New Developments in the Formulation of Dispersions
UMIST Manchester, UK, September 29 - October 1, 2003

# Formulation Design and Processing of Emulsion Systems

**Jean-Louis Salager**
*Lab. FIRP,*
*University of The Andes,*
*Mérida Venezuela*

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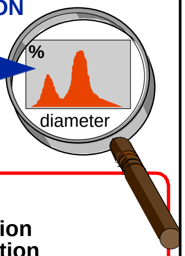
## EMULSION PROPERTIES

**TYPE** O/W, W/O, other… and **INVERSION**

**DROP SIZE** (Average & Distribution)
*>>> influences other properties*



**STABILITY** (against some Decay)

**VISCOSITY** (Rheological Behavior)

**depend on 3 kinds of**

**VARIABLES**
- **Formulation**
- **Composition**
- **Emulsification Protocol**

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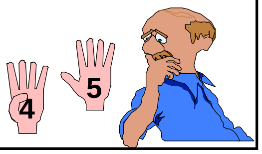
## 1 Physicochemical FORMULATION

Nature of each components: --> in general more than 3
- Electrolytes in aqueous phase (Na, Ca etc...)
- Oil Alkane Carbon Number ACN (complex mixture as crude)
- Surfactant Characteristics ..... often mixtures

Temperature (Pressure only in extreme cases)

**How many variables ?**



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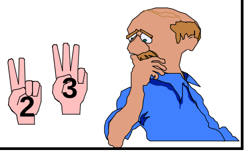
## 2 COMPOSITION

At least 2 independent
(Surf. Conc. + WOR) --> often more

**How many variables ?**



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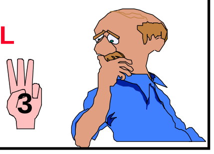
**How many variables ?**

## 3 Emulsification PROTOCOL

Phenomenon (shear, turbulence)
Emulsor Device (efficiency ?)
Energy Input (rpm)



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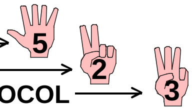
## 3 kinds of VARIABLES

**1. FORMULATION →**
**2. COMPOSITION →**
**3. Emulsification PROTOCOL →**



**Systematic Study with $\Sigma$ = 10 variables ?**

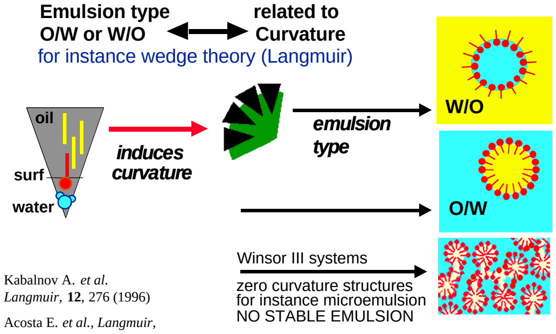
if 5 values for each variable
**>>> 100.000**
experiments are required

*Too many degrees of freedom !!!*

# Influence of FORMULATION

**Emulsion type O/W or W/O** ⟷ **related to Curvature**

for instance wedge theory (Langmuir)



Winsor III systems

zero curvature structures
for instance microemulsion
NO STABLE EMULSION

Kabalnov A. *et al.* *Langmuir*, **12**, 276 (1996)

Acosta E. *et al.*, *Langmuir*, **19**, 186 (2003)

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# Formulation Yardsticks

| | | |
|---|---|---|
| 1949 | **HLB** (Hydrophilic Lipophilic Balance) ....... | empirical |
| 1954 | **Winsor R ratio** ............................... | theoretical |
| 1964 | **PIT** (Phase Inversion Temperature) ........... | empirical |
| 1971 | **CER** (Cohesive Energy Ratio) ...................... | mixed |
| 1977 | **Correlations** for 3 phase behavior .... | empirical |
| 1988 | **SAD** (Surfactant Affinity Difference) ............ | mixed |

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# Surfactant Affinity Difference
# SAD = $\mu^*_W$ - $\mu^*_O$ = RT $\ln K_P$

(for instance for ionic systems)

$$\mathrm{SAD/RT} = \underset{\text{WATER SALINITY}}{\ln S} - K\,\underset{\text{OIL ALKANE CARBON NUMBER}}{\mathrm{ACN}} - \underset{\text{ALCOHOL TYPE \& CONC.}}{f(A)} + \underset{\text{SURFACTANT HYDROPHILE \& HYDROPHOBE}}{\sigma} - a_T\,\underset{\text{TEMPERATURE}}{\Delta T} \overset{>}{\underset{<}{=}} 0$$

☞ depends on all formulation variables as Winsor’s R ratio

☞ quantifies the physicochemical formulation at interface

***considerable reduction in number of degrees of freedom***

Salager J. L. *et al.*, *Langmuir*, **16**: 5534 (2000)

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# SAD has been generalized to many real systems

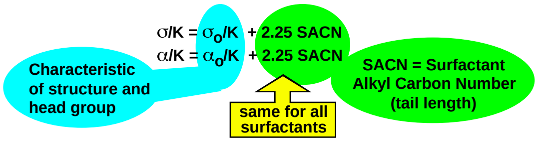
## e. g. Surfactant Parameters

(for “pure” or collective behavior surfactants)

**in SAD/RT expression, the surfactant parameter is :**

*(in same ACN units - used for comparison) :*

- $\sigma$/K for ionic surfactants
- ($\alpha$-EON)/K for nonionic surfactants



$\sigma/K = \sigma_o/K + 2.25\ \mathrm{SACN}$

$\alpha/K = \alpha_o/K + 2.25\ \mathrm{SACN}$

Characteristic of structure and head group

same for all surfactants

SACN = Surfactant Alkyl Carbon Number (tail length)

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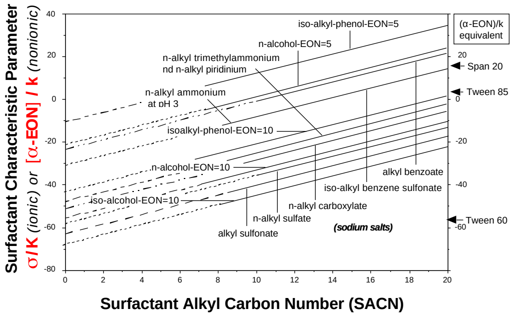
# Chart for Surfactant intrinsic hydrophilicity



Salager J. L. *et al.*, *Techniques de l'Ingénieur* ***J2**-157* (2001)

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# SAD has been generalized to many real systems

## e. g. Temperature Effect

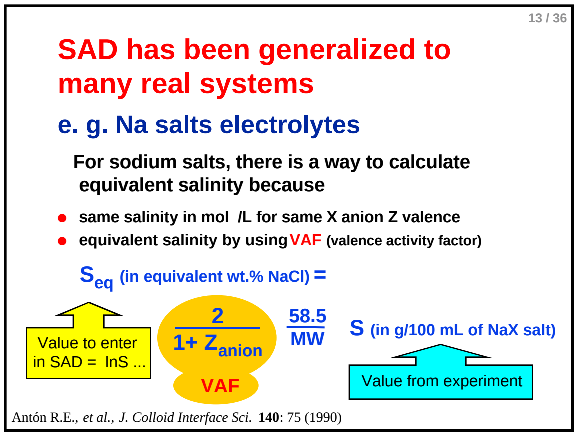
(for “pure” or collective behavior surfactants)

- $a_T$ = 0.01 (°C$^{-1}$) for anionic surfactants
- $a_T$ = 0.02 (°C$^{-1}$) for cationic surfactants
- $c_T$ = 0.04 - 0.08 (°C$^{-1}$) for nonionic surfactants actually it varies with EON and Temperature as $\Delta$H of transfer from water to oil.

$$c_T = \frac{2210 + 450\ \mathrm{EON}}{T^2} \qquad (\ T \text{ in K}\ )$$

*case of ethoxylated nonylphenols*

Skauge A., Fotland P., *SPE Reservoir Eng.*, **5**: 60 (1990)



## SAD has been generalized to many real systems

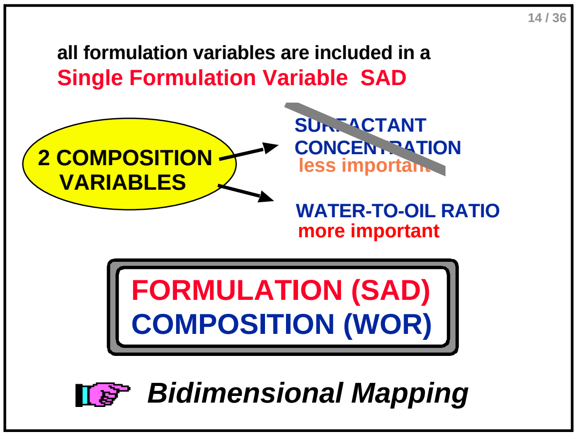
### e. g. Na salts electrolytes

For sodium salts, there is a way to calculate equivalent salinity because

- same salinity in mol /L for same X anion Z valence
- equivalent salinity by using VAF (valence activity factor)

$$S_{eq} \text{ (in equivalent wt.\% NaCl)} = \frac{2}{1+Z_{anion}} \frac{58.5}{MW} S \text{ (in g/100 mL of NaX salt)}$$

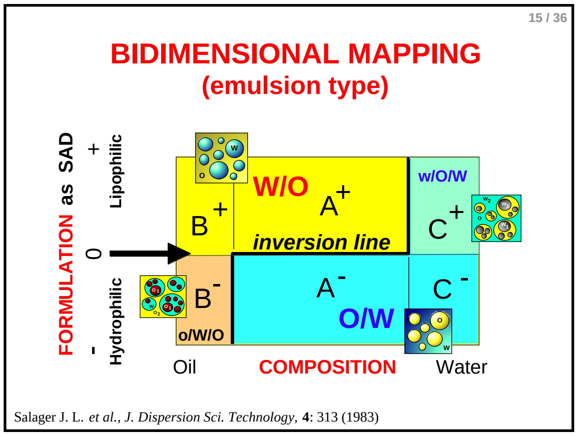
Antón R.E., *et al., J. Colloid Interface Sci.* **140**: 75 (1990)



all formulation variables are included in a Single Formulation Variable SAD

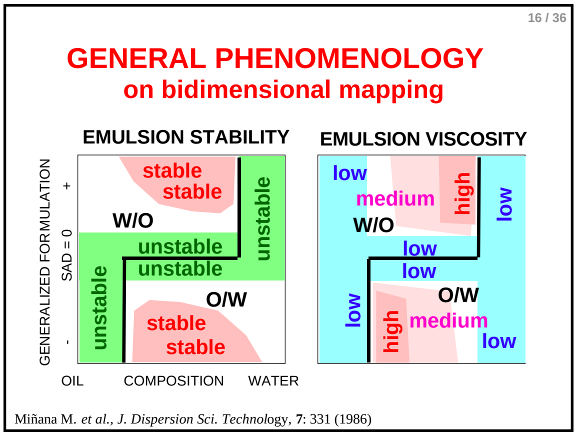
**FORMULATION (SAD)**
**COMPOSITION (WOR)**

☞ ***Bidimensional Mapping***



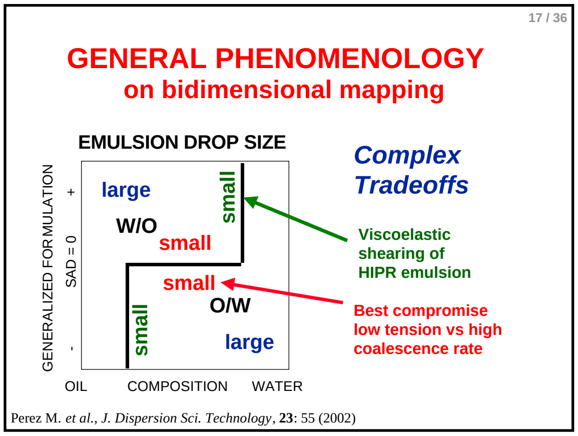
## BIDIMENSIONAL MAPPING
### (emulsion type)

Salager J. L. *et al., J. Dispersion Sci. Technology*, **4**: 313 (1983)



## GENERAL PHENOMENOLOGY
### on bidimensional mapping

Miñana M. *et al., J. Dispersion Sci. Technology*, **7**: 331 (1986)



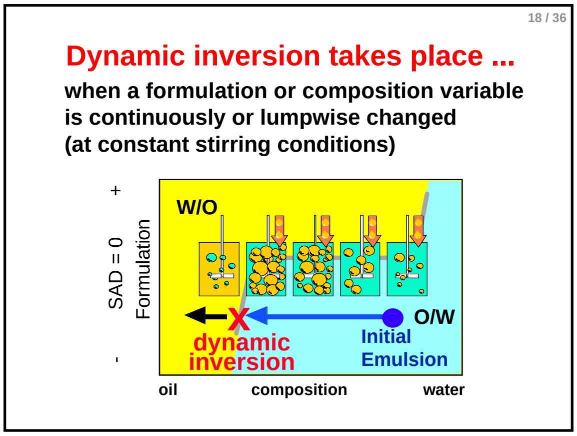
## GENERAL PHENOMENOLOGY
### on bidimensional mapping

***Complex Tradeoffs***

Viscoelastic shearing of HIPR emulsion

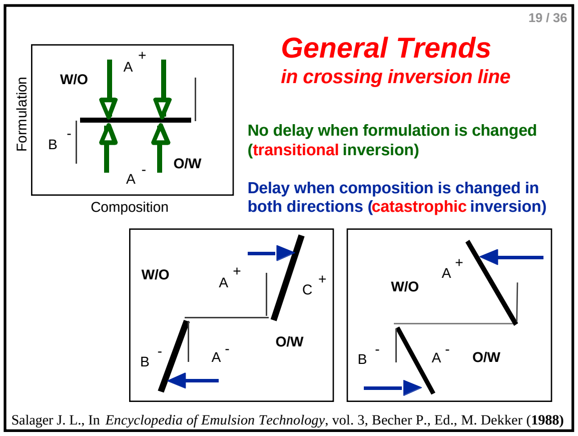
Best compromise low tension vs high coalescence rate

Perez M. *et al., J. Dispersion Sci. Technology*, **23**: 55 (2002)



## Dynamic inversion takes place ...

when a formulation or composition variable is continuously or lumpwise changed (at constant stirring conditions)

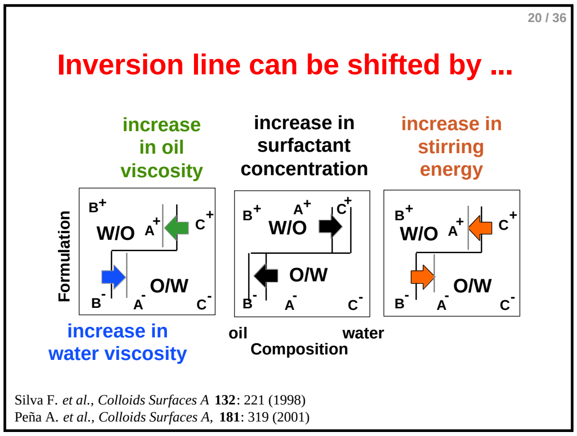


## *General Trends*
*in crossing inversion line*

**No delay when formulation is changed (transitional inversion)**

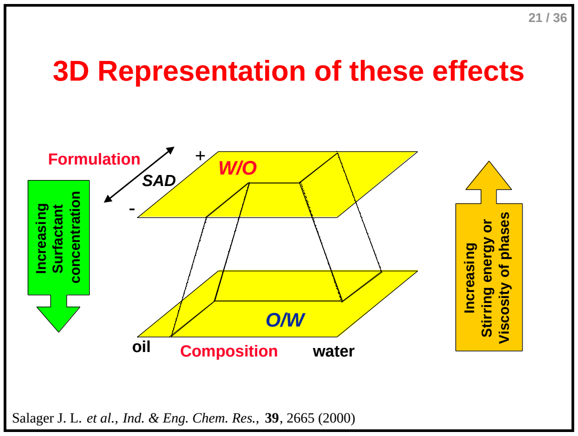
**Delay when composition is changed in both directions (catastrophic inversion)**

Salager J. L., In *Encyclopedia of Emulsion Technology*, vol. 3, Becher P., Ed., M. Dekker (**1988**)



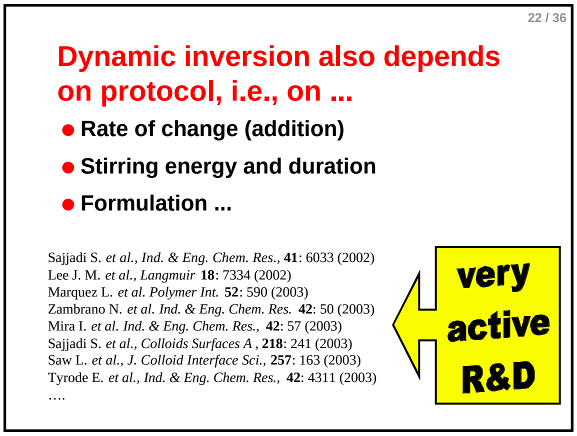
## Inversion line can be shifted by ...

Silva F. *et al.*, *Colloids Surfaces A* **132**: 221 (1998)
Peña A. *et al.*, *Colloids Surfaces A*, **181**: 319 (2001)



## 3D Representation of these effects

Salager J. L. *et al.*, *Ind. & Eng. Chem. Res.*, **39**, 2665 (2000)

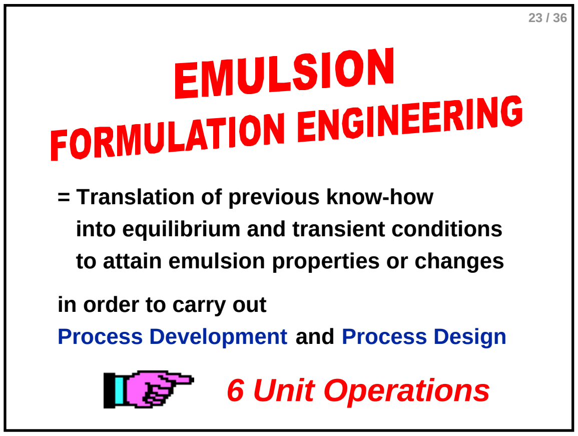


## Dynamic inversion also depends on protocol, i.e., on ...

- **Rate of change (addition)**
- **Stirring energy and duration**
- **Formulation ...**

Sajjadi S. *et al.*, *Ind. & Eng. Chem. Res.*, **41**: 6033 (2002)
Lee J. M. *et al.*, *Langmuir* **18**: 7334 (2002)
Marquez L. *et al. Polymer Int.* **52**: 590 (2003)
Zambrano N. *et al. Ind. & Eng. Chem. Res.* **42**: 50 (2003)
Mira I. *et al. Ind. & Eng. Chem. Res.*, **42**: 57 (2003)
Sajjadi S. *et al.*, *Colloids Surfaces A* , **218**: 241 (2003)
Saw L. *et al.*, *J. Colloid Interface Sci.*, **257**: 163 (2003)
Tyrode E. *et al.*, *Ind. & Eng. Chem. Res.*, **42**: 4311 (2003)
....

**very active R&D**

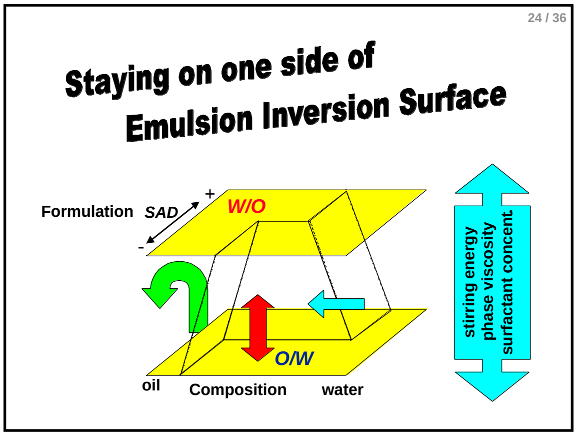


## EMULSION FORMULATION ENGINEERING

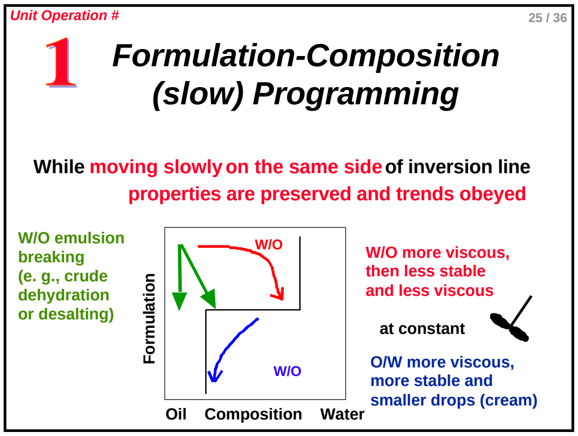
**= Translation of previous know-how into equilibrium and transient conditions to attain emulsion properties or changes**

**in order to carry out**
**Process Development and Process Design**

***6 Unit Operations***



## Staying on one side of Emulsion Inversion Surface



Unit Operation #

## 1 Formulation-Composition (slow) Programming

While moving slowly on the same side of inversion line properties are preserved and trends obeyed

W/O emulsion breaking (e. g., crude dehydration or desalting)

W/O more viscous, then less stable and less viscous

at constant

O/W more viscous, more stable and smaller drops (cream)

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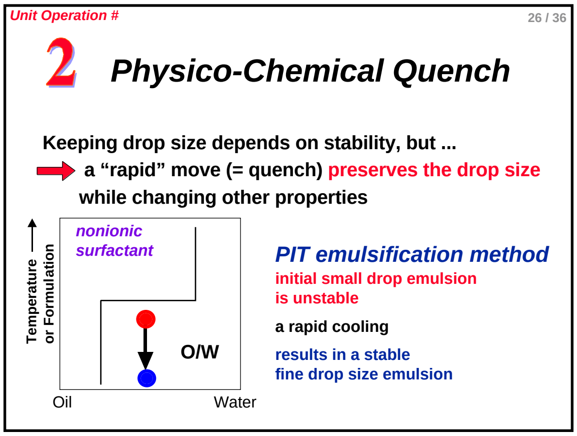

Unit Operation #

## 2 Physico-Chemical Quench

Keeping drop size depends on stability, but ...

➡ a “rapid” move (= quench) preserves the drop size while changing other properties

### PIT emulsification method

initial small drop emulsion is unstable

a rapid cooling

results in a stable fine drop size emulsion

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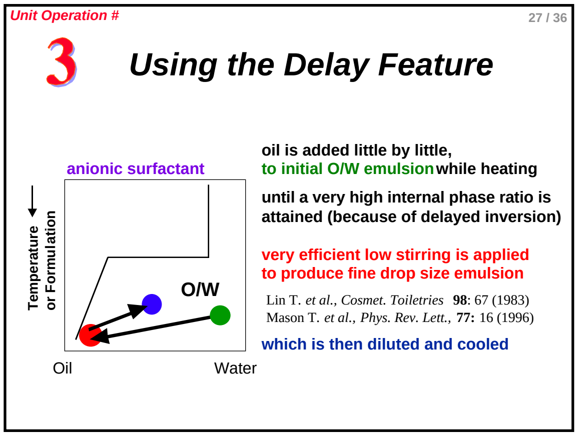

Unit Operation #

## 3 Using the Delay Feature

oil is added little by little, to initial O/W emulsion while heating

until a very high internal phase ratio is attained (because of delayed inversion)

very efficient low stirring is applied to produce fine drop size emulsion

Lin T. *et al.*, *Cosmet. Toiletries* **98**: 67 (1983)
Mason T. *et al.*, *Phys. Rev. Lett.*, **77:** 16 (1996)

which is then diluted and cooled

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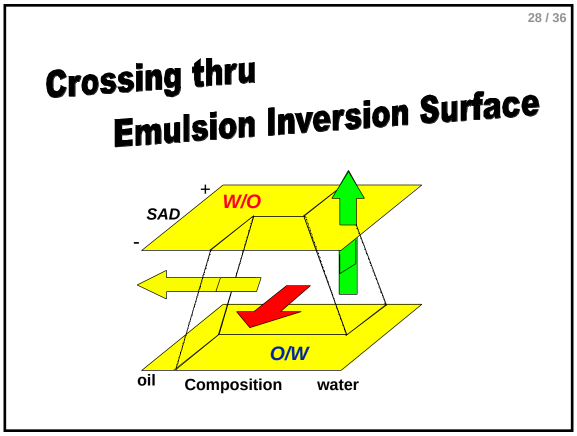

## Crossing thru Emulsion Inversion Surface

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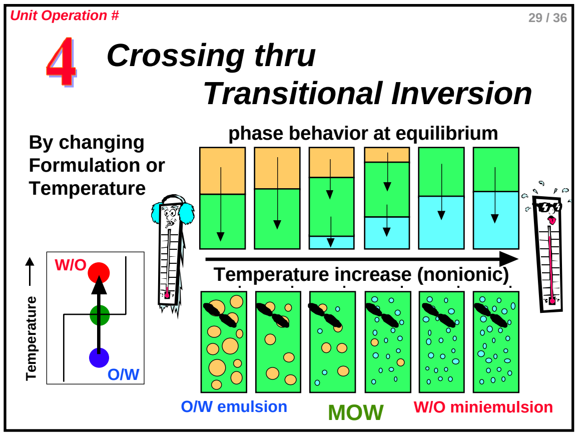

Unit Operation #

## 4 Crossing thru Transitional Inversion

By changing Formulation or Temperature

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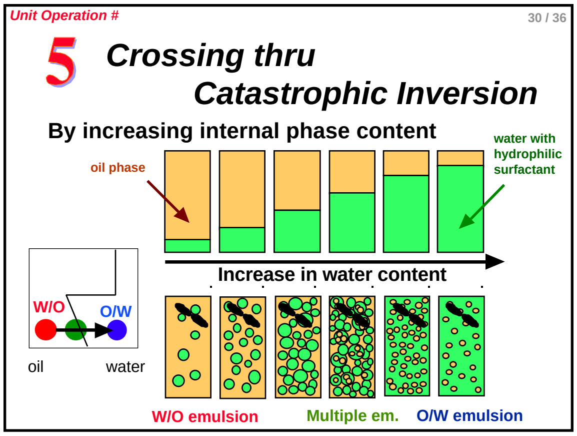


Unit Operation #

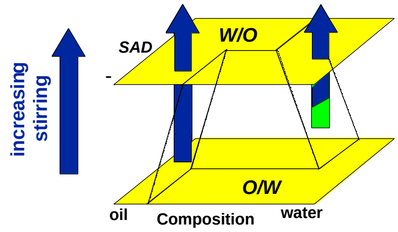
## 5 Crossing thru Catastrophic Inversion

By increasing internal phase content

*Unit Operation #*

## 6 *Crossing thru Catastrophic Inversion*

By increasing stirring energy ( ➡ )
and eventually stirring time

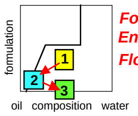


*In spite of current shortcomings*

## FORMULATION ENGINEERING

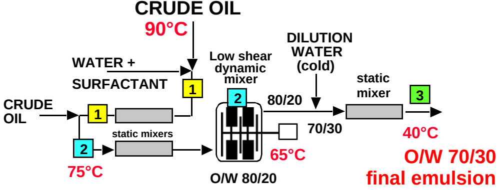
could help in developing and designing batch and continuous emulsification processes *for manufacturing food, paints, cosmetics and pharmaceuticals, dehydrating crude oil, treating liquid wastes etc...*

sometimes in large scale plants such as the production of *heavy crude oil-in-water emulsified fuel.* ➡



*Formulation Engineering Flow Chart*

## Emulsification Plant operated by BITOR a subsidiary of Petroleos de Venezuela



**Orimulsion™ current output 5.000.000 tons / year**

Salager J. L. at al., In *Encyclopedic Handbook of Emulsion Technology*, J. Sjöblom, Ed. (2001)

## Conclusion

Most emulsion manufacturing processes could be dealt with a Formulation Engineering Approach

*Probably as well as many other Product Engineering Problems*

## Formulation Engineering Approach

*will progress through*

> innovative conceptualization
> integration of multidisciplinary teams

## Research targets in the near future:

> Systematization of unit operations
> Understanding of complex cross effects
> Standardization of transient protocols

*A lot of work for many of us !*

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