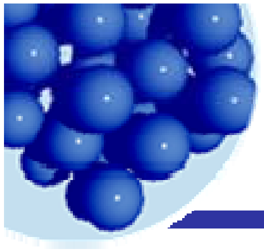


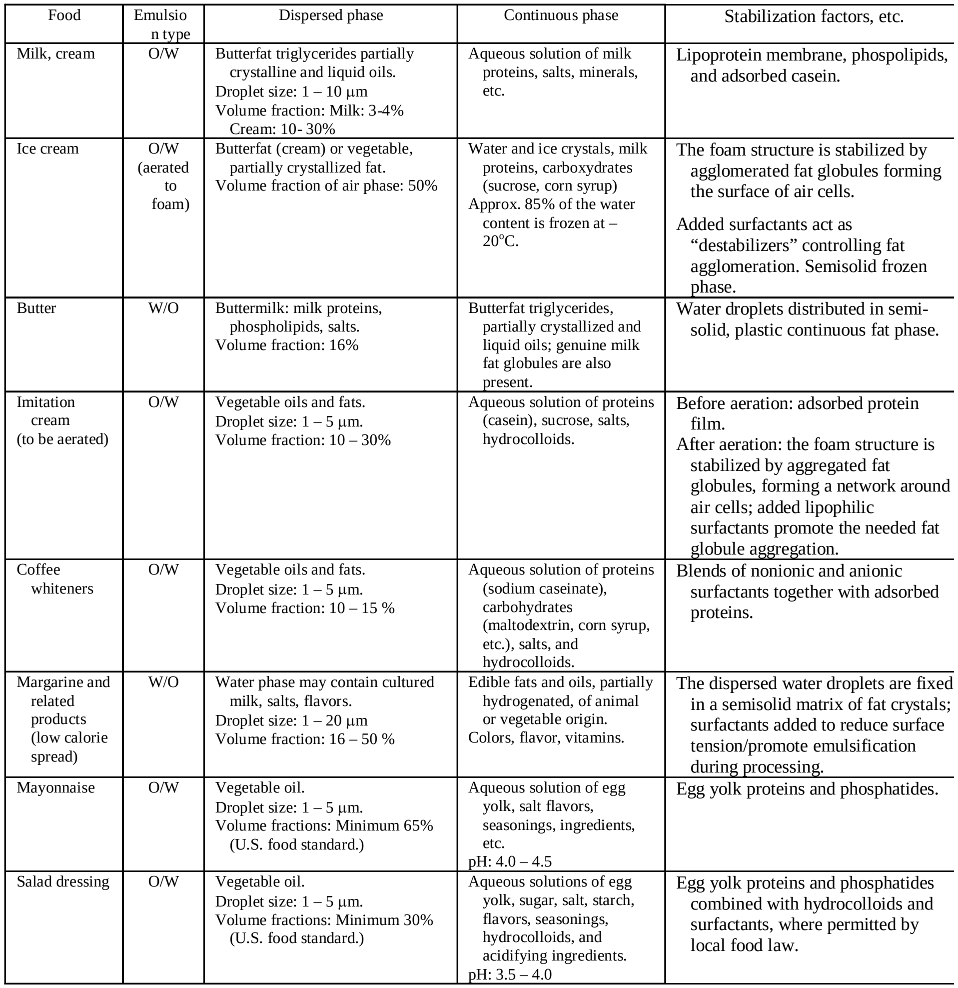
Emulsion Technology

Dispersions in liquids: suspensions, emulsions, and foams

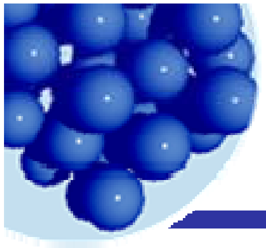
ACS National Meeting
April 9 – 10, 2008
New Orleans

Typical food emulsions

Dickenson, E.; McClements, D.J.; *Advances in Food Colloids*; Chapman & Hall: New York; 1996.

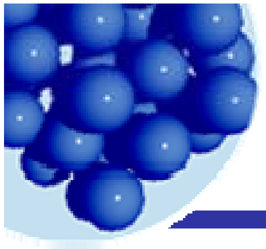


Food	Emulsion type	Dispersed phase	Continuous phase	Stabilization factors, etc.
Milk, cream	O/W	Butterfat triglycerides partially crystalline and liquid oils. Droplet size: 1 – 10 μm Volume fraction: Milk: 3-4% Cream: 10- 30%	Aqueous solution of milk proteins, salts, minerals, etc.	Lipoprotein membrane, 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.
Coffee whiteners	O/W	Vegetable oils and fats. Droplet size: 1 – 5 μm. Volume fraction: 10 – 15 %	Aqueous solution of proteins (sodium caseinate), carbohydrates (maltodextrin, corn syrup, etc.), salts, and hydrocolloids.	Blends of nonionic and anionic surfactants together with adsorbed proteins.
Margarine and related products (low calorie spread)	W/O	Water phase may contain cultured milk, salts, flavors. Droplet size: 1 – 20 μm Volume fraction: 16 – 50 %	Edible fats and oils, partially hydrogenated, of animal or vegetable origin. Colors, flavor, vitamins.	The dispersed water droplets are fixed in a semisolid matrix of fat crystals; surfactants added to reduce surface tension/promote emulsification during processing.
Mayonnaise	O/W	Vegetable oil. Droplet size: 1 – 5 μm. Volume fractions: Minimum 65% (U.S. food standard.)	Aqueous solution of egg yolk, salt flavors, seasonings, ingredients, etc. pH: 4.0 – 4.5	Egg yolk proteins and phosphatides.
Salad dressing	O/W	Vegetable oil. Droplet size: 1 – 5 μm. Volume fractions: Minimum 30% (U.S. food standard.)	Aqueous solutions of egg yolk, sugar, salt, starch, flavors, seasonings, hydrocolloids, and acidifying ingredients. pH: 3.5 – 4.0	Egg yolk proteins and phosphatides combined with hydrocolloids and surfactants, where permitted by local food law.



Terminology -I

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



Terminology - II

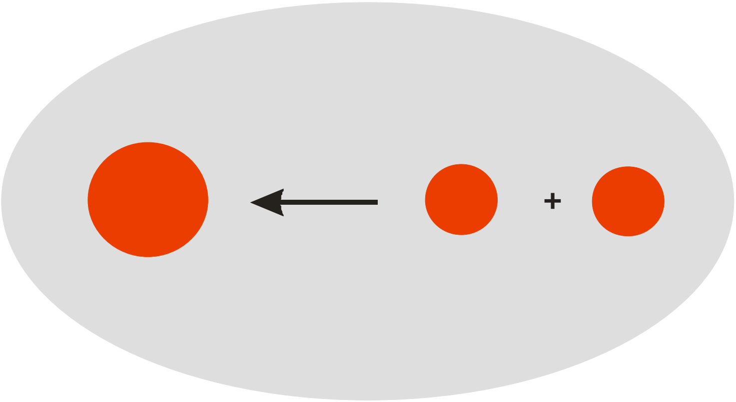
Macroemulsions – At least one immiscible liquid dispersed in another as drops whose diameters generally exceed 100 nm. The stability is improved by the addition of surfactants and/or finely divided solids. Considered only kinetically stable.

Miniemulsions – An emulsion with droplets between 100 and 1000 nm, reportedly thermodynamically stable.

Microemulsions – A thermodynamically stable, transparent solution of micelles swollen with solubilizate. Microemulsions usually require the presence of both a surfactant and a cosurfactant (e.g. short chain alcohol).

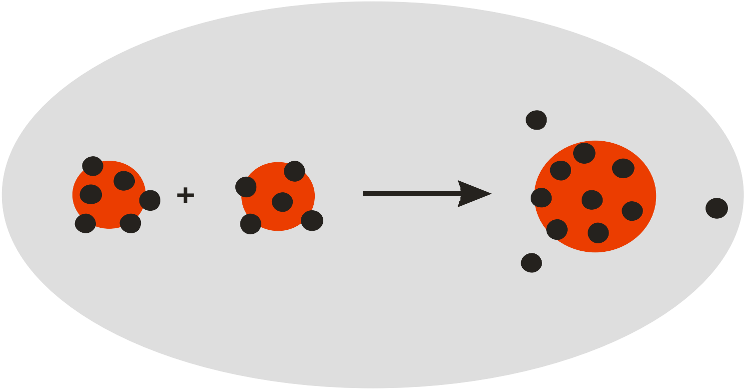
Becher, P. *Emulsions, theory and practice*, 3rd ed.; Oxford University Press: New York; 2001.

Emulsion stability



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

Drops coalesce spontaneously.



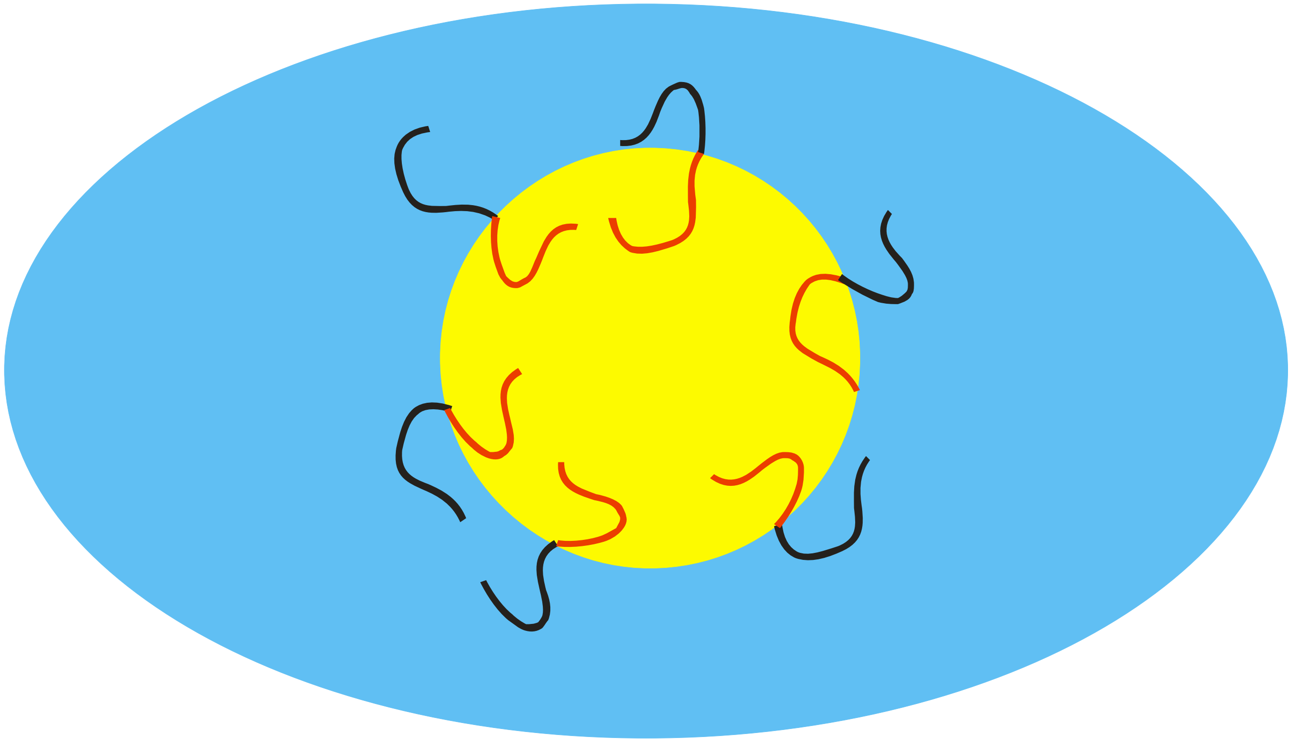
$$\Delta F = \sigma \Delta A + \text{ work of desorption}$$

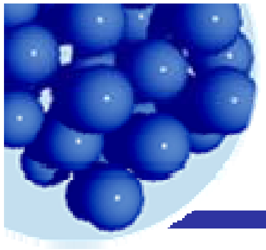
If the work of desorption is high, the coalescence is prevented.

Surface activity in emulsions

Emulsions are dispersions of droplets of one liquid in another.

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





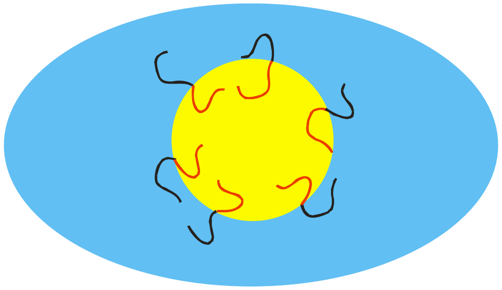
Emulsion stability

Electrostatic stabilization – at lower volume fractions

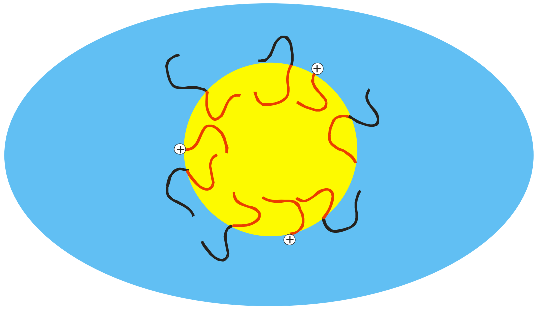
Steric stabilization – at all volume fractions

Additional factors –

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



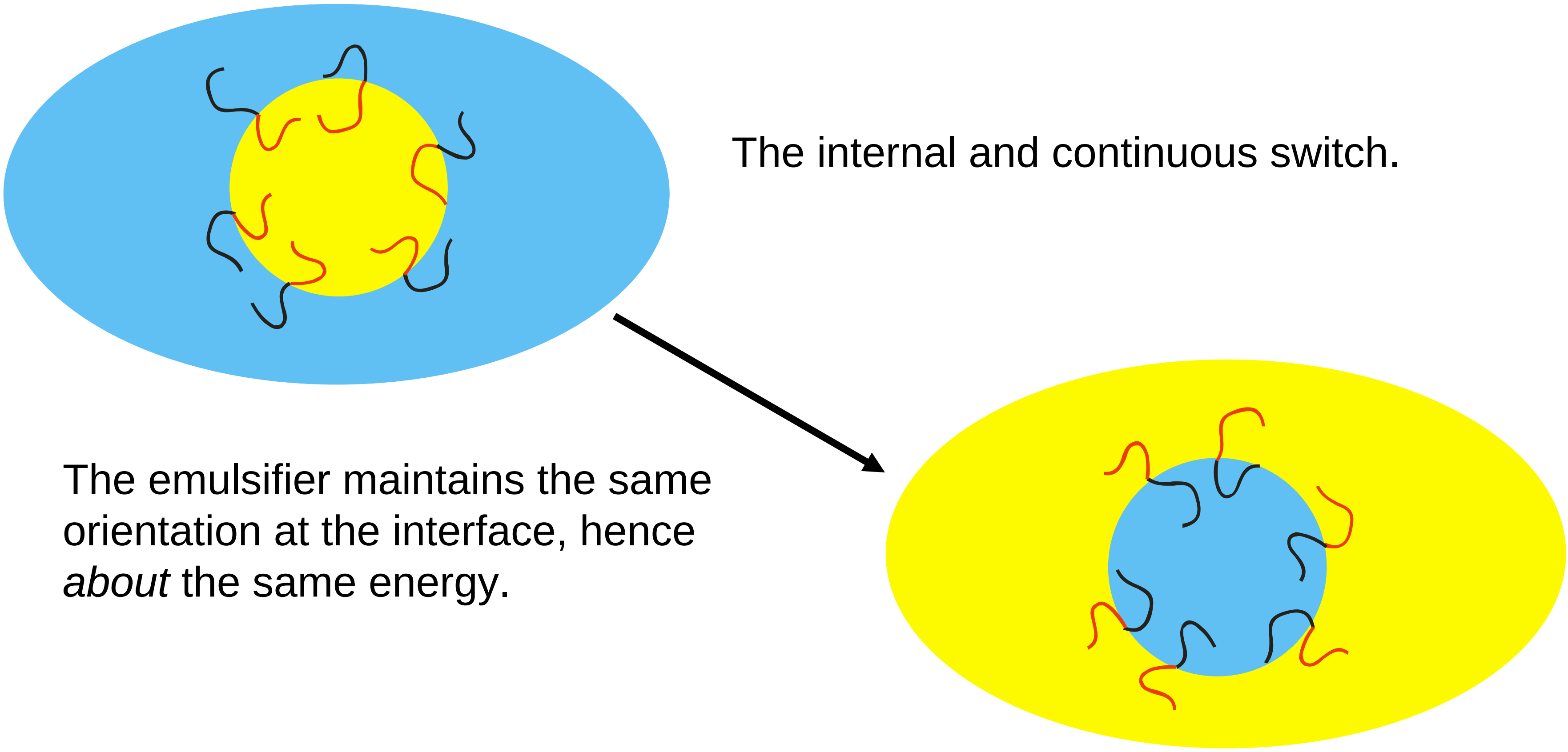
2. Mixed emulsifiers (cosurfactants) are common. They can come from either phase.



3. Temperature is important – solubility changes quickly.

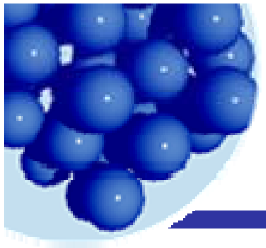
New

Emulsion inversion



The internal and continuous switch.

The emulsifier maintains the same orientation at the interface, hence *about* the same energy.

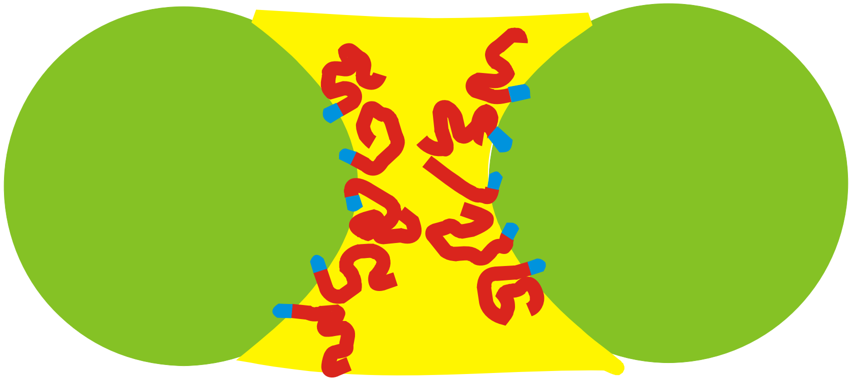


Newish

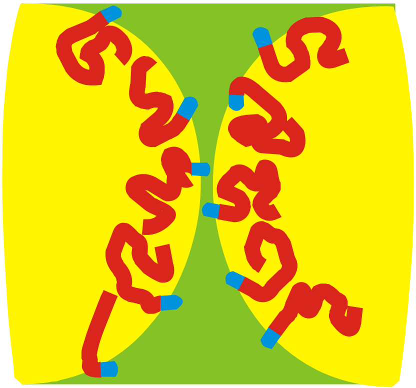
Bancroft’s Rule

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

The long tail on the surfactant is to represent the longer range interaction of a “hydrophobic” molecule through oil.



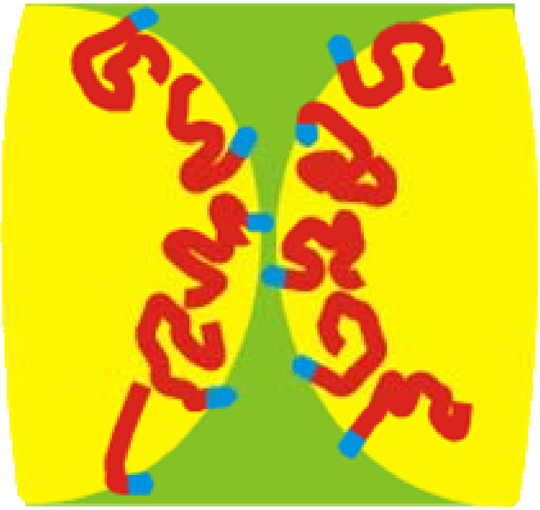
An oil-soluble emulsifier in a W/O emulsion.



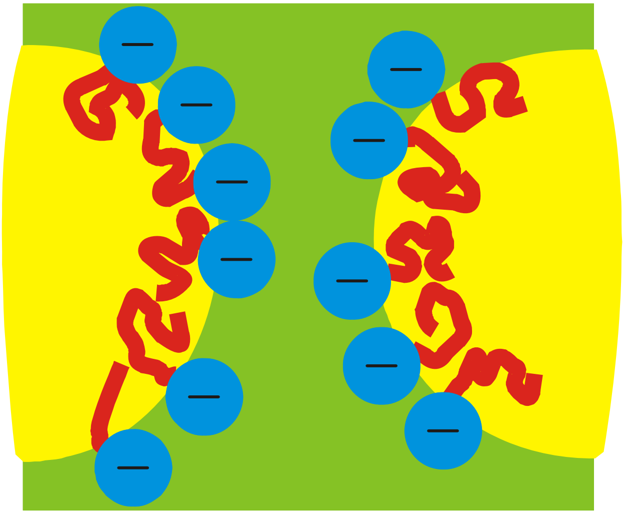
The same emulsifier in an O/W emulsion.

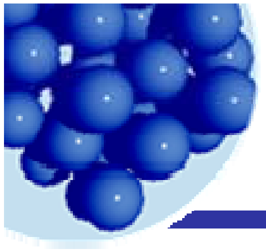
New

Bancroft’s rule - II



If the hydrophilic portion of the emulsifier is charged, its “effective” size is much larger.





Manufacture of butter*

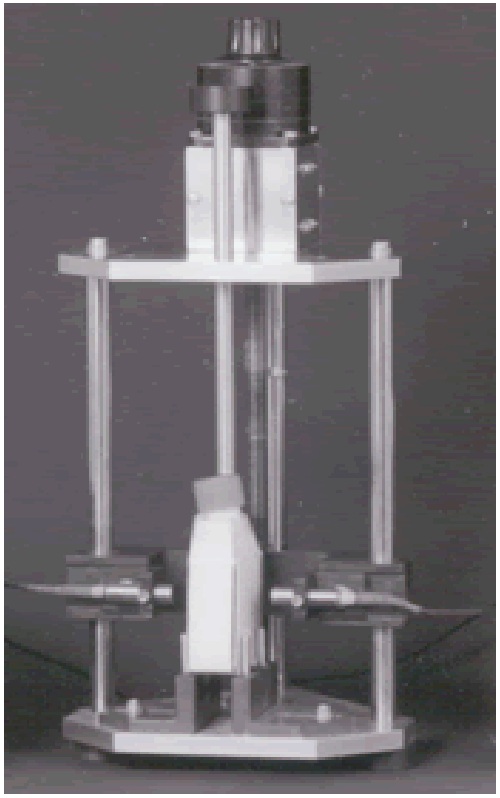
- Milk is a fairly dilute, not very stable O/W emulsion, about 4% fat.
- Creaming produces a concentrated, not very stable O/W emulsion, about 36% fat. And is skimmed off.
- Gentle agitation, particularly when cool, 13 – 18 C, inverts it to make a W/O emulsion about 85% fat.**
- Drain, add salt, and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

**Which might have happened 5000 years ago in the saddle bags of horsemen in Asia.

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

New

Measuring emulsion concentrations



The speed of sound is proportional to volume concentration.

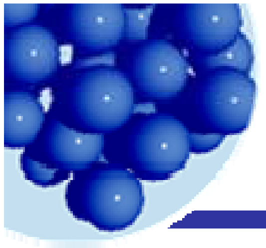
Even to very high concentrations.

A calibration curve of speed of sound *vs* concentration is easy to construct.

The measurement can be made through steel walls!

It just can’t be measured through air!

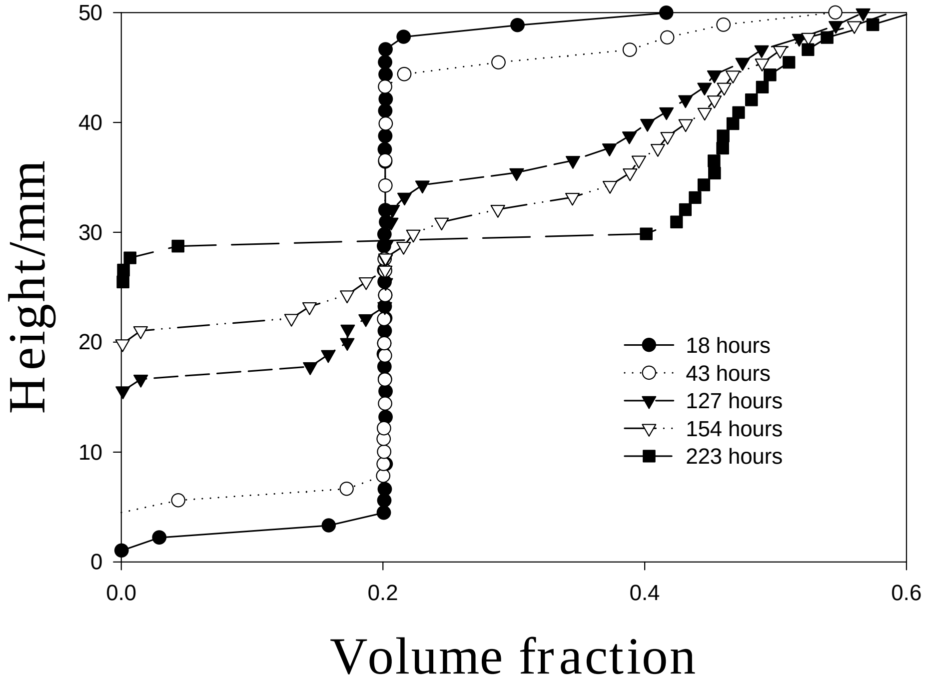
www.appliedsonics.com



Creaming of emulsions

The drops in emulsions are typically large, > 1 μm.

Therefore the drops will either rise, O/W emulsions or settle, W/O emulsions.



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

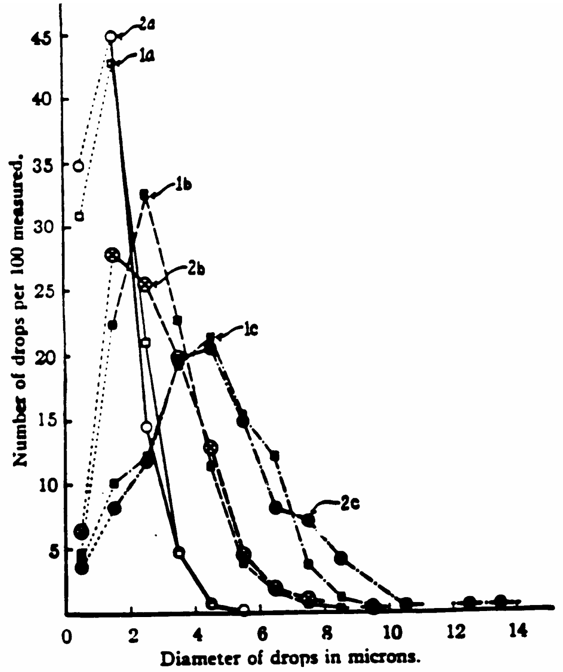
Newish

Ostwald ripening of emulsions

Smaller drops are at higher pressures:

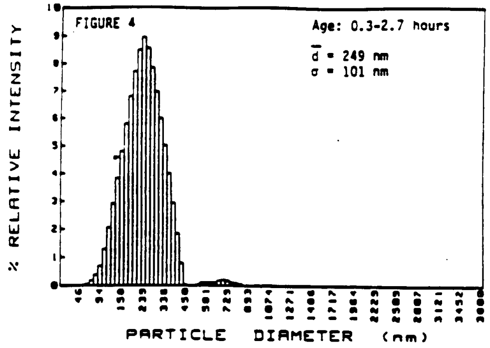
$$\Delta p = \frac{2\sigma}{r}$$

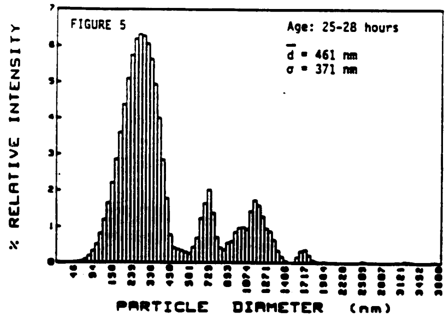
Therefore smaller ones gradually get even smaller and the large ones gradually get even larger,

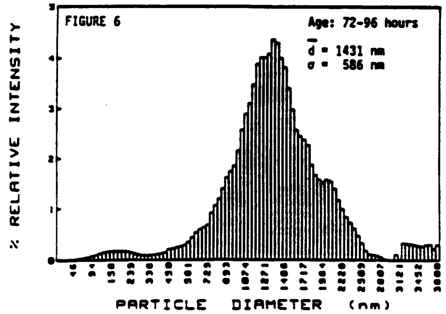


Change in size distribution with aging, 0.005 M sodium oleate and octane: 1*a*, measured on first day; 1*b*, measured on third day; 1c. measured on seventh day, 0.005M cesium oleate; 2a, measured on first day; 2b measured on third day; 2c. Measured on seventh day.

Coalescence of emulsions



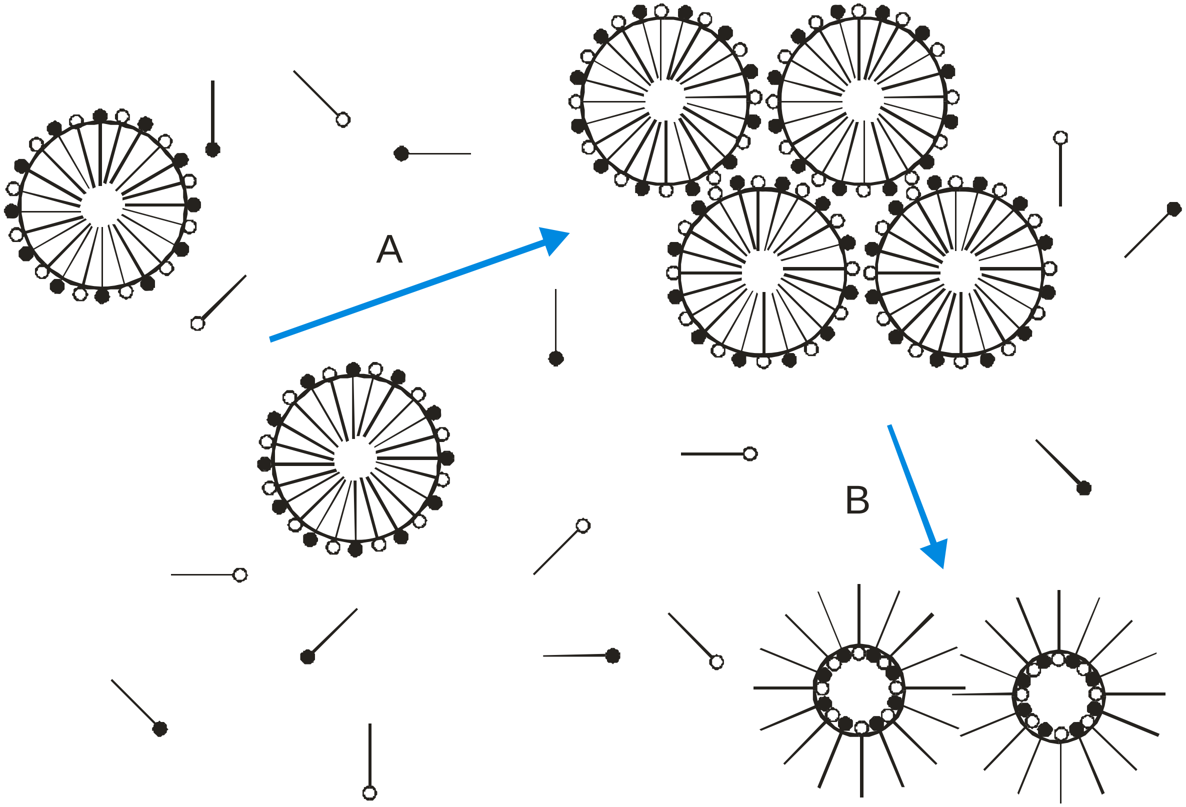




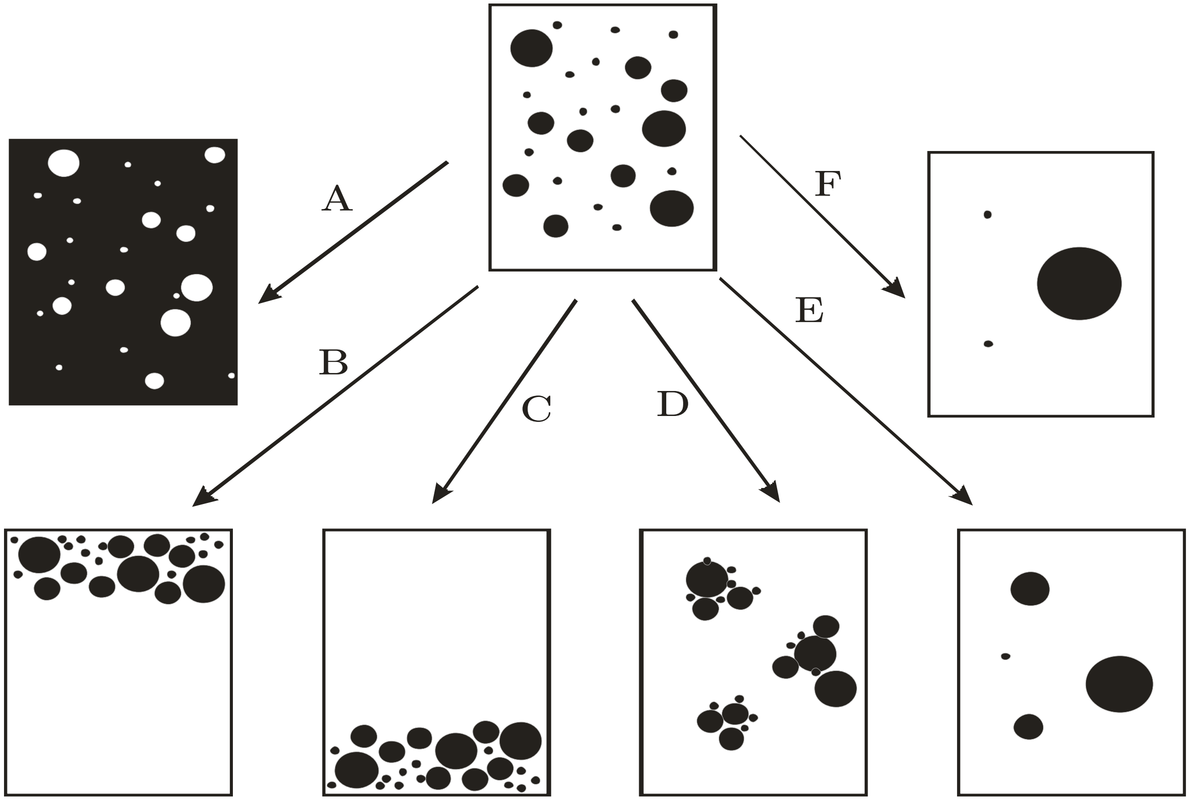
An emulsion system with an initial particle size of 235 *nm* was destabilized by dilution in a solution of an ionic surfactant opposite in sign to that of the particle charge. The three figures show the resulting distributions at times up to 4 days as reported in the figures.

Emulsion inversion

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



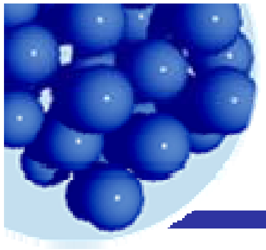
Emulsion processes



A – Inversion
B – Creaming

C – Sedimentation
D – Flocculation

E - Coalescence
F - Ripening

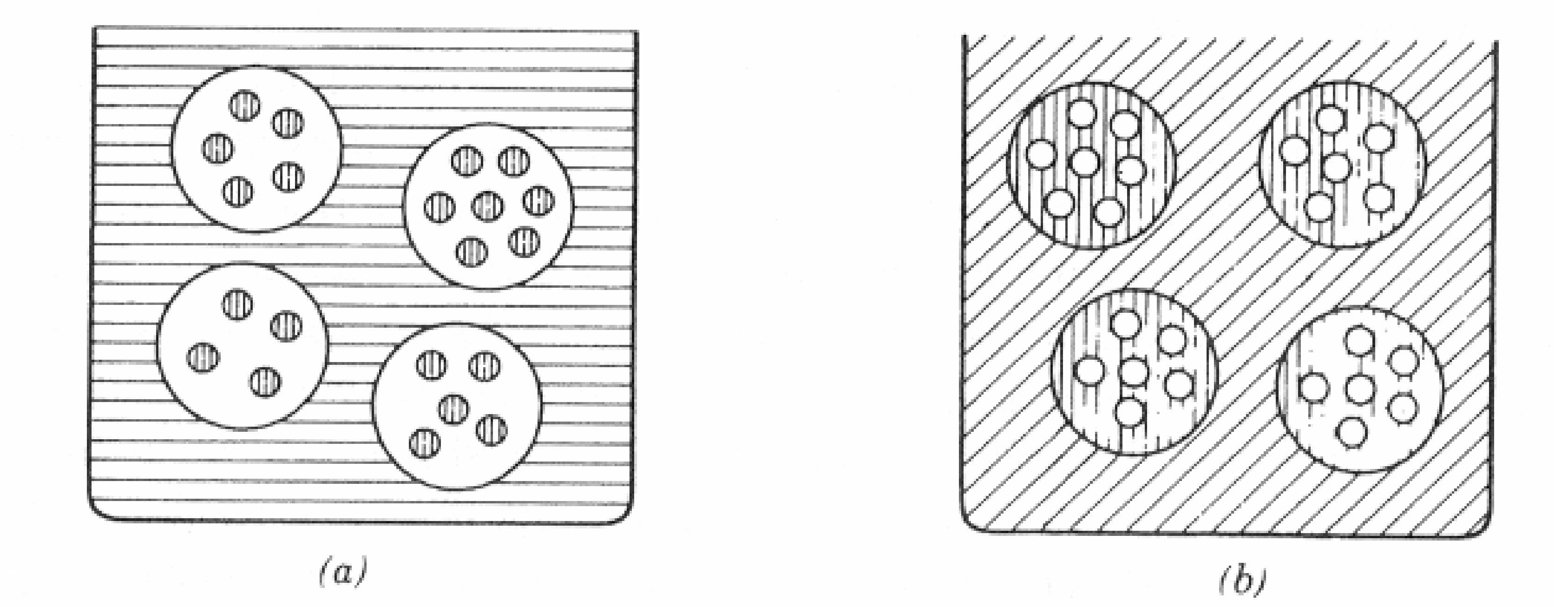


Demulsification – breaking emulsions

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.

Multiple emulsions



(a) W/O/W double emulsion

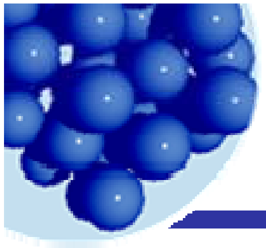
O/W/O double emulsion

Consider, for either diagram:

Each interface needs a different HLB value.

The curvature of each interface is different.

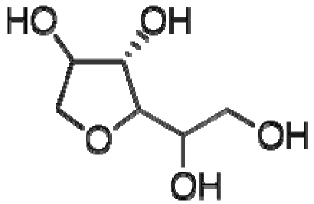
(Rosen, p. 313)



New

Emulsifiers come in graded series

Sorbitan (wikipedia)

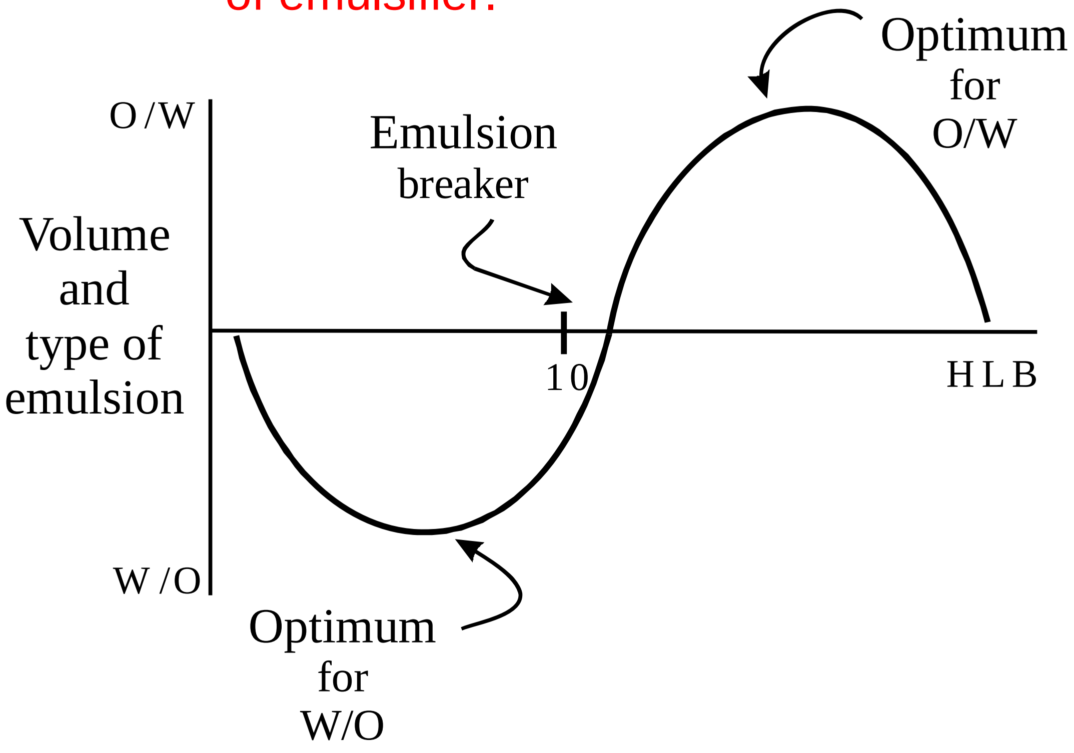


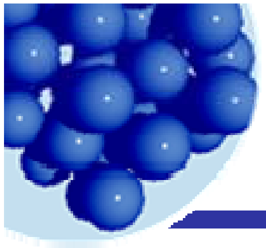
PEO (wikipedia)

Span 85	Sorbitan tri-oleate (3-C18, double bond)	HLB = 1.8	**Tween 85**	PEO(20)- Sorbitan tri-oleate	HLB = 11.0
Span 80	Sorbitan mono-oleate (C18, double bond)	HLB = 4.3	**Tween 80**	PEO(20)- Sorbitan mono-oleate	HLB = 15.0
Span 65	Sorbitan tristearate (3-C18, saturated)	HLB = 2.1	**Tween 65**	PEO(20)- Sorbitan tristearate	HLB = 10.5
Span 60	Sorbitan monostearate (C18, saturated)	HLB = 4.7	**Tween 60**	PEO(20)- Sorbitan monostearate	HLB = 14.9
Span 40	Sorbitan monopalmitate (C16, saturated)	HLB = 6.7	**Tween 40**	PEO(20)- Sorbitan monopalmitate	HLB = 15.6
Span 20	Sorbitan monolaurate (C12, saturated)	HLB = 8.6	**Tween 20**	PEO(20)- Sorbitan monolaurate	HLB = 16.7

The HLB Schema

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



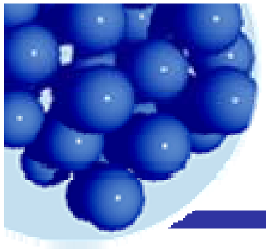


HLB Scale

Lipophilic End of Scale — Hydrophilic end of scale

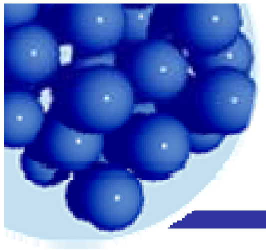
Stearane	Steric Acid	Sodium Stearate	Sodium Laurate	Sucrose	Sodium Sulfate
Soluble in oil; insoluble in water	Soluble in oil; insoluble in water	Soluble in oil; and in hot water	Slightly oil-soluble; soluble in water	Insoluble in oil; soluble in water	Insoluble in oil; soluble in water
Nonspreading on 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

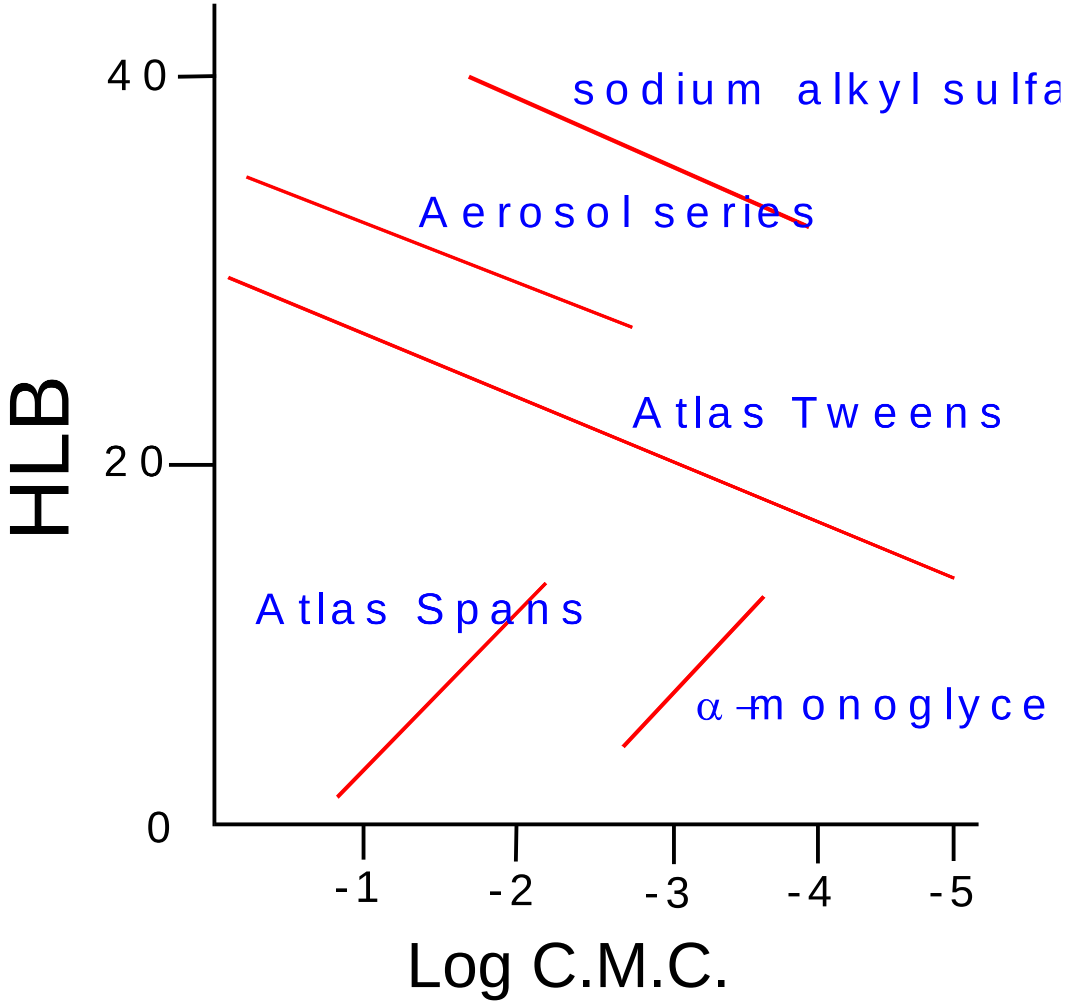


Group Numbers for Calculating HLB Values

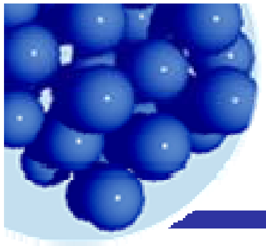
$$HLB = 7 + \sum(H) - \sum(L)$$

	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	
$-CH-$	0.475
$-CH_2-$	
CH_3-	
$=CH-$	
$(-CHCH_3CH_2O-)_n$	$0.15n$

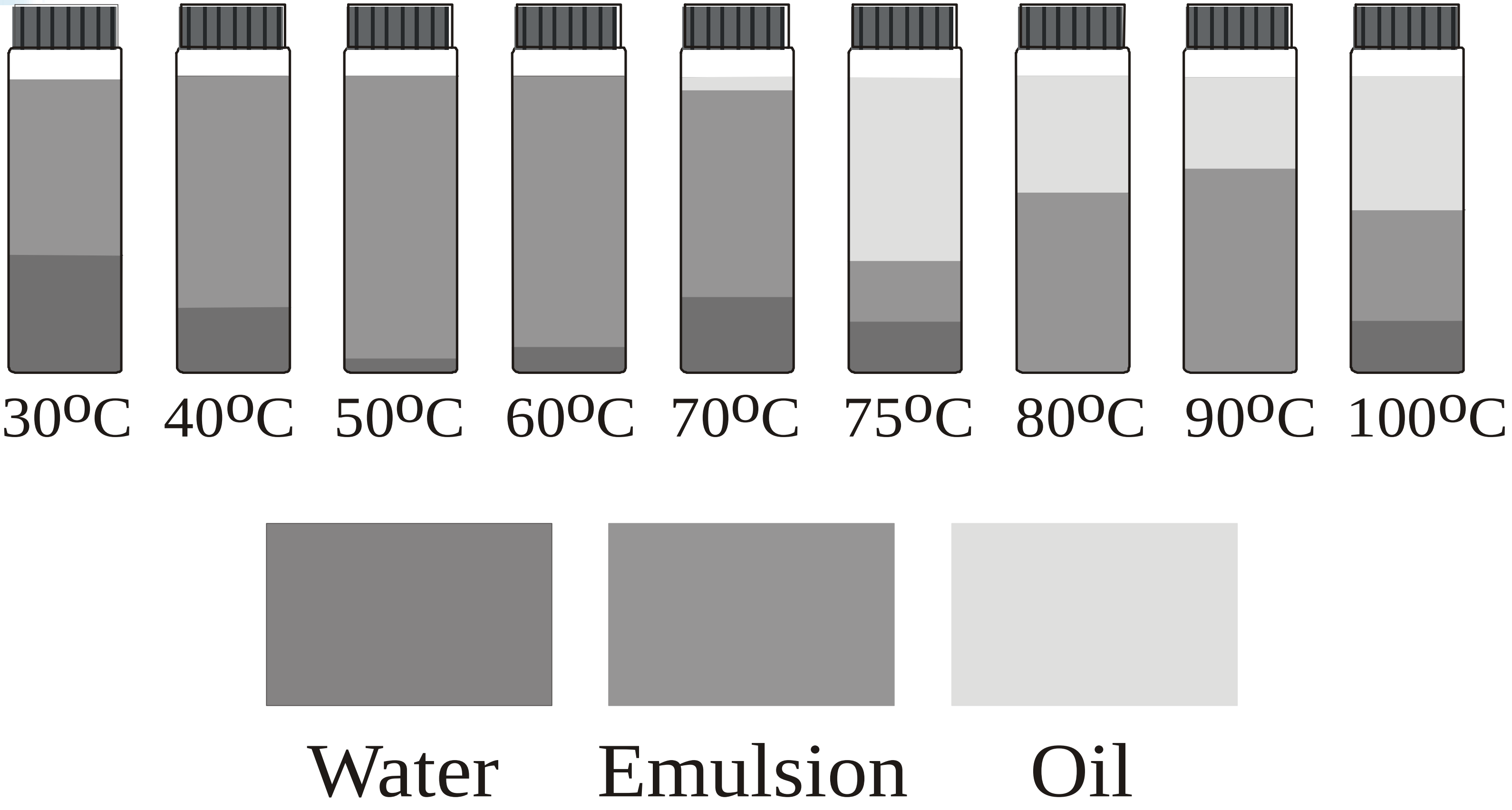
HLB and C.M.C.



40
20
0
HLB
sodium alkyl sulfa
Aerosol series
Atlas Tweens
Atlas Spans
α-monoglyce
-1
-2
-3
-4
-5
Log C.M.C.

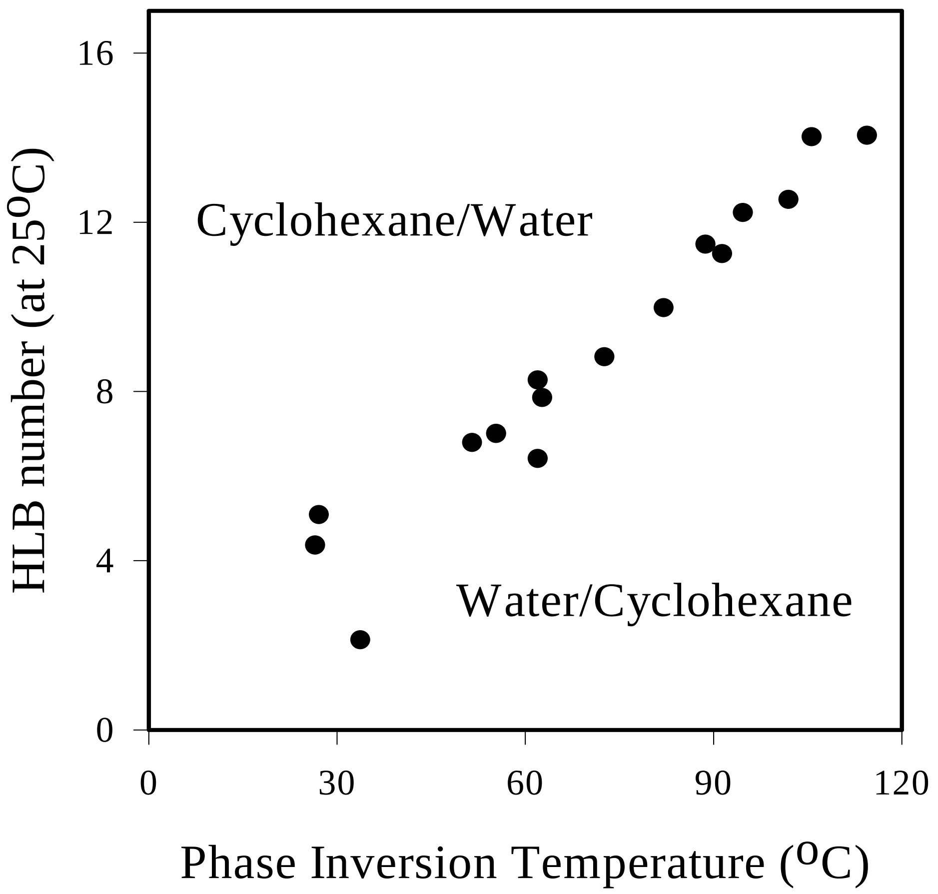


Phase inversion temperature

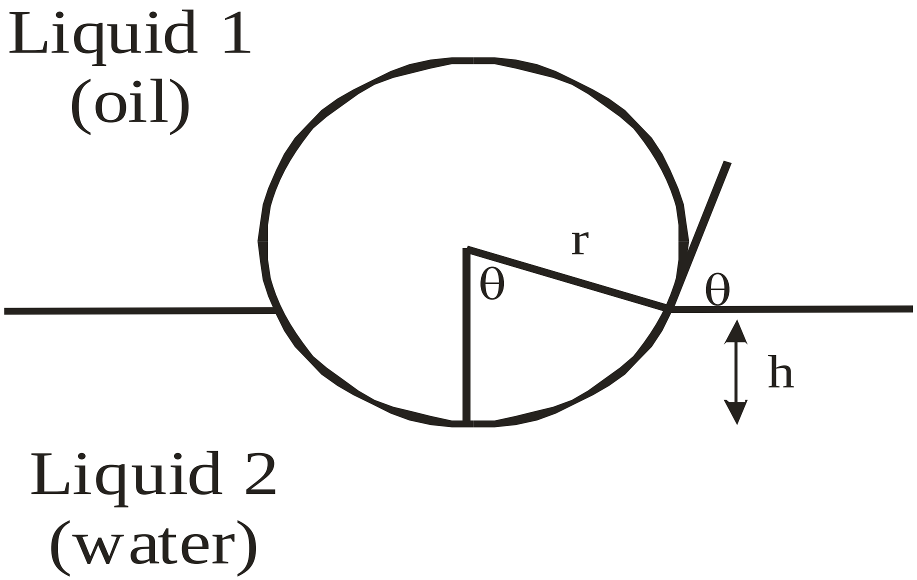


www.bias-net.com/chimica/pdf/set_baglioni.pdf

HLB and the Phase Inversion Temperature



Particles as emulsion stabilizers

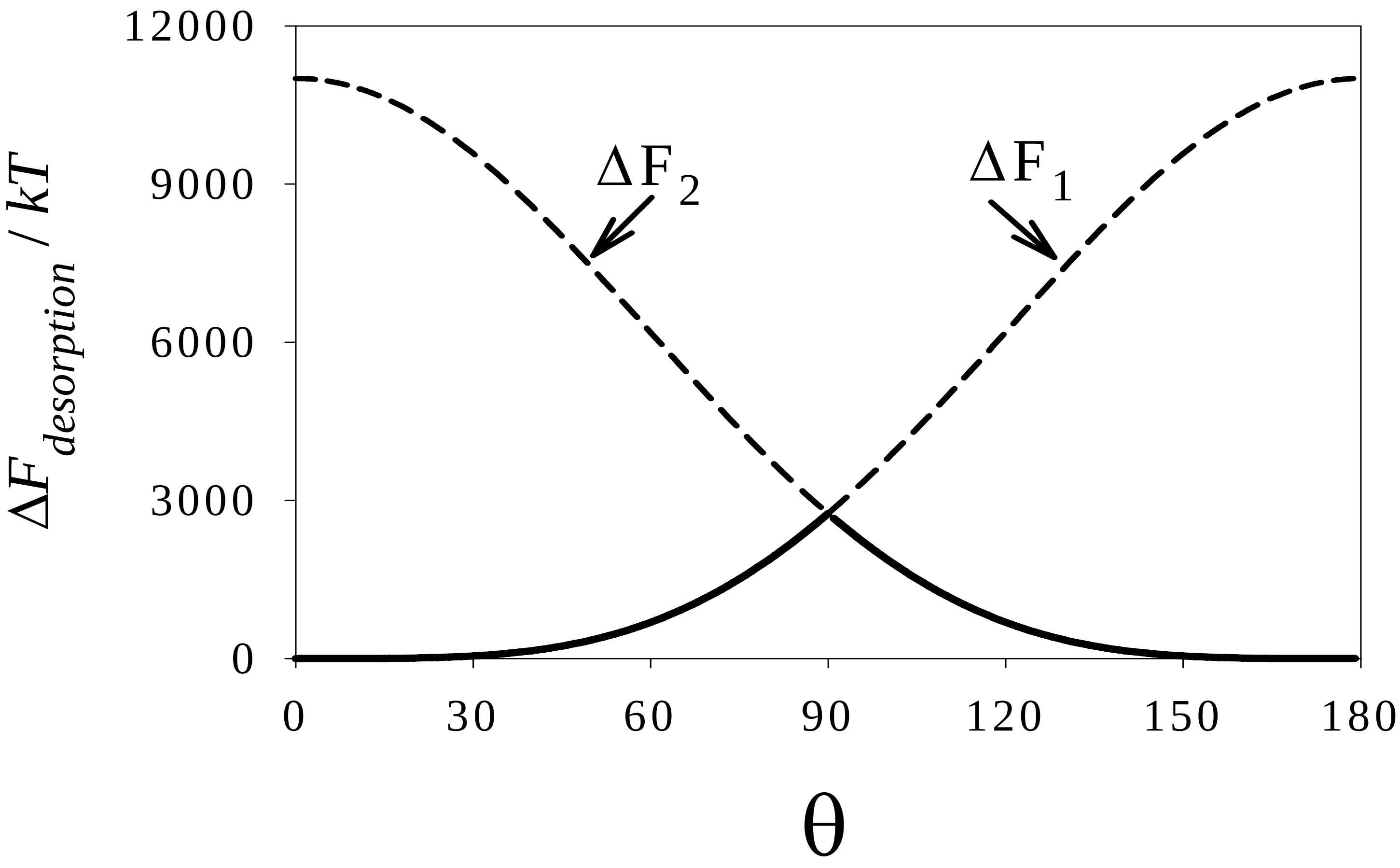


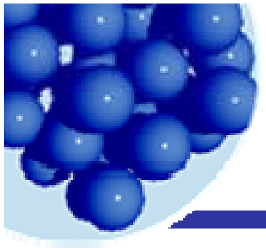
Almost all particles are only partially wetted by either phase.

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

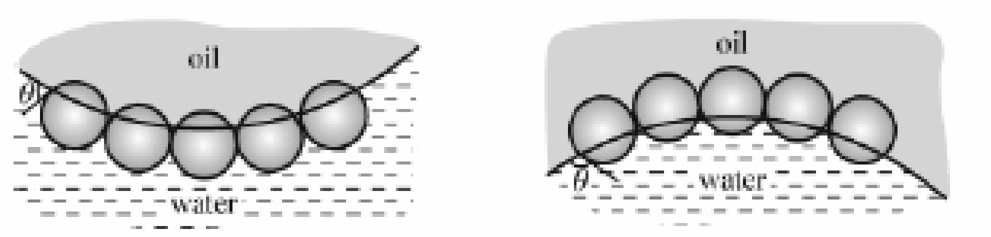
Crude oil is a W/O emulsion and is old!!

Stability as a function of contact angle





The thermodynamics is rich



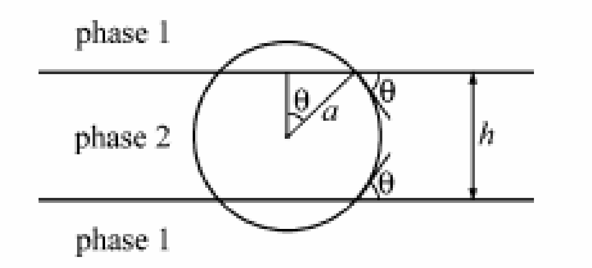


Figure 7. Sketch of a particle of radius *a*, which is bridging between the surfaces of a film from phase 2 formed between two drops of phase 1. *h* is the film thickness. õ is the contact angle.

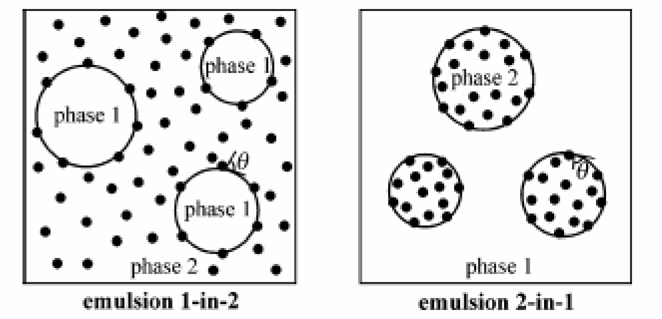


Figure 8. Definitions of phases, angles, and emulsions: By definition, the particles are initially dispersed in phase 2. The contact angle, õ, is always measured across phase 2. The emulsion 1-in-2 is a Bancroft-type emulsion, in which the particles are dispersed in the continuous phase. In contrast,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

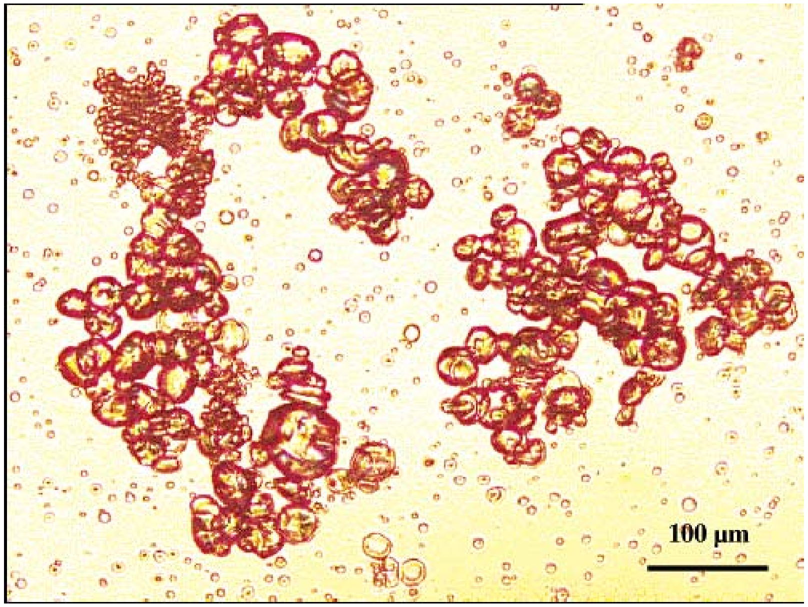


Figure 1. Microscopic image of a paraffin-in-water emulsion stabilized by CTAB alone. *T*) 25 °C.

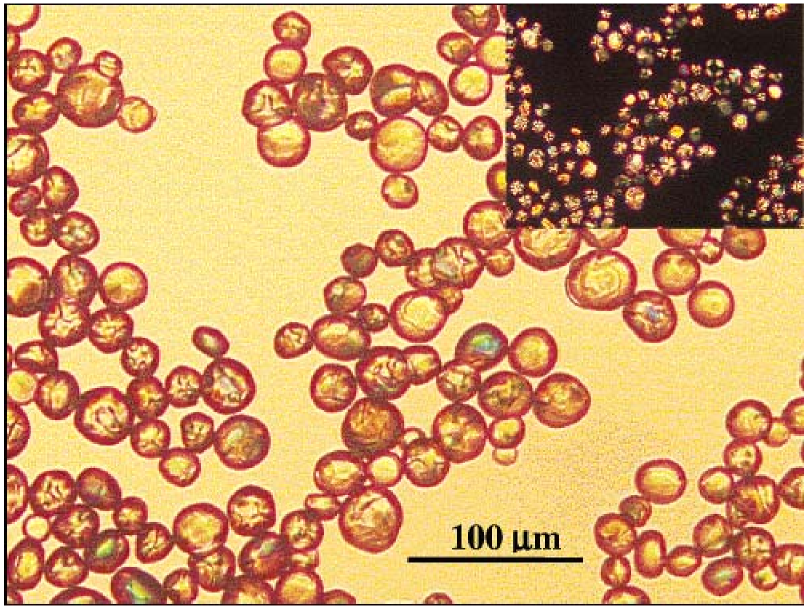


Figure 3. Microscopic image of a paraffin-in-water emulsion stabilized by P2 particles. Inset: same image taken at *T*) 25 °C under crossed polarizers, confirming the presence of crystals in the droplets.

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.

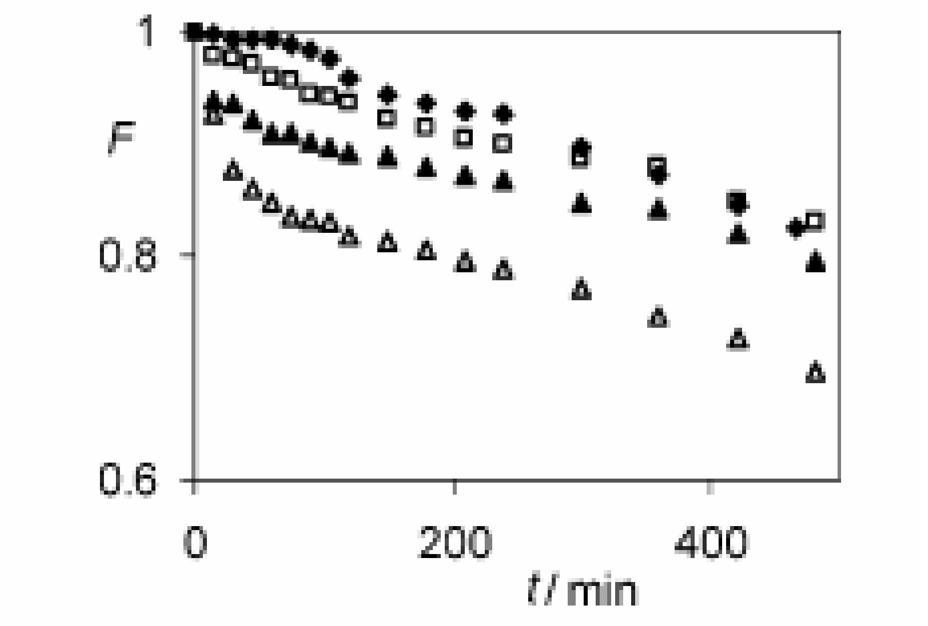
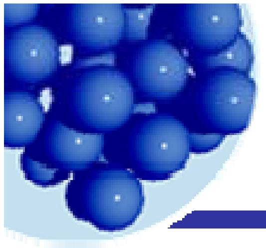


Figure 1. Fraction (*F*) of bubbles remaining as a function of time (*t*) formed in dispersions of 1wt%of 33% SiOR particles at different NaCl concentrations: 3 mol dm-3 ([), 2 mol dm-3 (0), 1 mol dm-3 (2), and 0.5 mol dm-3 (4).

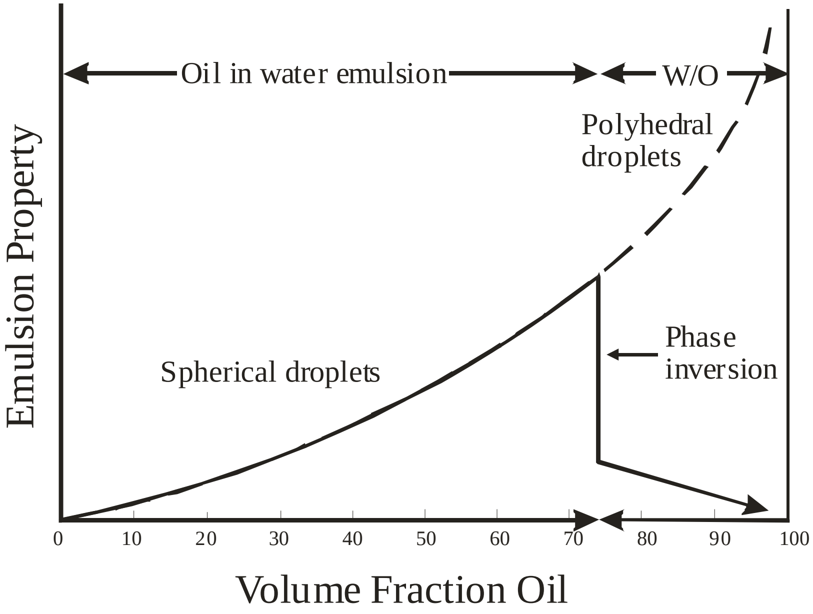
Thomas Kostakis, Rammile Ettelaie, and Brent S. Murray *Langmuir* **2006,** *22,* 1273-1280



Physical properties of emulsions

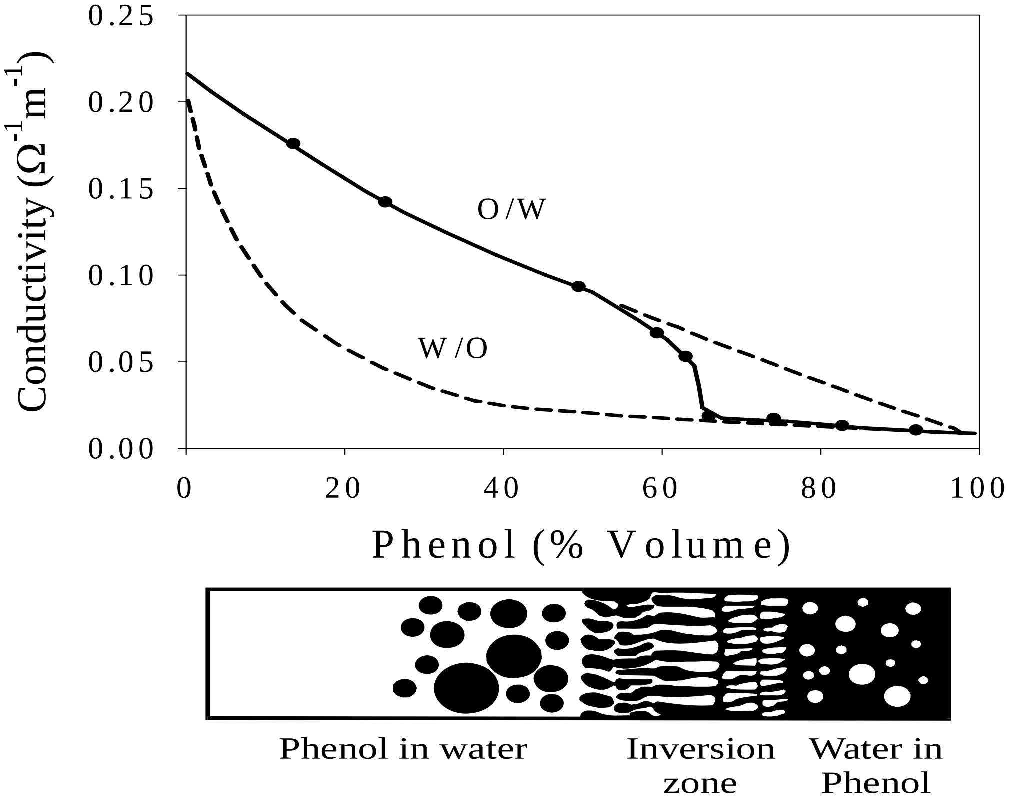
- **Identification** of “internal” and “external” phases; W/O or O/W
- **Droplet size and size distributions** – generally greater than a micron
- **Concentration of dispersed phase** – often quite high. The viscosity, conductivity, etc, of emulsions are much different than the continuous phase.
- **Rheology** – 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



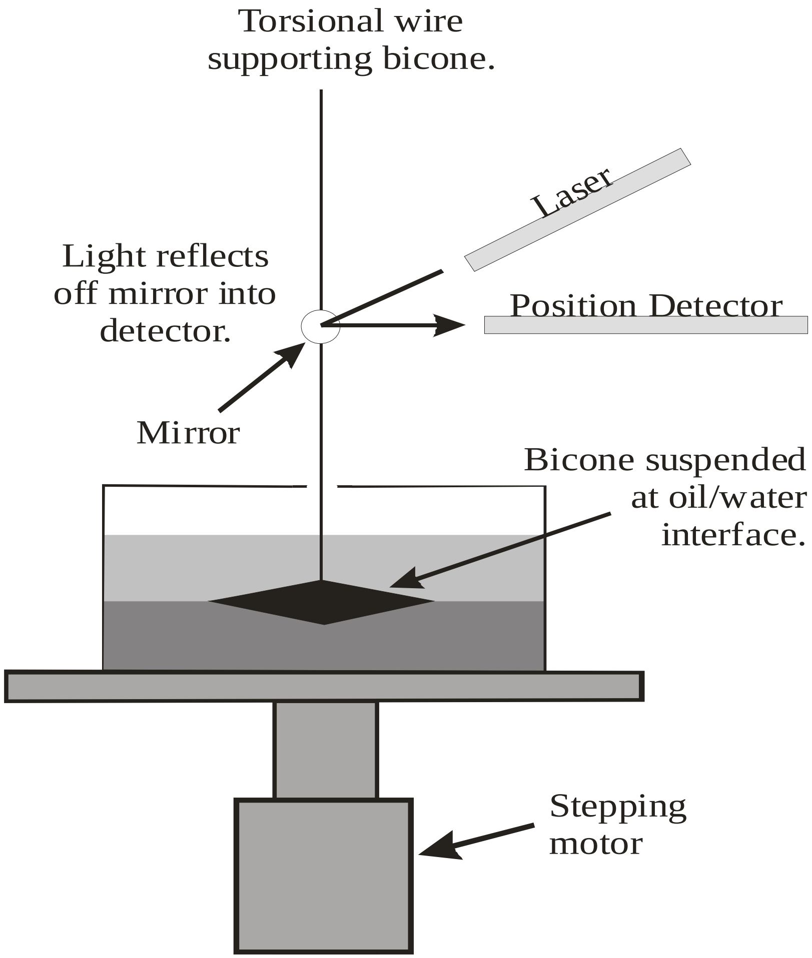
The variation of properties of emulsions with changes in composition. If inversion occurs, there is a discontinuity in properties, as they change from one curve to the other. Above 74% there is either a phase inversion or the droplets are deformed to polyhedra.

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

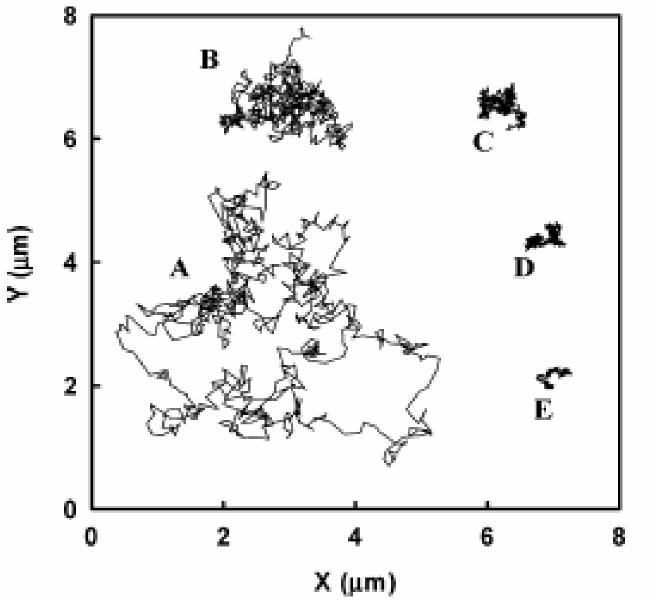


Figure 1. Typical trajectories of sulfate-treated PS (S-PS) particles at the oil−water interfaces for 756 s (700 frames) at 21 °C. The viscosities of the PDMS oil phase are (A) 350, (B) 1K, (C) 5K, (D) 20K, and (E) 60K cSt.

For viscous liquids:

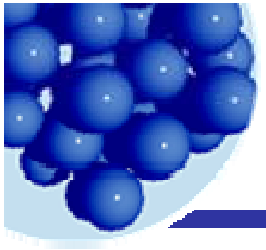
$$\left\langle \Delta r^2(\tau) \right\rangle = 4D\tau \quad \text{where} \quad D = \frac{k_B T}{4\pi\eta a}$$

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.

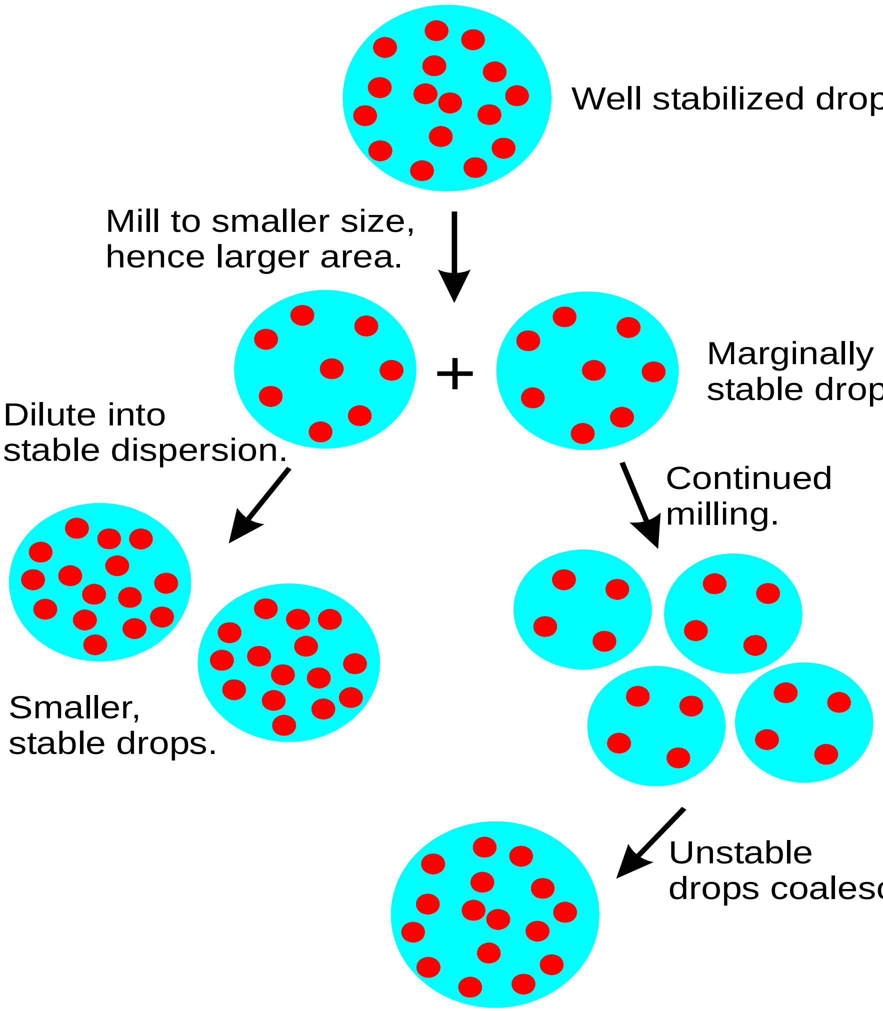
Wu and Dai, *Langmuir*, *23*, 4324 – 4331, **2007**.



Making emulsions

- Method of phase inversion
- PIT method
- Condensation methods - solubilize an internal phase in micelles
- Electric emulsification
- Intermittent milling

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.