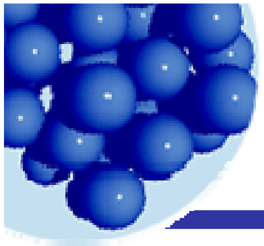


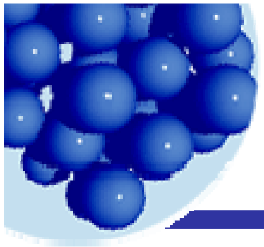
Emulsion Technology

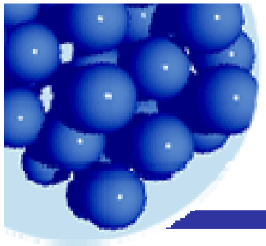
Dispersions in liquids: suspensions, emulsions, and foams

ACS National Meeting

March 21 – 22, 2009

Salt Lake City



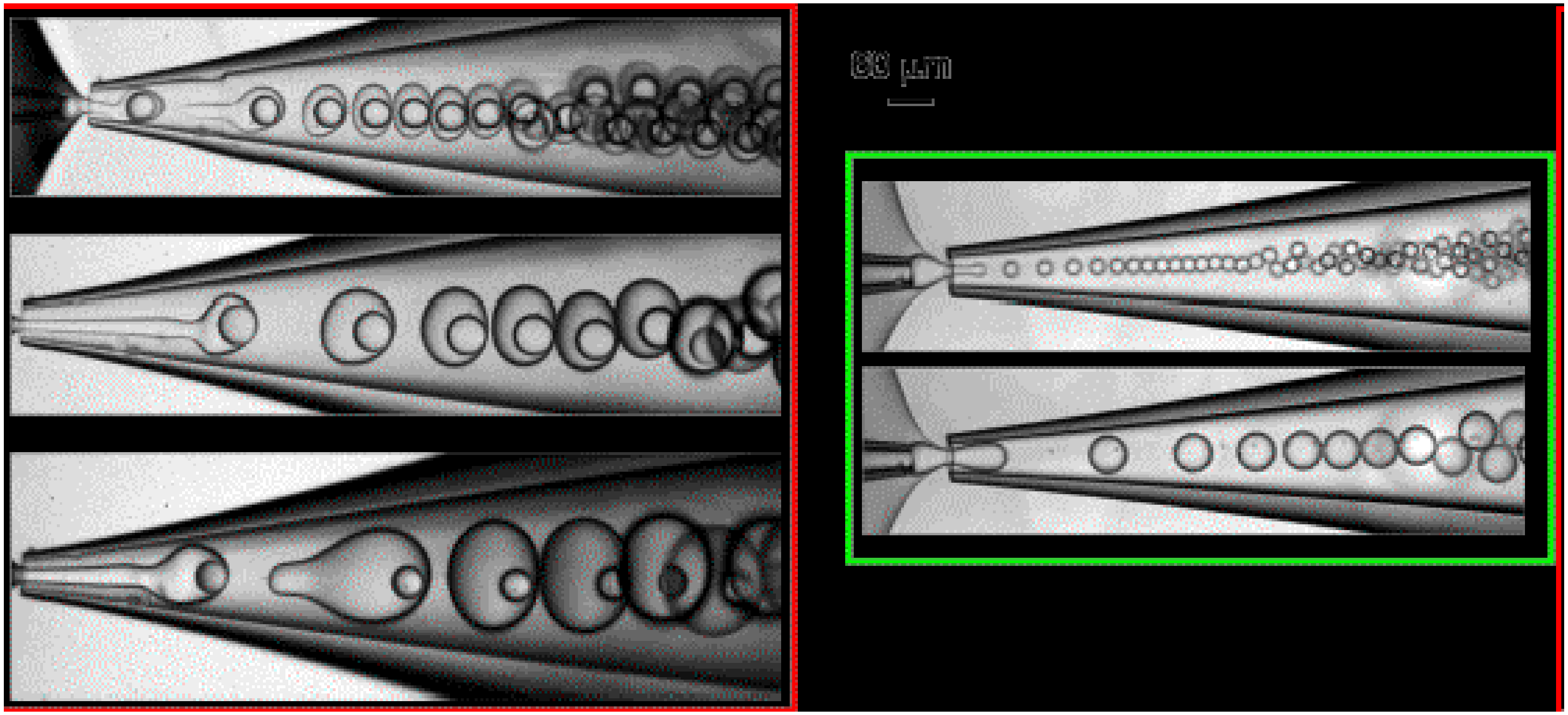


*Dickenson in ”Food Structure”; Butterworths; 1988.

Emulsions, e.g. food!

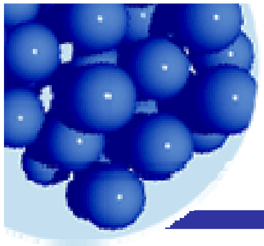
Food	Emulsion type	Dispersed phase	Continuous phase	Stabilization factors, etc.
Milk, cream	O/W	Butterfat triglycerides partially crystalline and liquid oils. Droplet size: 1 – 10 μm Volume fraction: Milk: 3-4% Cream: 10- 30%	Aqueous solution of milk proteins, salts, minerals, etc.	Lipoprotein membrane, phospolipids, and adsorbed casein.
Ice cream	O/W (aerated to foam)	Butterfat (cream) or vegetable, partially crystallized fat. Volume fraction of air phase: 50%	Water and ice crystals, milk proteins, carboxydrates (sucrose, corn syrup) Approx. 85% of the water content is frozen at –20°C.	The foam structure is stabilized by agglomerated fat globules forming the surface of air cells. Added surfactants act as “destabilizers” controlling fat agglomeration. Semisolid frozen phase.
Butter	W/O	Buttermilk: milk proteins, phospholipids, salts. Volume fraction: 16%	Butterfat triglycerides, partially crystallized and liquid oils; genuine milk fat globules are also present.	Water droplets distributed in semi-solid, plastic continuous fat phase.
Imitation cream (to be aerated)	O/W	Vegetable oils and fats. Droplet size: 1 – 5 μm. Volume fraction: 10 – 30%	Aqueous solution of proteins (casein), sucrose, salts, hydrocolloids.	Before aeration: adsorbed protein film. After aeration: the foam structure is stabilized by aggregated fat globules, forming a network around air cells; added lipophilic surfactants promote the needed fat globule aggregation.

Where’s the emulsion science*?



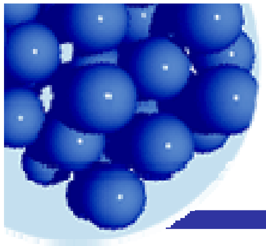
*To be respectful – where can we add the “magic” of emulsion science?

http://www.seas.harvard.edu/projects/weitzlab/andersonresearch/



Terminology - 1

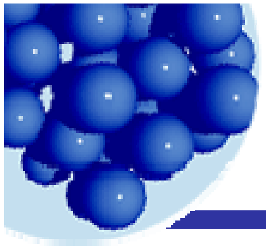
Phase 1	**Phase 2**
Droplet	Serum
Dispersed	Medium
Discontinuous	Continuous
Internal	External



Terminology - 2

Macroemulsions	At least one immiscible liquid dispersed in another as drops whose diameters generally exceed 1000 nm.	The stability by addition of surfactants and/or finely divided solids. Considered only kinetically stable.
Miniemulsions	An emulsion with droplets between 100 and 1000 nm.	Reportedly thermodynamically stable.
Microemulsions	A thermodynamically stable, transparent solution of micelles swollen with solubilizate.	Usually requires a surfactant and a cosurfactant (e.g. short chain alcohol).

Becher, P. *Emulsions, theory and practice*, 3rd ed.;
Oxford University Press: New York; 2001.

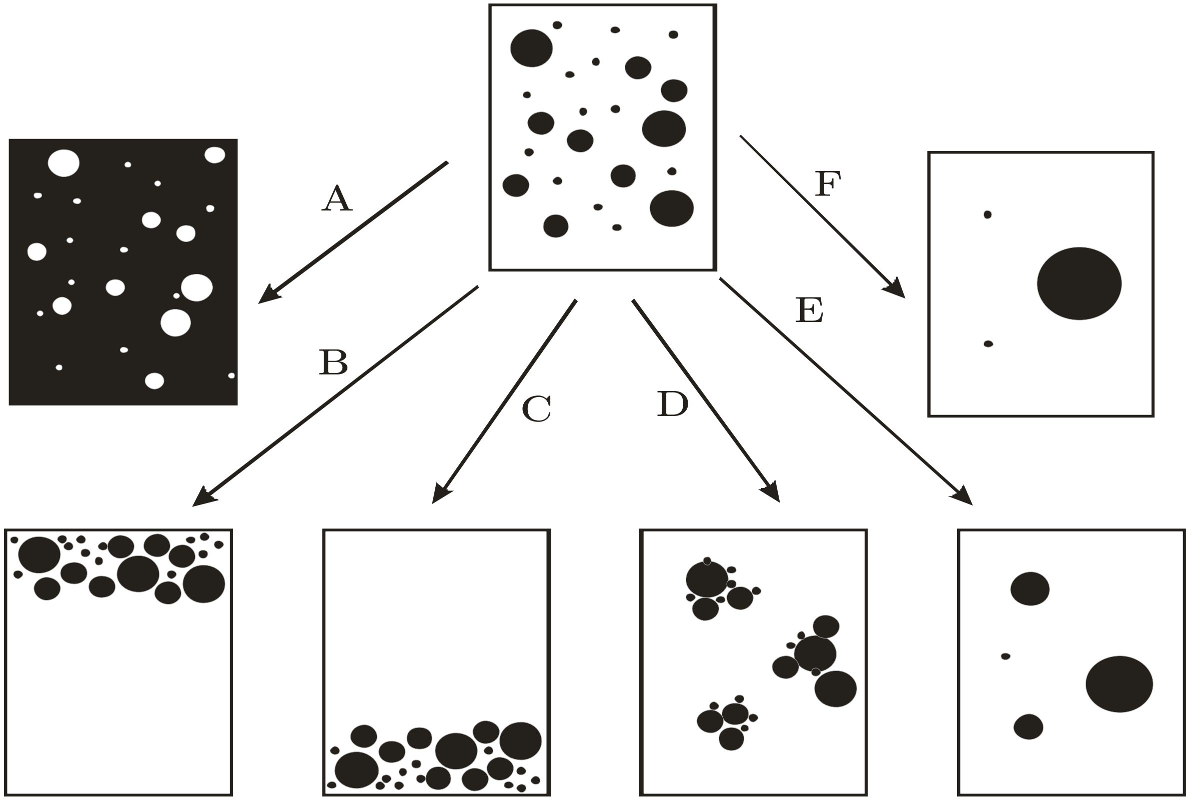


Manufacture of butter*

- Milk is a fairly dilute, not very stable O/W emulsion, about 4% fat.
- Creaming produces a concentrated, not very stable O/W emulsion, about 36% fat.
- Gentle agitation, particularly when cool, 13 – 18 C, inverts it to make a W/O emulsion about 85% fat.
- Drain, add salt, and mix well.
- Voila – butter!
- What remains is buttermilk.

*Becher, *Emulsions*; Oxford; 2001, p. 291

Emulsion processes

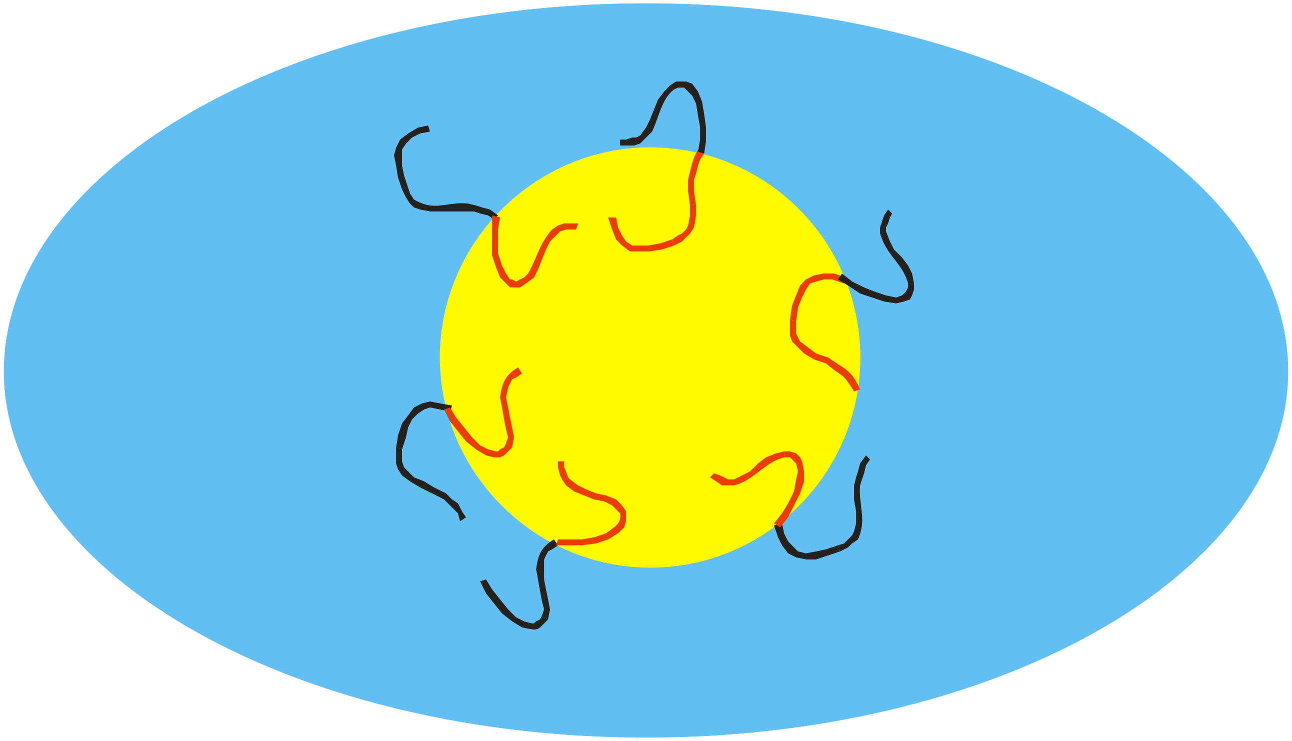


A – Inversion
B – Creaming
C – Sedimentation
D – Flocculation
E - Coalescence
F - Ripening

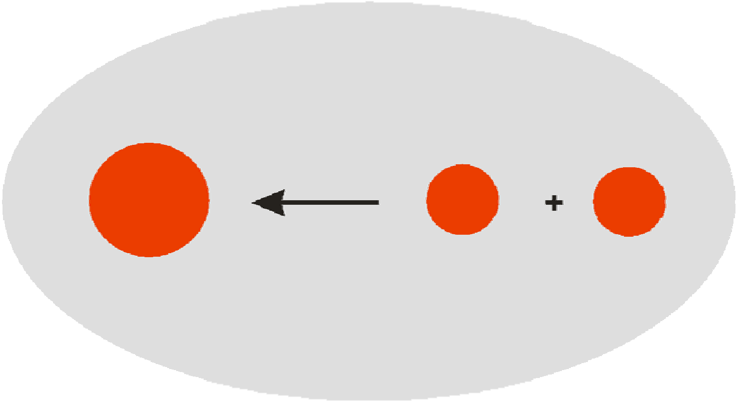
Surface activity in emulsions

Emulsions are dispersions of droplets of one liquid in another.

Emulsifiers are soluble, to different degrees, in both phases.

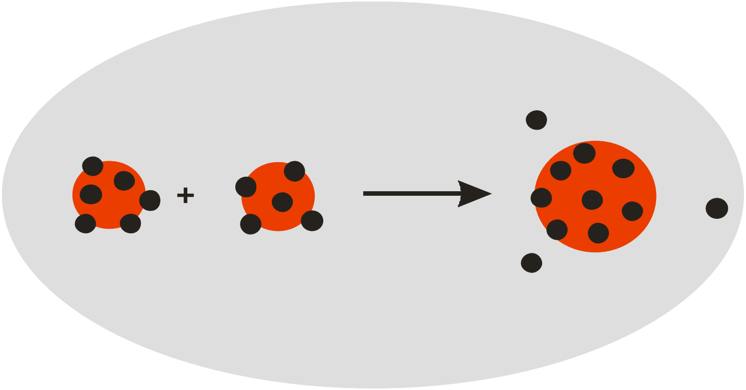


Emulsion stability



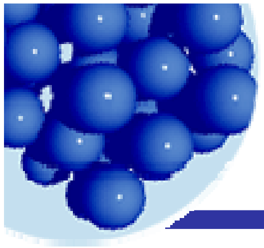
$$\Delta F = \sigma \Delta A < 0$$

Drops coalesce spontaneously.



$$\Delta F = \sigma \Delta A + \text{ work of desorption}$$

If the work of desorption is high, the coalescence is prevented.



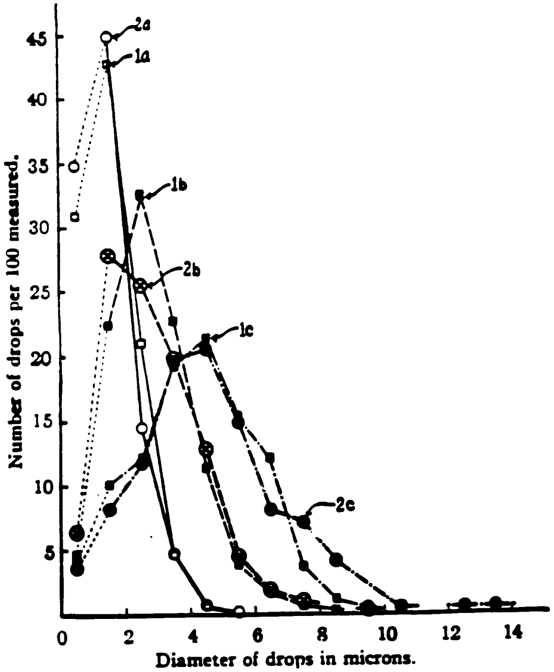
Stability of emulsions*

Types:

- Creaming – less dense phase rises
- Inversion – internal phase becomes external phase
- Ostwald ripening – small droplets get smaller
- Flocculation – droplets stick together
- Coalesence – droplets combine into larger ones

*Dickenson in ”Food Structure”; Butterworths; 1988; p. 43.

Ripening of Emulsions



Change in size distribution with aging, 0.005 M sodium oleate and octane: 1*a*, measured on first day; 1*b*, measured on third day; 1c. measured on seventh day, 0.005M cesium oleate; 2a, measured on first day; 2b measured on third day; 2c. Measured on seventh day.

Breaking of emulsions

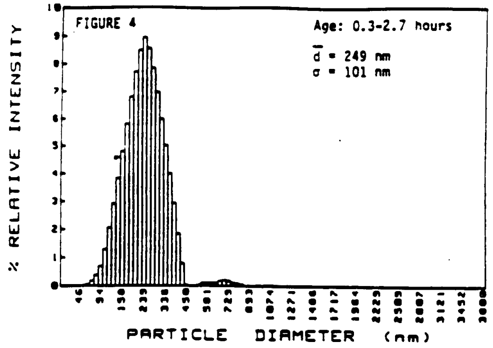


FIGURE 4

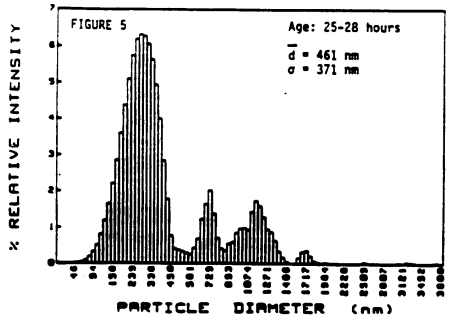


FIGURE 5

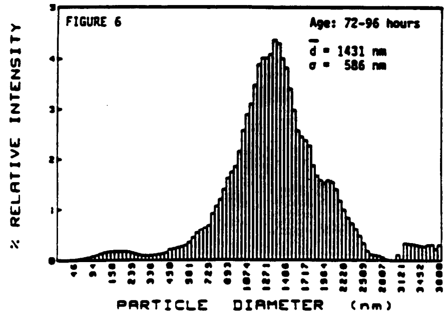
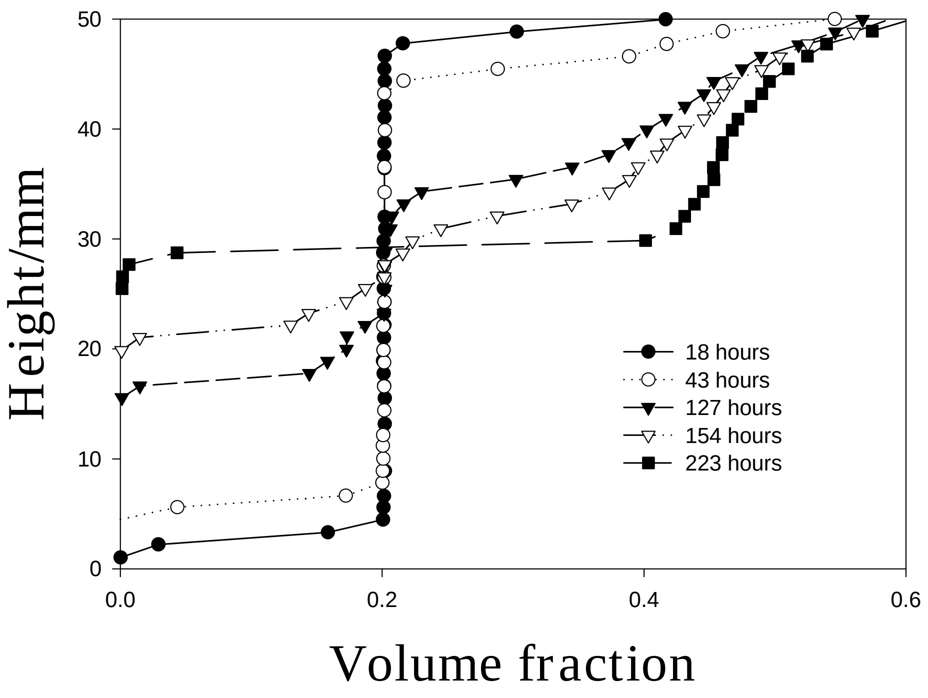


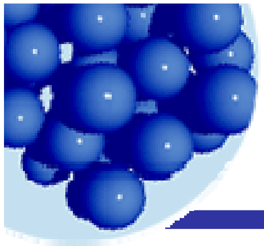
FIGURE 6

An emulsion system with an initial particle size of 235 *nm* was destabilized by dilution in a solution of an ionic surfactant opposite in sign to that of the particle charge. The three figures show the resulting distributions at times up to 4 days as reported in the figures.

Creaming of emulsions



Volume fraction at various heights and times was determined by measuring the speed of sound.



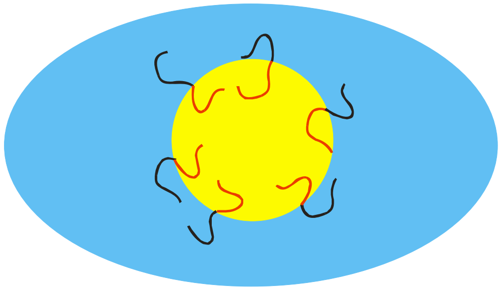
Stability of emulsions - II

Electrostatic stabilization – at lower volume fractions

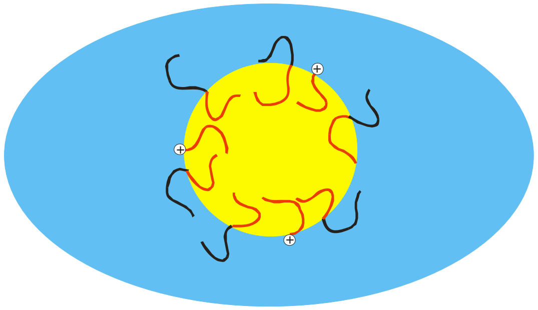
Steric stabilization – at all volume fractions

Additional factors –

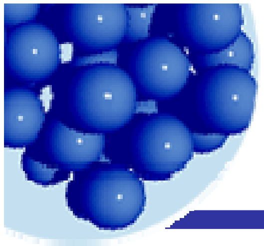
1. Steric stabilization is enhanced by solubility in both phases:



2. Mixed emulsifiers (cosurfactants) are common. They can come from either phase.



3. Temperature is important – solubility changes quickly.



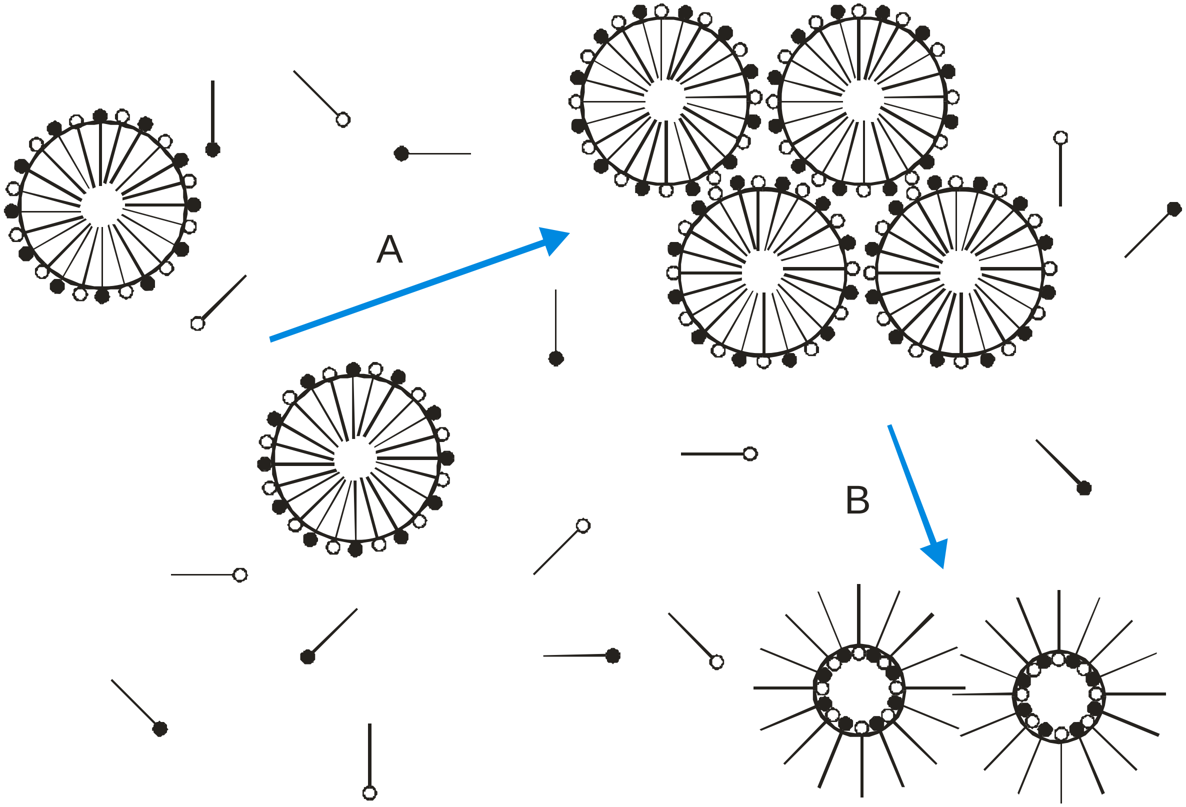
Demulsification – breaking emulsions

First, determine type, O/W or W/O. Continuous phase will mix with water or oil.

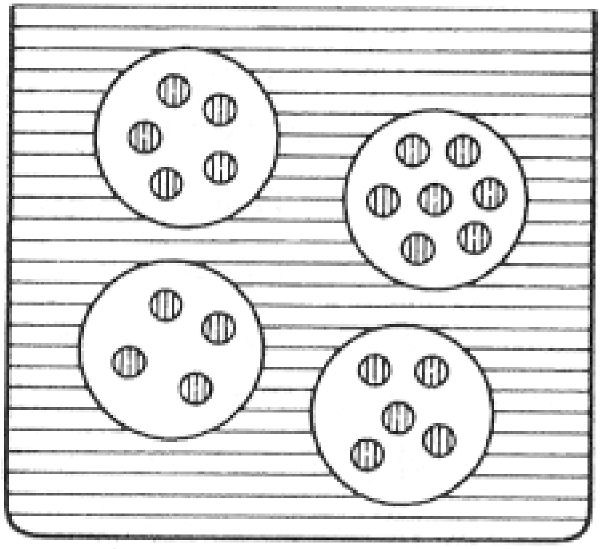
- Chemical demulsification, i.e. change the HLB
  - Add an emulsifier of opposite type.
  - Add agent of opposite charge.
- Freeze-thaw cycles.
- Add electrolyte. Change the pH.
- Raise temperature.
- Apply electric field.
- Filter through fritted glass or fibers.
- Centrifugation.

Emulsion inversion

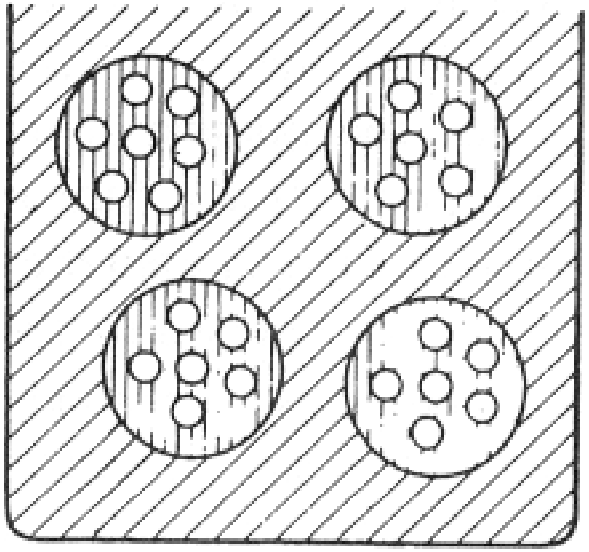
As the concentration increases (A) the droplets get closer until they pinch off into smaller, opposite type of emulsion (B).



Multiple emulsions


(a)

(a) W/O/W double emulsion


(b)

O/W/O double emulsion

Consider, for either diagram:

Each interface needs a different HLB value.

The curvature of each interface is different.

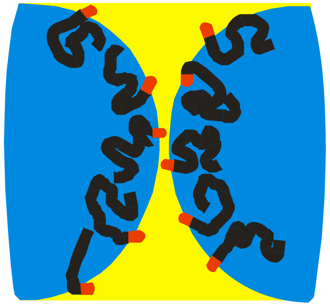
(Rosen, p. 313)

Bancroft's Rule

"The emulsifier stabilizes the emulsion type where the continuous phase is the medium in which it is most soluble."

A hydrophilic solute in an O/W emulsion.

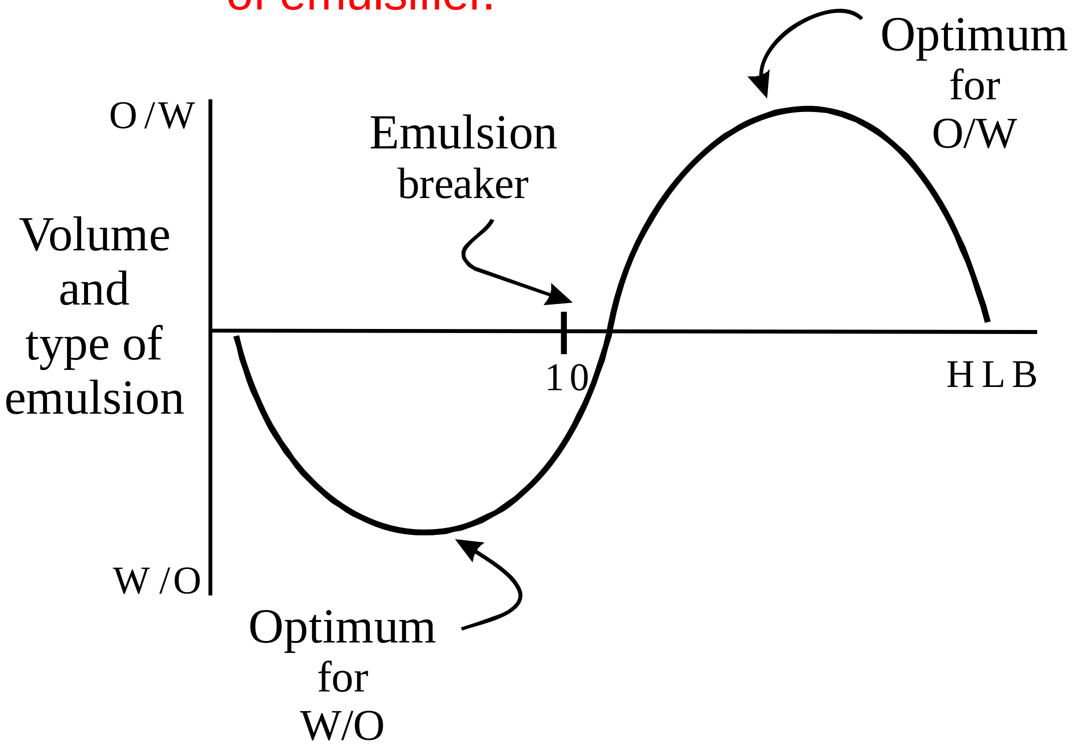
The long tail on the surfactant is to represent the longer range interaction of a "hydrophilic" molecule through water.

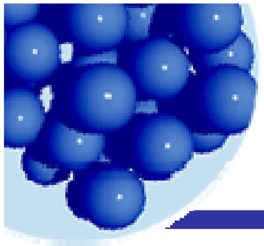


A hydrophilic solute in a W/O emulsion.

The HLB Schema

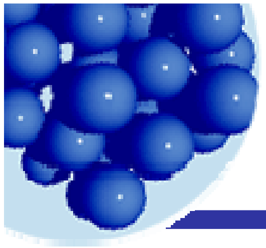
Variation of type and amount of residual emulsion with HLB number of emulsifier.





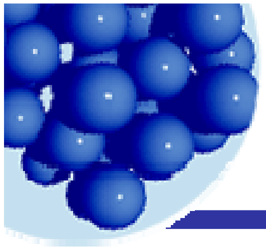
HLB Scale

Lipophilic End of Scale					Hydrophilic end of scale
Stearane	Steric Acid	Sodium Stearate	Sodium Laurate	Sucrose	Sodium Sulfate
Soluble in oil; insoluble in water	Soluble in oil; insoluble in water	Soluble in oil; and in hot water	Slightly oil-soluble; soluble in water	Insoluble in oil; soluble in water	Insoluble in oil; soluble in water
Nonspreading on water substrate	Spreads on water substrate	Spreads on water substrate	Reduces surface tension of aqueous solutions	Does not affect the surface tension in aqueous solution	Increases surface tension in aqueous solution
Does not affect interfacial tension at oil–water interface	Reduces interfacial tension at oil–water interface	Reduces interfacial tension at oil–water interface	Reduces interfacial tension at oil–water interface	Does not affect interfacial tension at oil–water interface	Increases interfacial tension at oil–water interface
Does not stabilize emulsions	Stabilizes water in oil emulsions	Stabilizes either type of emulsion	Stabilizes oil in water emulsions	Does not stabilize emulsions	Decreases the stability of emulsions
	1	HLB Scale	20		



Applications of the HLB scale

HLB Range	Application
3.5–6	W/O emulsifier
7–9	Wetting agent
8–18	O/W emulsifier
13–15	Detergent
15–18	Solubilizer

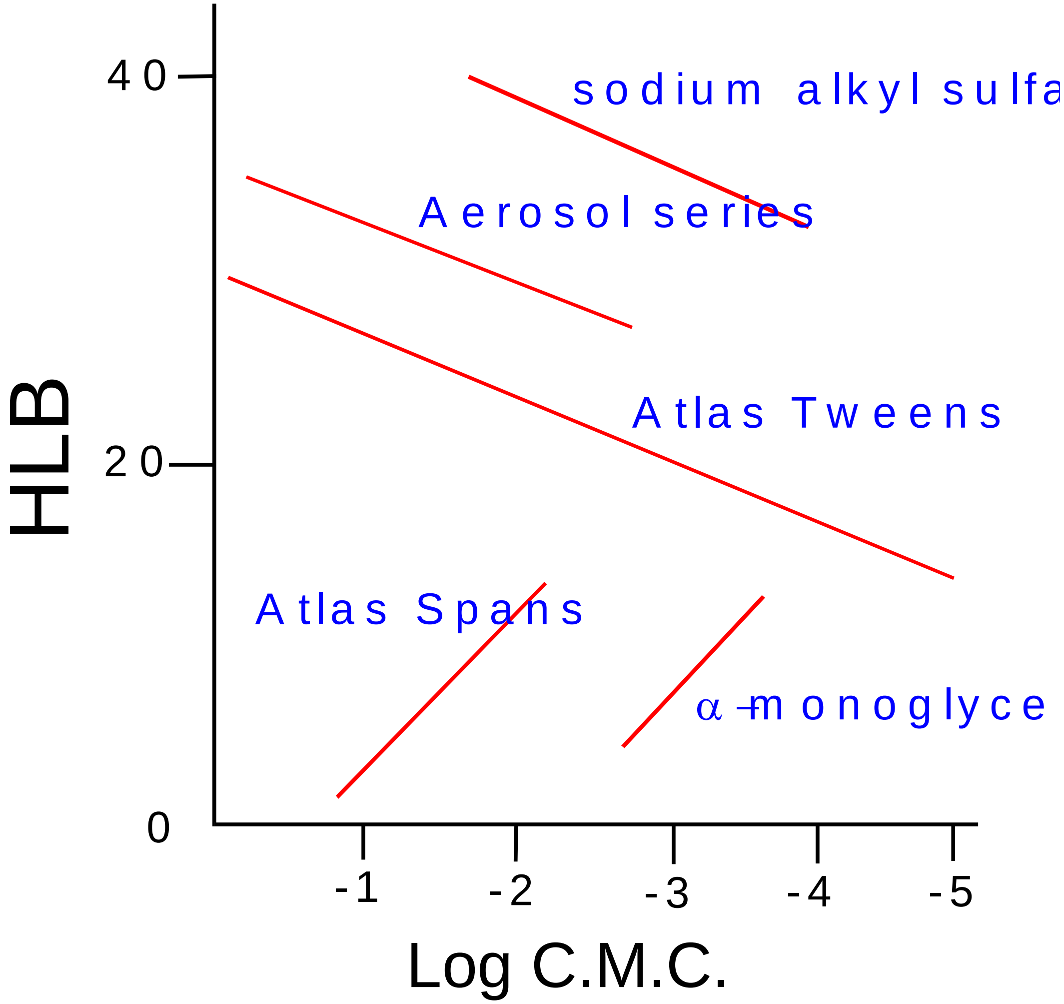


Group Numbers for Calculating HLB Values

$$HLB = 7 + \sum(H) - \sum(L)$$

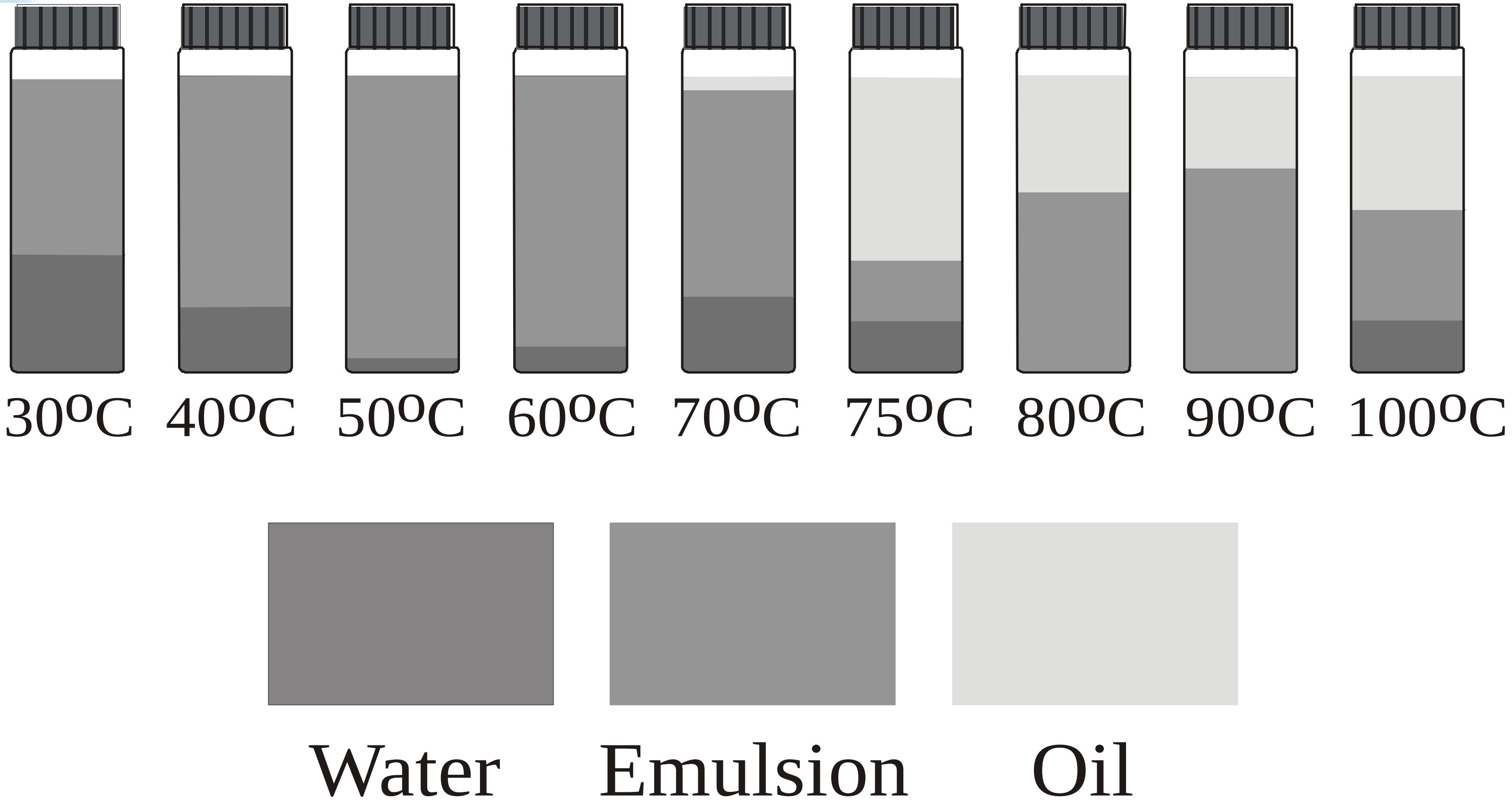
	Group Number
Hydrophilic Groups	
$-OSO_3^-Na^+$	38.7
$-COO^-K^+$	21.1
$-COO^-Na^+$	19.1
N (tertiary amine)	9.4
Ester (sorbitan ring)	6.8
Ester (free)	2.4
$-COOH$	2.1
$-OH$ (free)	1.9
$-O-$	1.3
$-OH$ (sorbitan ring)	0.5
$(-CH_2CH_2O-)_n$	$0.33n$
Lipophilic Groups	
$-CH-$ $-CH_2-$ CH_3- $=CH-$	0.475
$(-CHCH_3CH_2O-)_n$	$0.15n$

HLB and C.M.C.



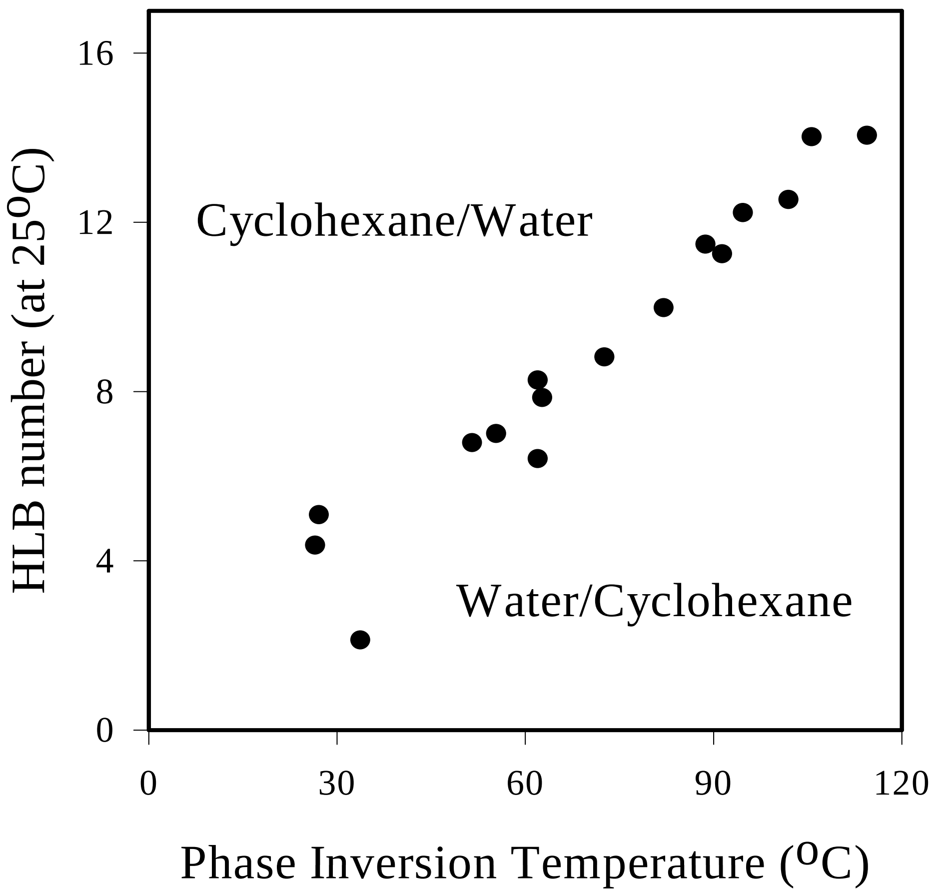
Ian Morrison© 2009

Phase inversion temperature

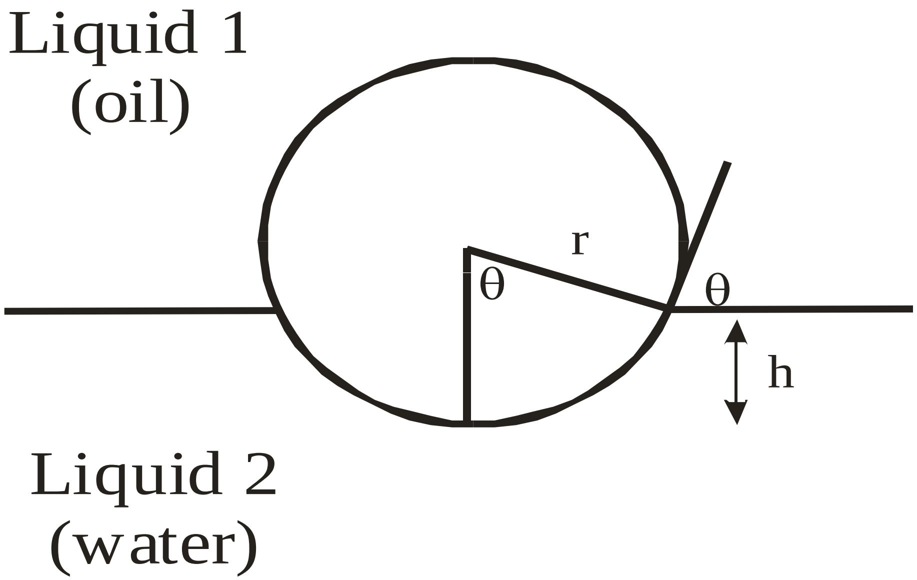


www.bias-net.com/chimica/pdf/set_baglioni.pdf

HLB and the Phase Inversion Temperature



Particles as emulsion stabilizers

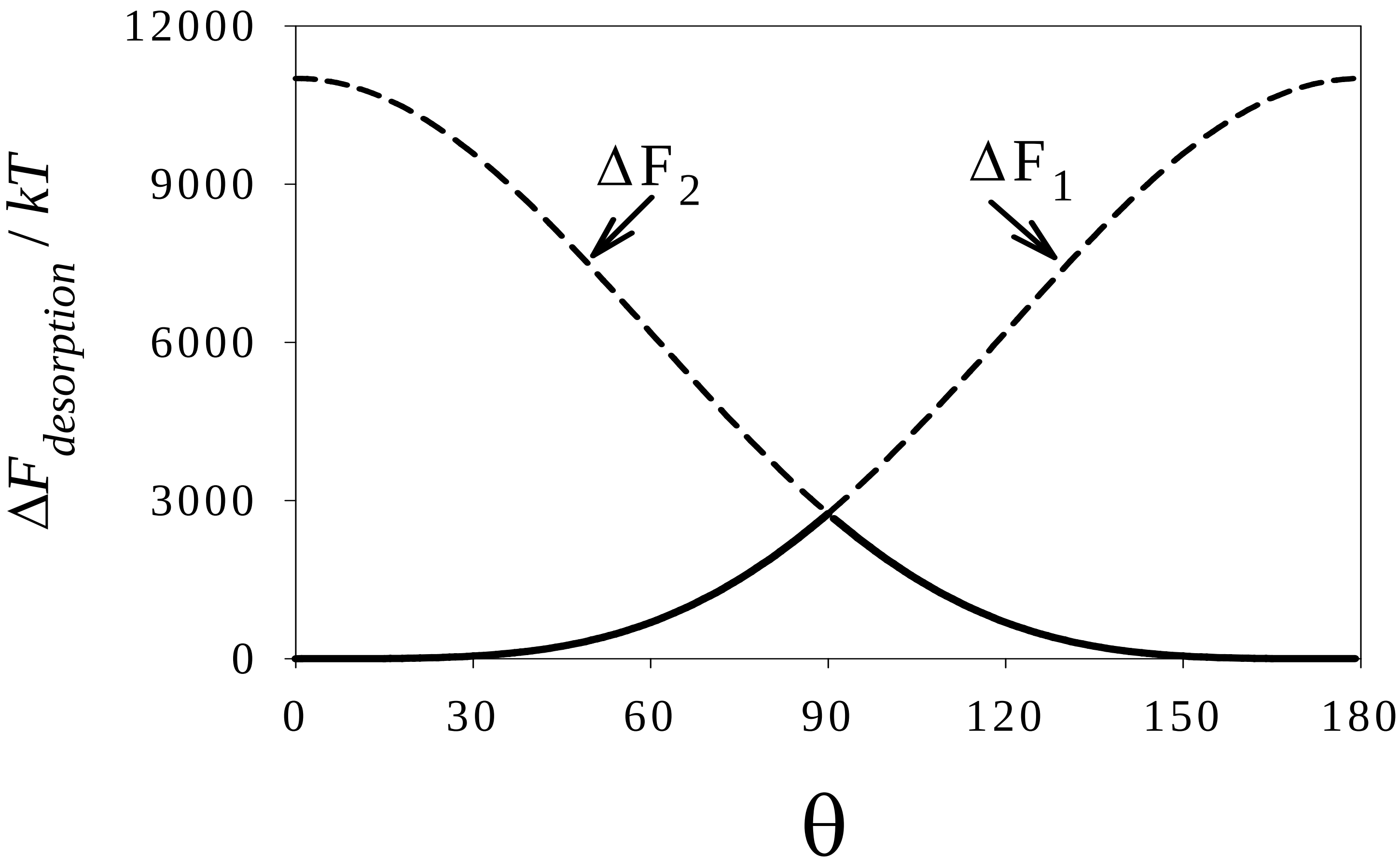


Almost all particles are only partially wetted by either phase.

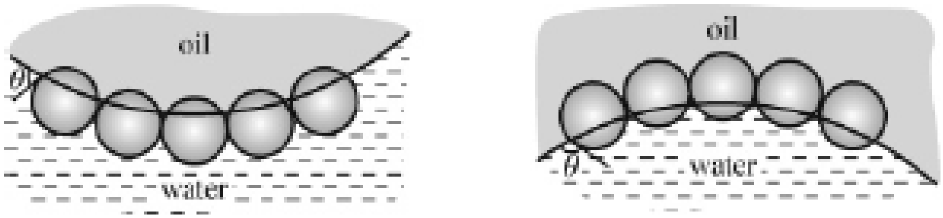
When particles are “adsorbed” at the surface, they are hard to remove – the emulsion stability is high, sometimes thousands of *kT*.

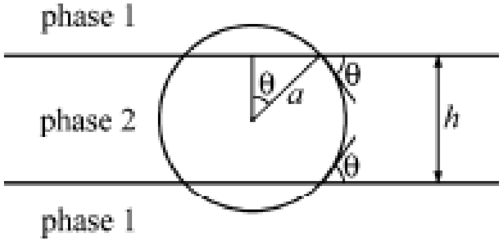
Crude oil is a W/O emulsion and is old!!

Stability as a function of contact angle



The thermodynamics is rich





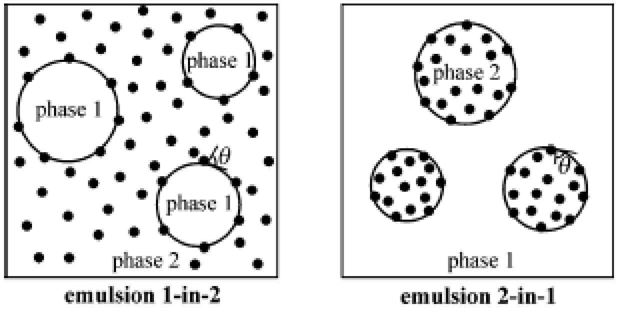


Figure 7. Sketch of a particle of radius *a*, which is bridging between the surfaces of a film from phase 2 formed between two drops of phase 1. *h* is the film thickness. õ is the contact angle.

Figure 8. Definitions of phases, angles, and emulsions: By definition, the particles are initially dispersed in phase 2. The contact angle, õ, is always measured across phase 2. The emulsion 1-in-2 is a Bancroft-type emulsion, in which the particles are dispersed in the continuous phase. In contrast, the emulsion 2-in-1 is of anti-Bancroft type.

P. A. Kralchevsky,*,† I. B. Ivanov,† K. P. Ananthapadmanabhan,‡ and A. Lips‡ *Langmuir* **2005,** *21,* 50-63

Wax dispersed with fumed silica

Hydrophilic silica stabilizing a wax/water emulsion

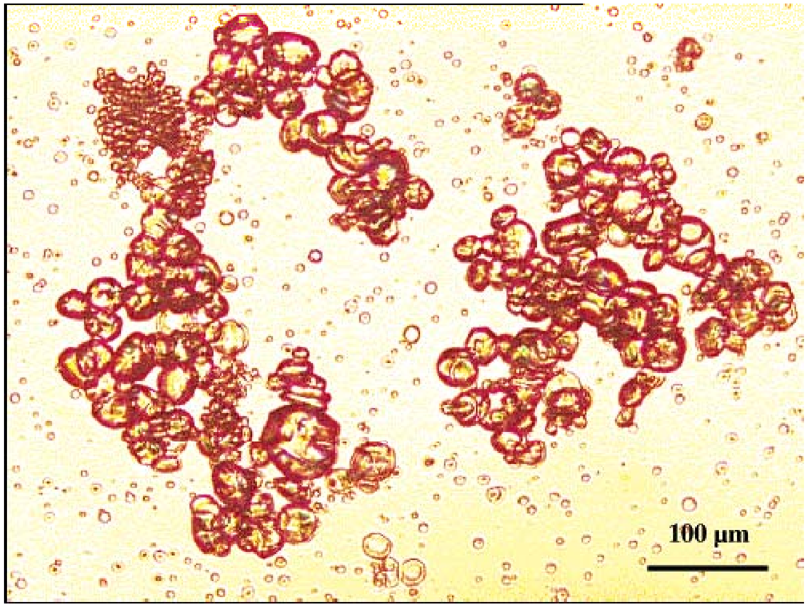


Figure 1. Microscopic image of a paraffin-in-water emulsion stabilized by CTAB alone. *T*) 25 °C.

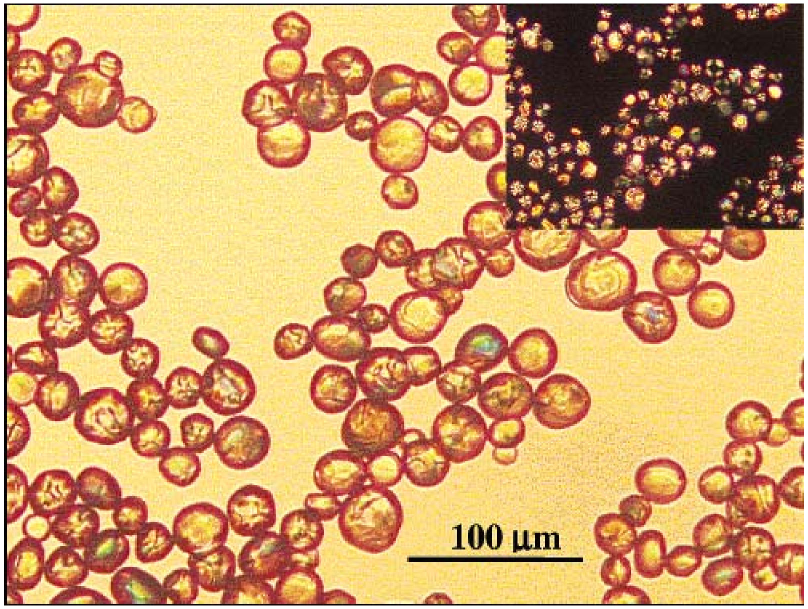


Figure 3. Microscopic image of a paraffin-in-water emulsion stabilized by P2 particles. Inset: same image taken at *T*) 25 °C under crossed polarizers, confirming the presence of crystals
in the droplets.

J. Giermanska-Kahn,† V. Laine,† S. Arditty,† V. Schmitt,† and F. Leal-Calderon

Langmuir **2005,** *21,* 4316-4323

Bubbles stabilized with fumed silica

Hydrophobic silica stabilizing a foam in water with added salt.

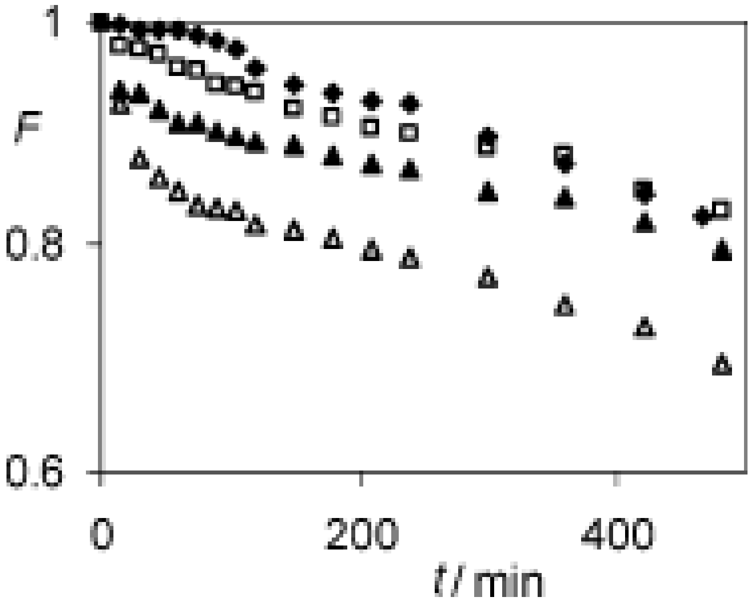
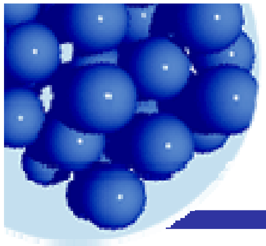


Figure 1. Fraction (*F*) of bubbles remaining as a function of time (*t*) formed in dispersions of 1wt%of 33% SiOR particles at different NaCl concentrations: 3 mol dm-3 ([), 2 mol dm-3 (0), 1 mol dm-3 (2), and 0.5 mol dm-3 (4).

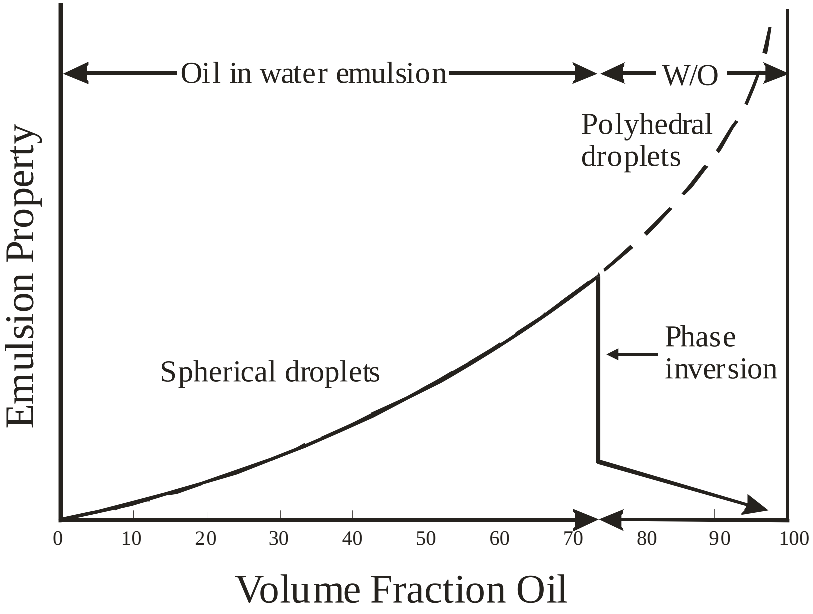
Thomas Kostakis, Rammile Ettelaie, and Brent S. Murray *Langmuir* **2006,** *22,* 1273-1280



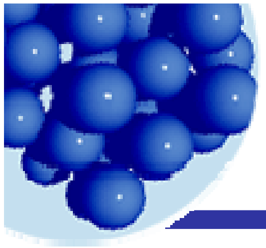
Physical properties of emulsions

- **Identification** of “internal” and “external” phases; W/O or O/W
- **Droplet size and size distributions** – generally greater than a micron
- **Concentration of dispersed phase** – often quite high. The viscosity, conductivity, etc, of emulsions are much different than the continuous phase.
- **Rheology** – complex combinations of viscous (flowing) elastic (when moved a little) and viscoelastic (when moved a lot) properties.
- **Electrical properties** – useful to characterize structure.
- **Multiple phase emulsions** – drops in drops in drops, …

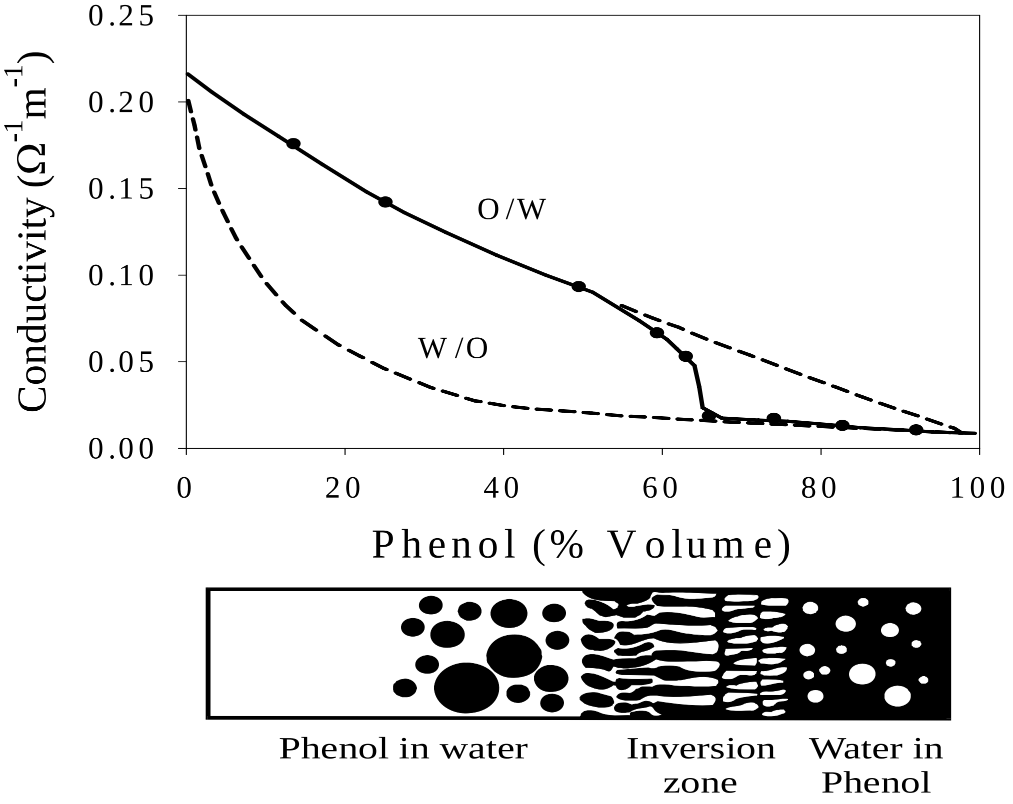
Variation in properties with concentration



The variation of properties of emulsions with changes in composition. If inversion occurs, there is a discontinuity in properties, as they change from one curve to the other. Above 74% there is either a phase inversion or the droplets are deformed to polyhedra.

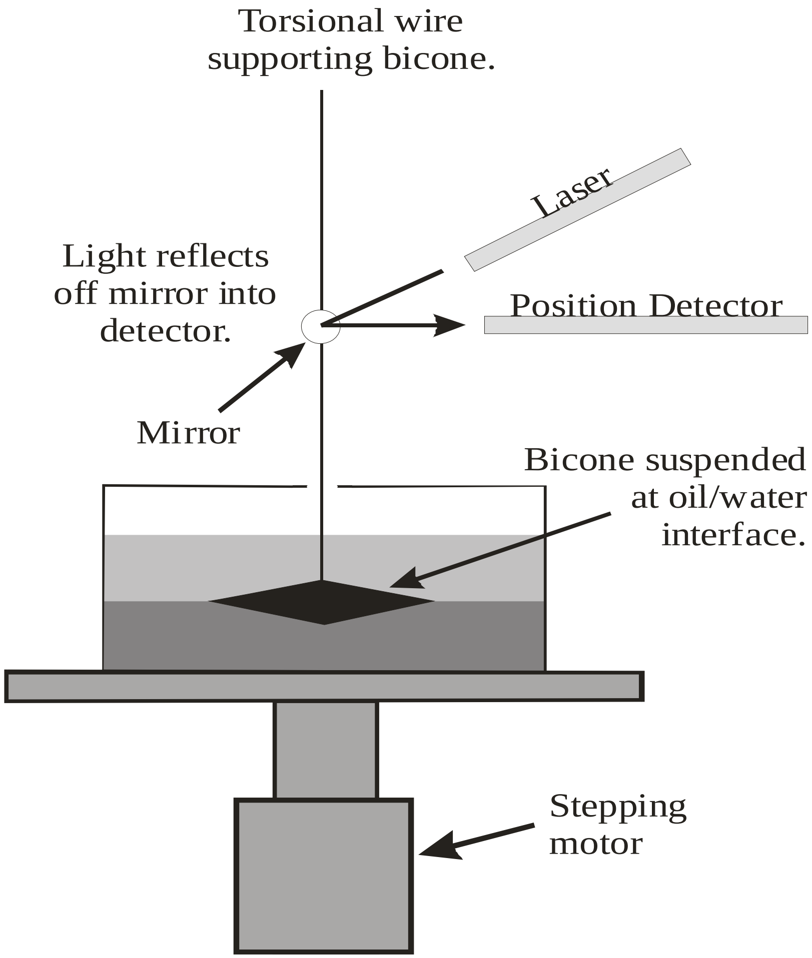


Conductivity of emulsions



The specific conductivity of aqueous potassium iodide and phenol emulsions as a function of composition (Manegold, p. 30).

Interfacial viscometer



Rheology of O/W interfaces

By single-particle tracking

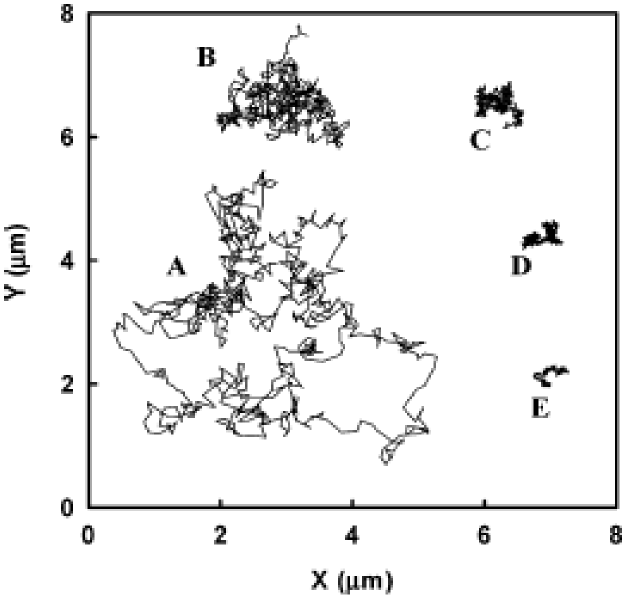


Figure 1. Typical trajectories of sulfate-treated PS (S-PS) particles at the oil−water interfaces for 756 s (700 frames) at 21 °C. The viscosities of the PDMS oil phase are (A) 350, (B) 1K, (C) 5K, (D) 20K, and (E) 60K cSt.

For viscous liquids:

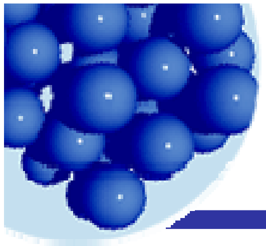
$$\left\langle \Delta r^2(\tau) \right\rangle = 4D\tau \quad \text{where} \quad D = \frac{k_B T}{4\pi\eta a}$$

For elastic liquids:

$$\left\langle \Delta r^2 \right\rangle = \frac{2k_B T}{3\pi a G'}$$

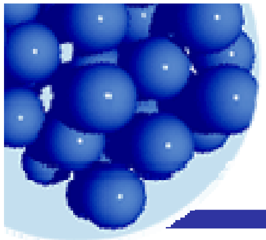
The particles have to sit properly at the O/W interface.

Wu and Dai, *Langmuir*, *23*, 4324 – 4331, **2007**.



Making emulsions

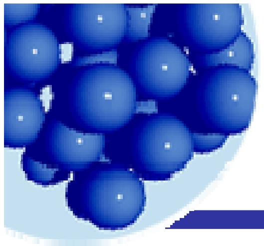
Method of phase inversion	*e.g.* Use a poor O/W emulsifier, go to high volume fractions, the emulsion inverts to smaller droplets of W/O
Phase-inversion-temperature method	*e.g.* Heat and emulsify O/W 2-4^{o} below the PIT, creates low σ and small drops, cool to room temperature.
Solubilize vapor in micelles	The energies driving the condensation, drive Ostwald ripening, therefore a formulation challenge.
Electric emulsification	Charging the surface produces electrohydrodynamic instabilities.
Intermittent milling	Surfactant adsorption is slow – waiting helps.



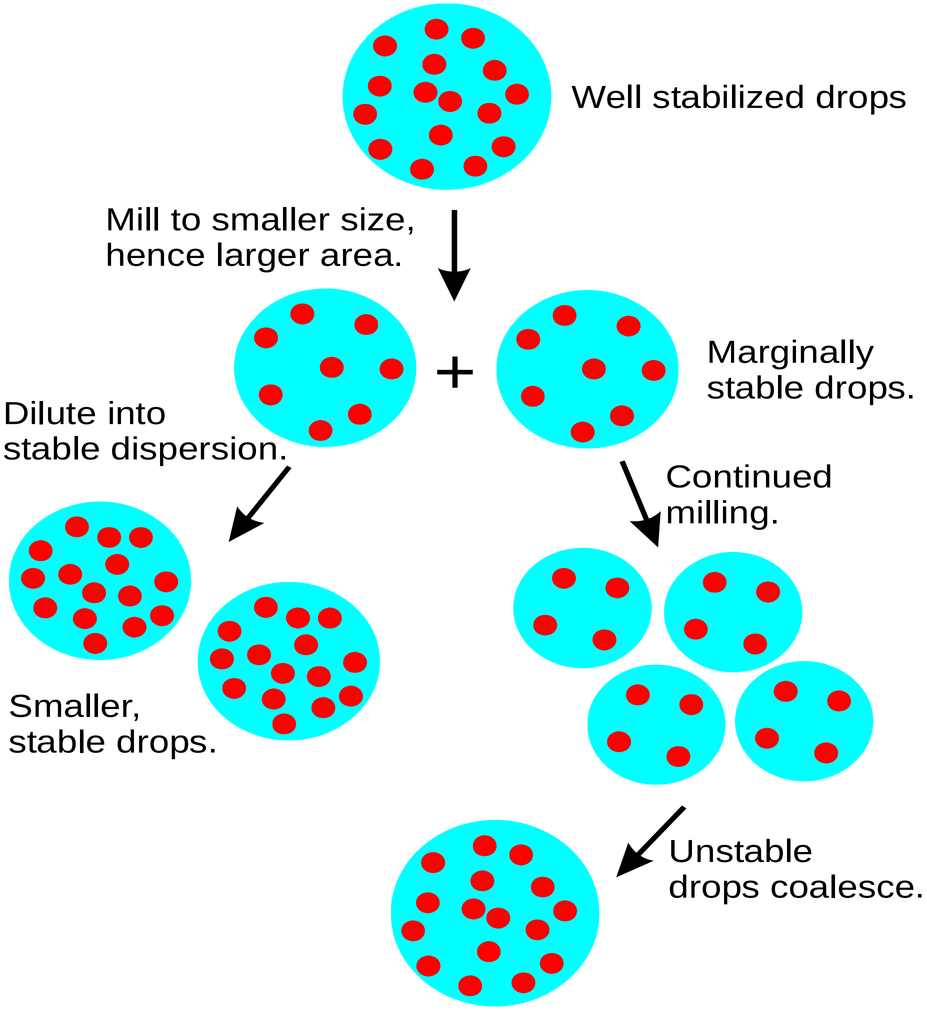
Breaking emulsions

Creaming	Especially with a centrifuge, taking advantage of temperature and salt.
Mechanical	Sometime high shear; filtering through bed whose surfaces are wetted by internal phase; ultrafiltration; dialysis;
Thermal	Most emulsion a less stable hot; At the PIT many are quite unstable; freeze-thaw.
Chemical	Chemically change the emulsifier; mismatch of HLB, pH; replace with strong surfactant but not strong emulsifier; addition of other solvents.

Menon, V.B.; Wasan, D.T. *Demulsification*, in *Encyclopedia of emulsion technology*; Becher, P., Ed.; Marcel Dekker: New York; **1985**, Vol. 2; pp 1-75.



Intermittent milling



Well stabilized drops

Mill to smaller size,
hence larger area.

+

Marginally
stable drops.

Dilute into
stable dispersion.

Continued
milling.

Smaller,
stable drops.

Unstable
drops coalesce.