What is Solubilization?

- it is the ability of a surfactant to produce a monophasic system containing both oil and water

**Diagram:**
- Surfactant (+ alcohol)
- Monophasic zone
- Polyphasic zone
- Water
- Oil

All phase diagrams contain a monophasic zone

**Diagram:**
- S + A
- W III
- W I
- W II
- Phase behavior
- Optimum Formulation

The height of polyphasic zone at fixed oil/water composition (e.g. 50/50) is monitored

- Formulation Scan
- S + A
- Lowest height = maximum solubilization at optimum formulation

Formulation Scan

**Diagram:**
- S + A
- W III
- W I
- W II
- Phase behavior
- Optimum Formulation

Bicontinuous Structures with zero curvature

- Random bicontinuous structure
- Schwartz surface


Bicontinuous Structure with zero mean curvature

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

Solubilization Parameters

Maximum Solubilization at crossing

Tension-Solubilization Relationship

- Solubilization varies as the inverse of interfacial tension
- many applications of optimum formulation
  - Enhanced oil recovery
  - Crude oil dehydration
  - Emulsion breaking
  - Detergency
  - Remediation
  - Solubilization in microemulsion ...

Winsor Ratio (1954)

between molecular interaction energies

\[ R = \frac{A_{CO}}{A_{CW}} \]

- \( R = 1 \) at optimum formulation
- \( R < 1, R = 1 \) or \( R > 1 \) related to phase behavior


Winsor R

Maximum Solubilization when \( N = D \)

\[ R = \frac{A_{CO}}{A_{CW}} = \frac{N}{D} = 1 \]

but ... various cases

\[ R = 1 = \frac{2}{2} = \frac{5}{5} = \frac{10}{10} \]

Is it the same thing? No!
According to Winsor’s premise, solubilization increases when interactions increase on both sides of the interface.

- When the chain reaches 18-20 carbon atoms, the surfactant precipitates (Krafft Temperature).

But there is a limit.

In some cases, Winsor’s premise does not explain the observed increase in solubilization.

Examples of lipophilic linkers:
- Long chain n-alcohols (> 8)
- Long chain alkylphenols (> 8)
- Slightly ethoxylated (EON < 2)
- Single chain esters (ethyl oleate)
- Probably other linear lipophilic amphiphiles.

Proposed mechanism:
- The lipophilic link increases interactions on the oil side by ordering the molecules deeper inside the oil bulk phase.

This lipophilic additive was called "Lipophilic Linker".

The Lipophilic Linker:
- Does not adsorb at the interface (it is not a cosurfactant).
- Is a slightly polar oil (or a very lipophilic amphiphile).
- Is located inside the oil phase near the interface (interfacial segregation).
- Gets oriented perpendicular to the interface.
- Stretches the reach of surfactant in oil without producing precipitation.

Lipophilic Linker Role

The L.L. “stretches” (in situ)... ...the surfactant hydrophobic “tail”

The L.L. produces a slightly polar zone inside the oil phase, near the interface

Hydrophilic Linker

Same role on the water side

di-hexyl-sultosuccinate

The H.L. produces a slightly less polar zone in the water phase, close to the interface

Hydrophilic Linker

- Di-butyl Naphtalene Sulfonate = hydrophilic surfactant
- Mono/Dimethyl Naphtalene Sulfonate = hydrophilic linker

Lipophilic and Hydrophilic Linkers

Combining LL and HL increases solubilization performance in many systems:

- Hydrocarbons, mono, di and triesters, natural oils, tri and tetrachloroethylene (denser-than-water oils), motor oil, terpenes, squalane etc

For various applications:

- Detergency, hard surface cleaning, remediation processes, drilling fluids, completion, spacer and workover fluids, etc

Go-thru amphiphilic Linker

- It extends interactions on both sides of interface (low MW diblock polymer)
- At low concentration there is no solubility problem
- Considerable Enhancement of Solubilization

Lipophilic and Hydrophilic Linkers

produce:

Better match (oil does not contact water)

Continuous polarity variation

what can be concluded as far as solubilization is concerned?

Favorable factors are:
- Continuity in interfacial transition
- And a good match on both sides

Surfactant + Lipophilic Linker

= "extended" Surfactant

Extended Surfactants

Extended Surfactant Properties

<table>
<thead>
<tr>
<th>PPO Chain</th>
<th>Property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrophobic but slightly polar</td>
<td>Spacer arm is hydrophobic but slightly polar</td>
</tr>
<tr>
<td>Hydophilic group</td>
<td>Hydrophilic group</td>
</tr>
</tbody>
</table>

Extended Surfactant Properties

Extended Surfactant Properties

Extended Surfactant Properties

Extended Surfactant Properties

Conclusion:
- When PON increases ...
  - Surfactant becomes more lipophilic

PPO chain is part of the "tail"
Micellar aggregation of extended surfactant

computer simulation courtesy Alvaro Fernández

Potential Applications

- Single phase water-oil mixtures
  - bladder stone dissolution
  - single phase dressing
  - vegetable oil extraction
  - environmental remediation
  - petroleum well cleaning

- Microemulsions for injection in blood stream
  (most pharmaceutical products are oil soluble)

- Soak-only Detergent Formulation
  (no stirring required)

2nd Generation of extended surfactants for biocompatible applications

nice polar group
taylored spacer arm
Fatty acid derivative (hydrophobic tail)

Physico-chemical Properties of these products are under study

Recent Publications

- Scorzza C. et al., Synthesis de dérivés polypropilèneglycol à tête glucidyl ou ityl comme surfactants, XVIe Journées Chimie des Glucides, Tregastel, France, June 1999
- Scorzza C. et al., New amphiphilic polypropylene glycol derivatives with carbohydrate polar head, 24th Congr. As. Comité Español Detergencia, Barcelona, Spain, May 1999
- Goethals G. et al., Spacing arm influence on gluco-amphiphilic compound properties, 20 International Meeting of the Portuguese Carbohydrate Chemistry Group and 11 European Carbohydrate Meeting, Aveiro, Portugal, Sept 19-23, 1999
- Goethals G. et al., Carbohydrate Polymers, 45: 147-154 (2001)
- ... 2 publications waiting...
Semicommercially available compounds

Sasol (Comvista)
Seppic
Hunstman

Polar heads (simple or combined) currently synthesized and tested in Lab. FIRP

Linear C12-C18 chain attached at end or center saturated or unsaturated
- sulfate
- ethoxy-sulfate
- carboxylate
- ethoxy-carboxylate
- C6 sugars
- xylitol (C5 sugar)
- di-xylitol
- ethoxy-xylitol
- carboxylate & xylitol
- carboxylate & glucose
- Others...

Spacer to be tested
Poly C20/C30/C40
Cellulose compounds
Gradual polarity change

Extended soaps

Lipophilic tail
Lipophilic linker
Spacer
Hydrophilic linker
Facilitates synthesis

Extended glycoside

Hydrophilic linker

R = alkyl tail

Lipophilic Linker

Sugar polar group

Extended di-xylitol

Increase in water solubility and HLB
Current best solubilization:
1 gram of high performance extended surfactant might solubilize almost 50 g of hexadecane or ethyl oleate and 15 g of C18 triglyceride.

Thank you for your Attention.