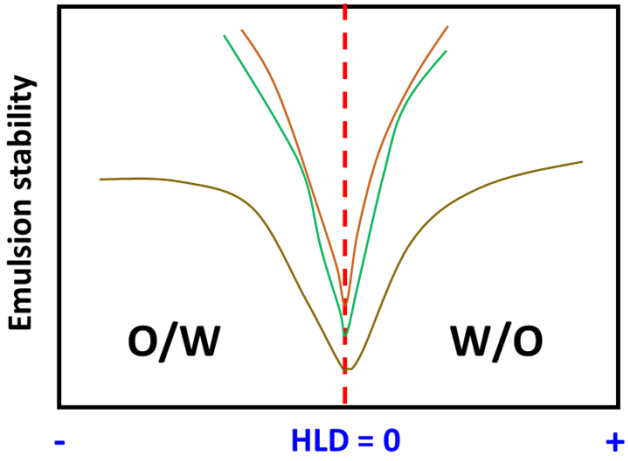
## Minimum stability is attained with different scans




**Variable that can be scanned:**

- Salinity.
- Surfactant (SCP), e.g., HLB (hydrophilic lipophilic balance) or EON (ethylene oxide number).
- Temperature.

**Stability can be determined by bottle tests**

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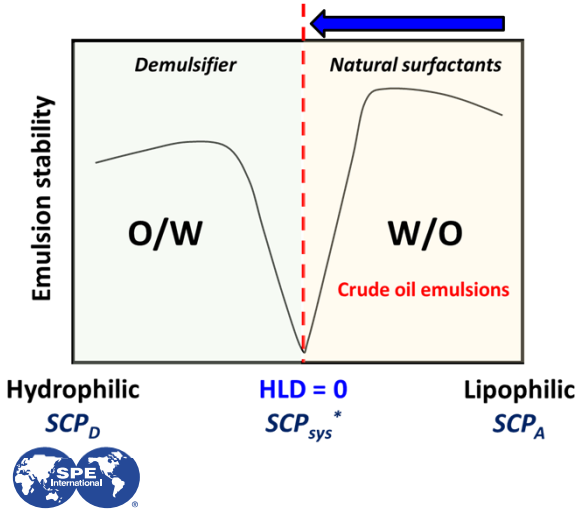
## Demulsifier modifies the interfacial formulation

**Change induced by demulsifiers (hydrophilic surfactants)**




Demulsifier changes the interfacial formulation to attain HLD = 0 (optimum formulation).

$$\mathbf{SCP^{*}_{sys} = X_D SCP_D + X_A SCP_A}$$

$SCP^{*}_{sys}$ = Surfactant parameter of interfacial mixture at optimum formulation.

$SCP_D$ = Surfactant parameter of demulsifier (D).

$SCP_D$ = Surfactant parameter of asphaltenes (A, natural surfactants).

$X_D$ and $X_A$ = molar fractions of D and A at interface.

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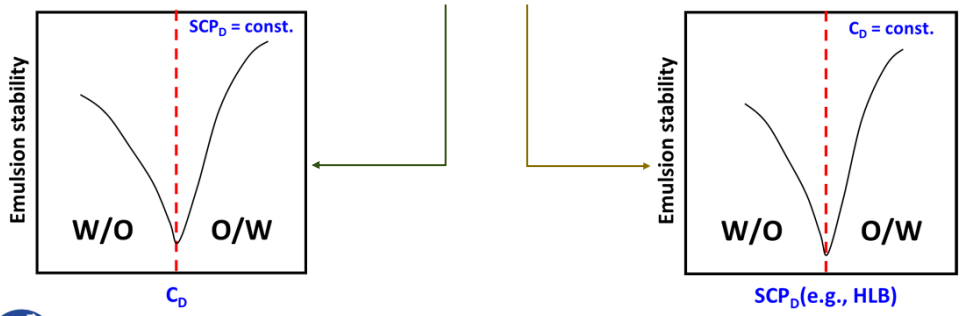
# HLD = 0 can be attained varying demulsifier concentration ($C_D$) or demulsifier nature ($SCP_D$)

depends on crude oil

$$SCP^*_{sys} = X_D SCP_D + X_A SCP_A$$




$X_D$ is the interfacial concentration that can be related to bulk concentration ($C_D$)

Rondon et al. 2006. Energy & Fuels, 20: 3485-349
Delgado-Linares et al. 2016. Energy & Fuels, 30: 7065-7073

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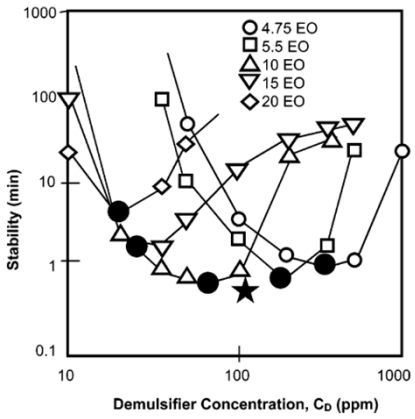
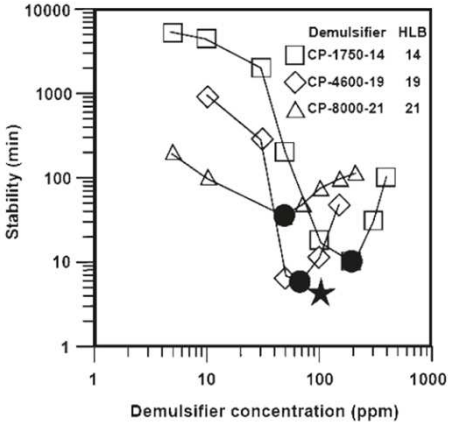
# The best of all optima (Optimum Optimorum)

Ethoxylated nonylphenols




Adapted with permission from Rondon et al. 2006. Energy & Fuels, 20: 3485-3490. Copyright 2006 ACS.

Triblock copolymers




Adapted with permission from Pereira, Delgado-Linares et al. 2011,. Energy & Fuels, 25: 1045-1050. Copyright 2011 ACS.

**The best-of-all conditions for breaking emulsion occurs when using a not-too-hydrophilic demulsifier in a not-too-small concentration**

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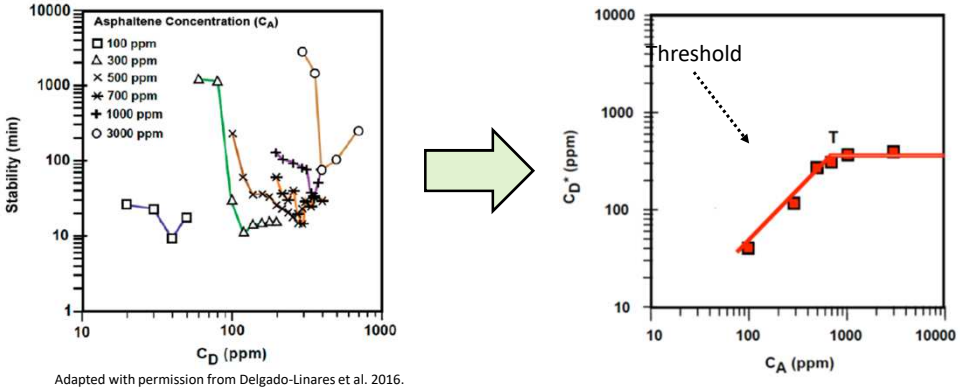
# Asphaltene concentration can be varied by dilution with a solvent (e.g., cyclohexane). Map $C_D^*$ vs $C_A$

$$SCP^*_{sys} = X_D SCP_D + X_A SCP_A$$

For the same oil ($SCP_A$ = constant) a change in $X_A$ induces a change in $X_D$ at HLD = 0

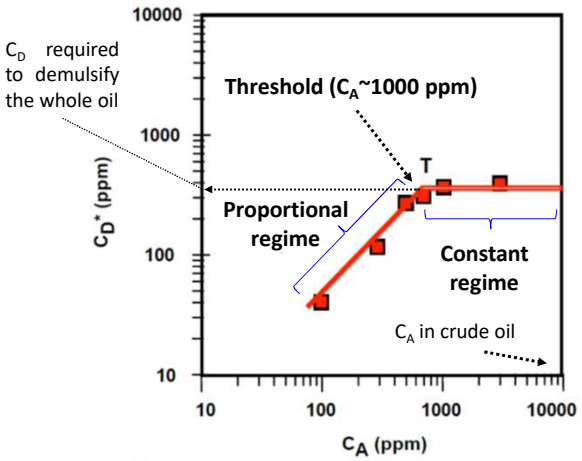
Extended surfactant




Adapted with permission from Delgado-Linares et al. 2016. Energy & Fuels, 30: 7065-7073. Copyright 2016 ACS.



# Map $C_D^*$ vs $C_A$ gives information about interfacial relative composition




## In the proportional regime:

Unit slope (log-log plot).

$$\frac{X_A}{X_D} = K\frac{C_A}{C_D}$$ ⇒ Interfacial concentrations are proportional to bulk concentrations.

## In the constant regime:

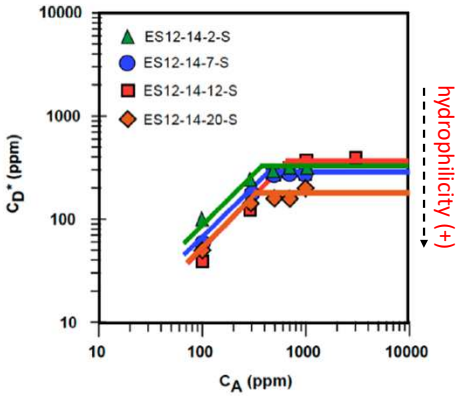
Interface is saturated with asphaltenes. The excess of asphaltenes is located near interface in bulk solution.

In this regime, there is not change in the interfacial formulation

Salager et al. 2022. Energy & Fuels, 36: 711-730

# Map $C_D$* vs $C_A$ for different demulsifiers

Extended surfactants with sulfate head

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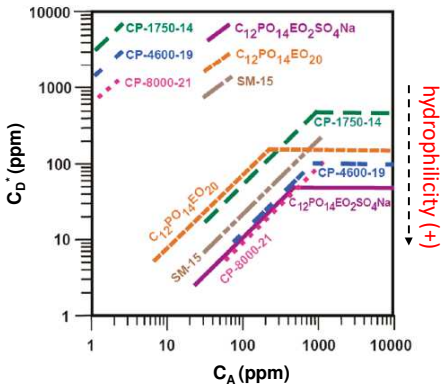
Demulsifier of different nature

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**Demulsifier hydrophilicity ↑ : $C_D$* ↓**

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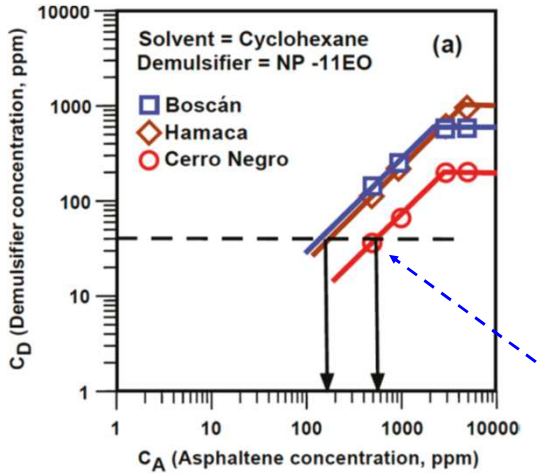
# $SCP_A$ can be changed by changing crude oil nature




One surfactant and three different oils.

**Demulsifier performance ($C_D$*) also depends on crude oil nature.**

The $C_A$ "neutralized" with a $C_D$* is a function of $SCP_A$.

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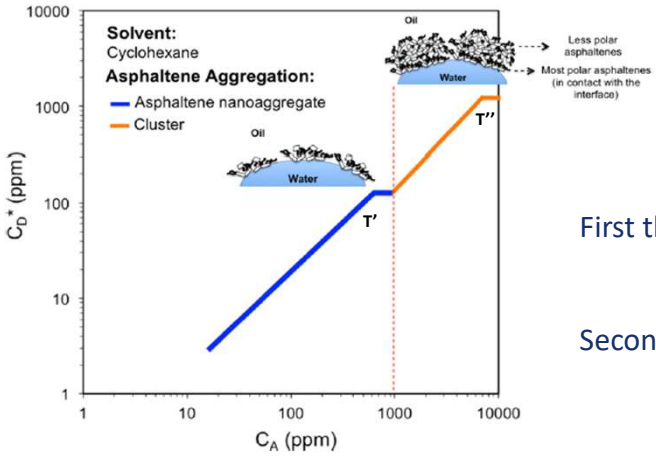
## Some systems show two proportional regimes associated with different asphaltene association levels




First threshold (T'): $C_A$ = 700 ppm

Second threshold (T''): $C_A$ = 7000 ppm

Adapted with permission from Alvarado, Delgado-Linares et al. 2019. Energy & Fuels, 33: 1928-1936. Copyright 2019 ACS.

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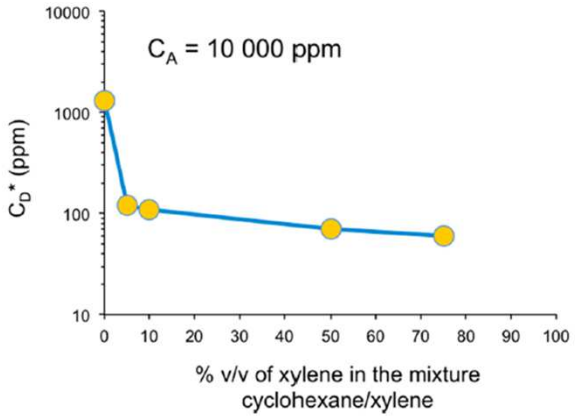
## Addition of a small amount of aromatics decreases $C_D^*$ significantly.

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- Xylene can segregate at interface*.
- Aromatics are good solvent for asphaltenes.
- Good reason to add aromatics to demulsifier formulation.

*Graciaa et al. 1993. Langmuir, 9: 1473-1478

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# Final considerations

- Generalized formulation, HLD, applies to demulsifier-natural surfactant (asphaltenes) mixtures.
- Demulsifier concentration at optimum formulation (desired condition for demulsification) depends on hydrophilicity, structure, asphaltene content, asphaltene structure and polarity, and solvent nature.
- Emulsion stability at $C_D^*$ must be considered in comparing different demulsifiers.
- Ions present in water could play a key role in demulsifier performance.
- Crude oil composition (e.g., aromaticity) affect asphaltene aggregation and demulsifier performance.
- Robustness in emulsion stability at optimum is key to avoid overdosage of demulsifiers.

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# Acknowledgments


- SPE for inviting me to present this talk.
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# Thank you!

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