**From Micro/Macro-Emulsions to Nano-Emulsions**

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**EMULSION** = liquid-liquid dispersed system
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**reasonably stable**
which could mean ➤ 1 hour? 1 day? 1 year?

- 2 non-miscible phases
  - so-called water and oil
  - + surfactant (emulsifier)
    - located at interface

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**Phase Behavior at equilibrium**

- **Surfactant**
- **Water**
- **Oil**

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**Surface Area** = \(4 \pi R^2\)

**Volume** = \((4/3) \pi R^3\)

**Specific Surface Area** = \(S/V = \sigma = 3/R\)

1 mm drop \(\sigma = 3 \times 10^3 \text{ m}^2/\text{m}^3 = 3 \text{ m}^2/\text{liter}\)
1 µm droplet \(\sigma = 3 \times 10^6 \text{ m}^2/\text{m}^3 = 3,000 \text{ m}^2/\text{liter}\)
10 nm droplet \(\sigma = 3 \times 10^9 \text{ m}^2/\text{m}^3 = 300,000 \text{ m}^2/\text{liter}\)

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**Emulsion Energy** = tension x surface area

**Surface Area per unit volume** = \(3/R\)

**Mechanical Efficiency** is very low (typically < 5%)

**This means that very fine droplets can’t be produced by brute force unless very extreme conditions are allowed.**

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**Required Stirring Energy** = x 50 times larger

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**Beware of the Terminology**

- d > 1 mm drops visible with naked eye
- 200 µm > d > 1 µm **macromulsions**
- --- Limit of action of gravity ---
- --- Upper limit of colloid range 0.1 µm (= 1000Å) ---
- d < 0.5 µm **mini/nanoemulsions** (= 2 phases)
- d < 0.5 µm **microemulsions** (= 1 phase)
- ≈ 100 Å micelles, macromolecules
- ≈ 10 Å molecules

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**Surface Energy** = tension x surface area

**Surface Area per unit volume** = \(3/R\)
Emulsion Energy = tension x surface area
Surface Area (3/R) can be large ... and drops can be small ... if tension is very low

Low tension is associated with so-called optimum formulation for 3 phase behavior

Zero tension (= single phase microstructure) ... can be attained at equilibrium

Method # 1:
Phase Transition by Formulation Change

Mechanical Efficiency can be high in a very peculiar situation ... so-called viscoelastic HIPR stirring

Method # 2:
Phase Inversion by Composition Change

Low tension ... can be transient (mass transfer)

Method # 3:
Phase Transition/Inversion (spontaneous emulsification)

This is not straightforward!

Because emulsions made at phase transition are extremely unstable

They coalesce quickly droplets >>> large drops

Something should be done to avoid coalescence!

Let's put some order into that!

Formulation
Microstructures
Phase Transition
Emulsion Inversion
Stabilization by LC

Physico-Chemical Formulation

Influence of formulation on emulsion type (wedge theory)

Langmuir
O/W or W/O

Scale 20 Å

W/O

Scale 10 μm

O/W

oil
surfactant
water

zero curvature
no stable structures

Scale 20 Å
**Generalized Formulation**

**Surfactant Affinity Difference (SAD)**

Deviation from optimum formulation for 3 phase behavior

\[
\text{ionic} \quad \frac{\text{SAD}}{RT} = \ln S - K \text{ACN} - f(A) + \sigma - a_T \Delta T \leq 0
\]

\[
\text{nonionic} \quad \frac{\text{SAD}}{RT} = \alpha - EON + b S - k \text{ACN} - \phi(A) + c_T \Delta T \leq 0
\]

*complex but quantitative*

\[
\frac{\text{SAD}}{RT} = \ln \text{(Partition Coefficient)}
\]

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**Winsor’s research**

showed a relation between **Formulation and Phase Behavior**

- liquid crystal
- microemulsion
- Winsor type III

- complex phase behavior

**Winsor’s type III Diagram**

- microemulsion or liquid crystal structure?

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**MICROEMULSIONS**

= high solubilization structures

- “mixture” of swollen micelles and swollen inverse micelles

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**MICROEMULSIONS**

= high solubilization structures

- Schwartz surface
- Random

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Mean Curvature = 0

Characteristics of microemulsion and of oil-water interface in a Winsor’s type III diagram

Another zero curvature structure ... lamellar liquid crystal ... not a liquid ... nor a crystal

It is not stochiometric and can take up water or oil

Microemulsion or liquid crystal depending on disorder

Macroemulsions depend on both formulation & composition

There are many ways to (dynamically) cross the inversion line which are used in actual processes ...

... a few (4) can result in nanoemulsions
CASE # 1: crossing of horizontal branch
dynamic inversion coincides with SAD = 0 line

Transitional inversion in zone A through a change in formulation (or temperature)

Phenomenology ↔ Formulation
- Interfacial Tension
- Conductivity (type)
- Emulsion Stability
- Emulsion Viscosity

Formulation Scan

CASE # 2 & 3: approaching & crossing a vertical branch by a change in composition

Dynamic (catastrophic) inversion lags whatever the direction when crossing a vertical branch of the inversion line (change in composition)
**CASES # 2 & 3:**
Dynamic (catastrophic) inversion lags whatever the direction when crossing a vertical branch of the inversion line (change in composition)

![Diagram of formulation and composition transitions](image)

**Dynamic inversion**
Inversion delay (hysteresis) = memory can be modeled thru Catastrophe Theory

![Diagram of formulation and composition transitions](image)

**CASE # 2**
Approaching the Catastrophic Inversion Branch from normal to abnormal morphology

![Diagram of formulation and composition transitions](image)

**CASE # 2**
Slow “HIPR” Emulsification
“High Internal Phase Ratio”

At a high internal phase ratio (HIPR)
The emulsion is very viscous
A slow motion mixing can result in very tiny droplets

A trick used to make ...
... Cosmetics, Orimulsion® ...

**CASE # 3**
Crossing the Catastrophic Inversion Branch from abnormal to normal morphology

![Diagram of formulation and composition transitions](image)

**Formulation**

- Increase in water content
- O/W emulsion
- Multiple O/W/O
- LC not required

**Compositions**

- W/O emulsion
- Water
- Oil
- O/W emulsion

**Mathematical Expression**

\[ \dot{\gamma} = \frac{\Delta V}{\Delta y} \]

when \( \Delta y \rightarrow 0 \) \( \dot{\gamma} \rightarrow \infty \)

**High Internal Phase Ratio (HIPR)**
Emulsion is Viscous and exhibits Viscoelastic Behavior

- Emulsion is very viscous
- A slow motion mixing can result in very tiny droplets
- A trick used to make ...
  ... Cosmetics, Orimulsion® ...
"Inversion + mass transfer change in formulation and composition SPONTANEOUS EMULSIFICATION"
Summary on how to make a nanoemulsion

- Pass thru a favorable situation (single phase, low $\gamma$, high $\dot{\gamma}$)
- Produce a (transient) microstructure
- Avoid coalescence of microstructure
- Stabilize droplets by changing formulation

must be a dynamic process because of inherent instability

Mini/Nano Emulsions in the Petroleum Industry?

- Drilling fluids (LIPR, high $h$)
- Deep Aquaconversion Catalyst
- Emulsified Products
  - Diesel (or other) Fuel with water droplets
  - Cutting/Laminating Lube Oils
  - High Pressure Brake Fluids
- Asphalt Coatings
- Templates for microstructures
- Imaging of structures ...

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