

Chapter 2. Methodology of Nanomaterial

2.1 Template Method

2.1.1. Microemulsion

2.1.2. Nanostructured Polymer (Copolymer, DNA)

2.1.3. Nanostructured Ceramics (AAO, Porous Silica, Zeolite)

2.2. Non-template Method

2.2.1. Sol-gel Method

2.2.2. Vapor Deposition (Physical, Chemical)

2.2.3. Electrospinning



Chapter 2.1. Template Method



2.1.1. Microemulsion

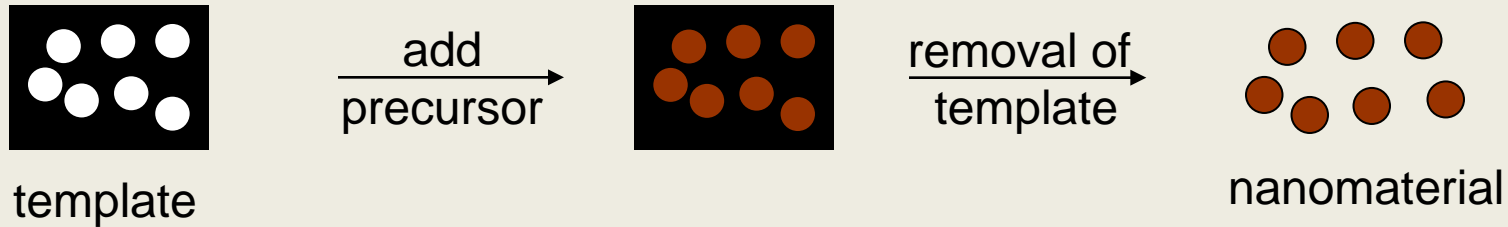
1. Introduction
2. Stability of microemulsions
3. Formation Mechanisms of micelles and microemulsions
4. Synthesis of organic nanomaterials from o/w microemulsions



1. Introduction

Template method to prepare the nanomaterials

- Concept



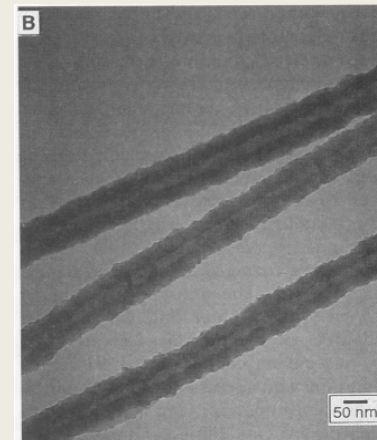
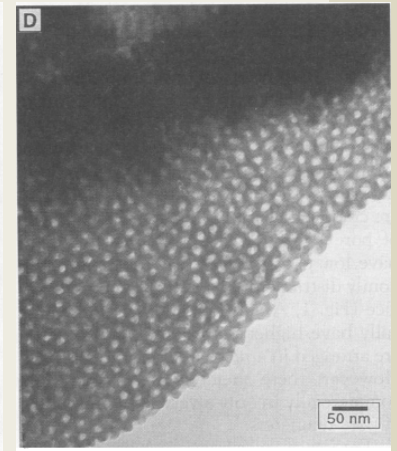
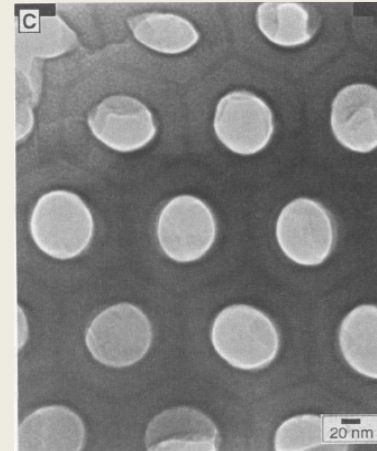
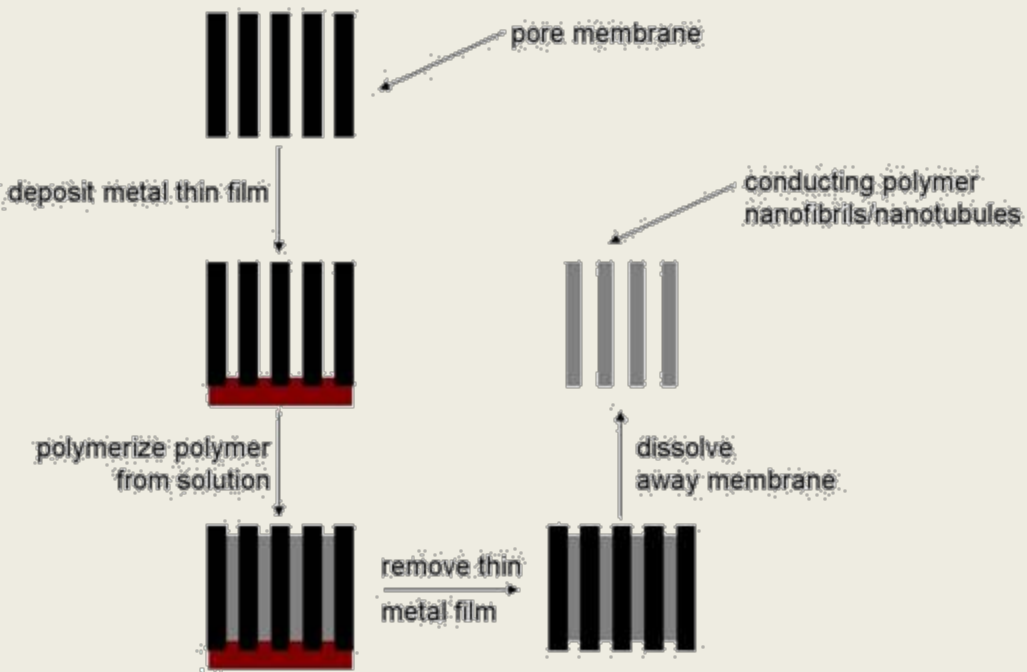
- Kinds of template

Anodized aluminum oxide (AAO)
Zeolite
Porous silicate
Colloidal particle
Polycarbonate membrane



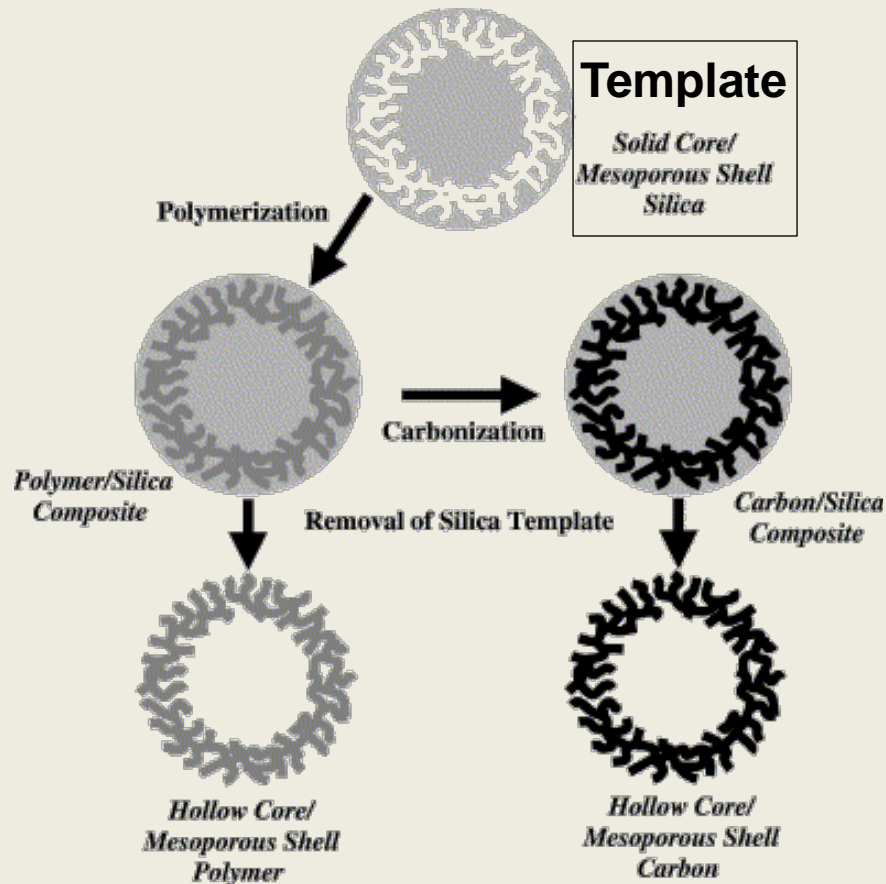
1. Introduction

Examples of template method



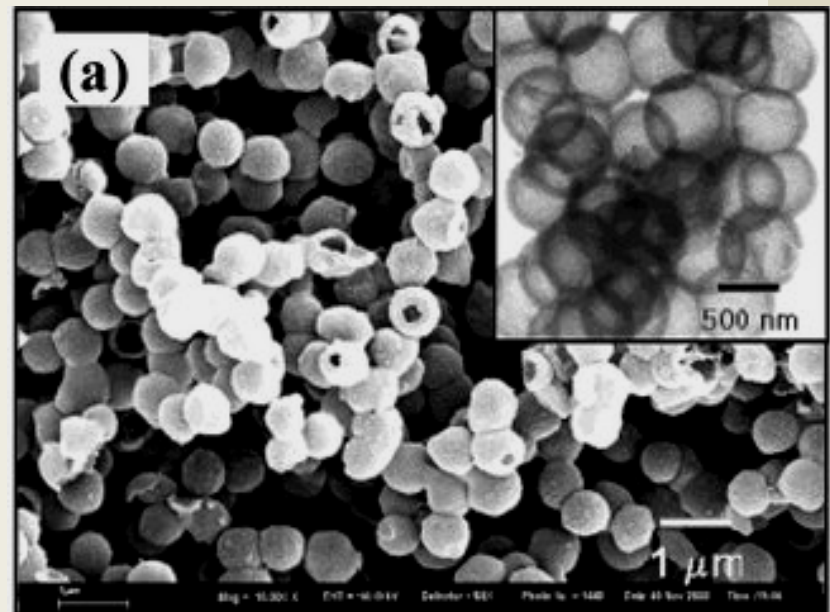
1. Introduction

Examples of template method



Hollow polymer and carbon spheres
using silica template

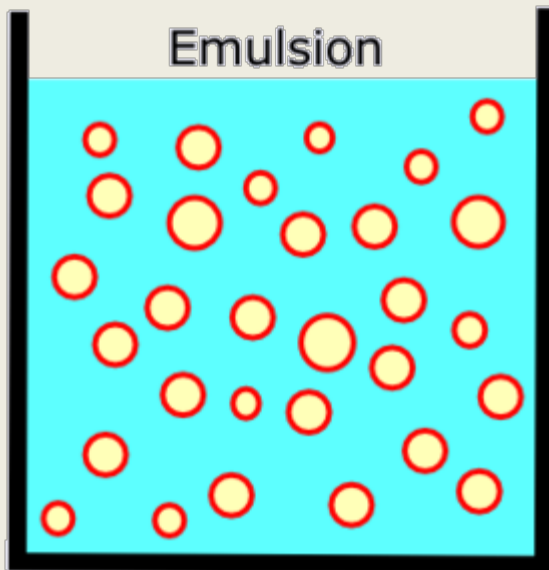
Microporous and Mesoporous Materials,
63 (2003) 1-9
*J. Mater. Chem.***14** (2004) 478–486



1. Introduction

1.1. What is emulsion?

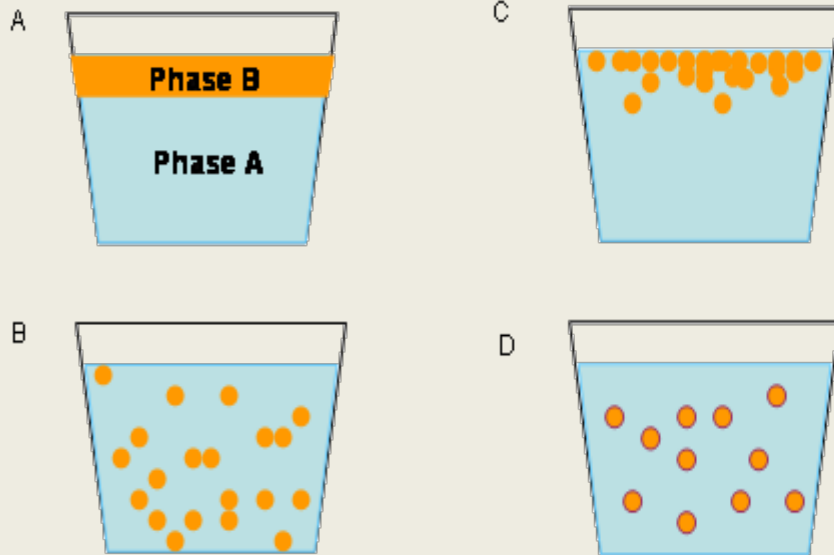
- IUPAC (International Union of Pure and Applied Chemistry) :
A state of liquid whereby liquid droplets and/or liquid crystals are dispersed in a liquid
- An emulsion is a thermodynamically unstable system consisting of at least two immiscible liquid phases, one of which is dispersed as globules in the other liquid phase, stabilized by the presence of an emulsifying agent.



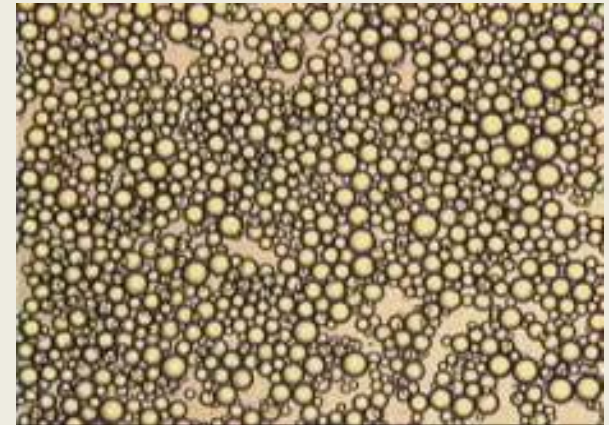
Ref. Wikipedia, the free encyclopedia

1. Introduction

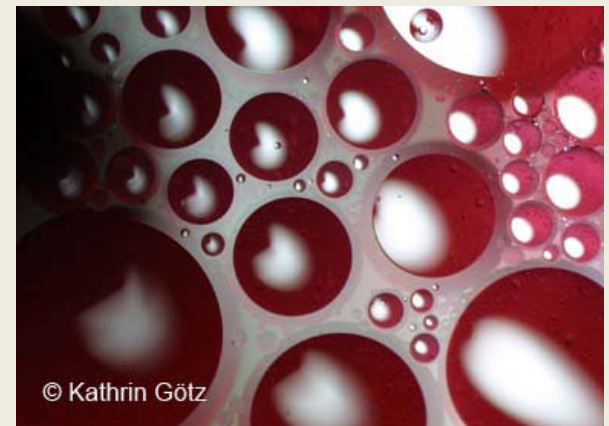
1.1. What is emulsion?



- A. Two immiscible liquids, not emulsified
- B. An emulsion of Phase B dispersed in Phase A
- C. The unstable emulsion progressively separates
- D. The (purple) surfactant positions itself on the interfaces between Phase A and Phase B, stabilizing the emulsion



<http://www.micropore.co.uk/images/200emulsion.jpg>



© Kathrin Götz
http://www.uni-bayreuth.de/departments/ddchemie/experimente/effekt/bilder/emulsion_11a.jpg



1. Introduction

1.1. What is emulsion?

※ **Colloids** : a colloid or colloidal dispersion is a substance with components of one or two phases. The size of dispersed phase particles in a colloid range from one nanometer to one micrometer

▪ Classification of colloids

		Dispersed Medium		
		Gas	Liquid	Solid
Continuous Medium	Gas	None*	Liquid Aerosol (Fog, mist)	
	Liquid	Foam (Whipped cream)	Emulsion (mayonnaise, hand cream)	Sol or Suspension (blood, pigmented ink)
	Solid	Solid Foam (Aerogel, styrofoam, pumice)	Gel (Gelatin, jelly, cheese, opal)	Solid Sol (ruby glass)

* All gases are soluble

1. Introduction

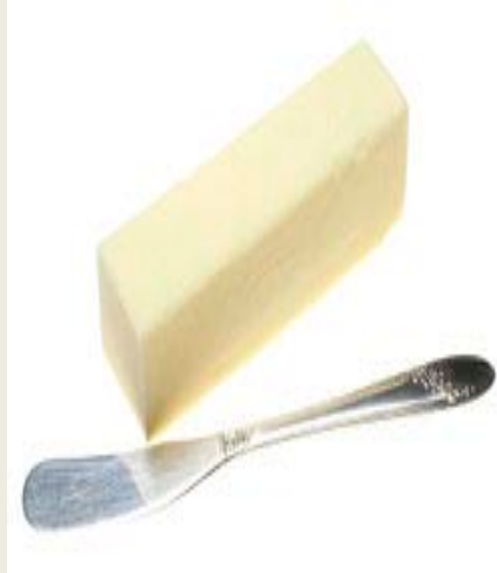
1.1. What is emulsion?

▪ Practical applications of emulsion

Foods: Butter (w/o), Mayonnaise

Home applications: Latex paints (o/w), Floor/glass waxes (o/w)

Cosmetics and medications: many cosmetic and personal-care preparations and medications



1. Introduction

1.2. Types of emulsion

- “dispersed phase” in “continuous phase”

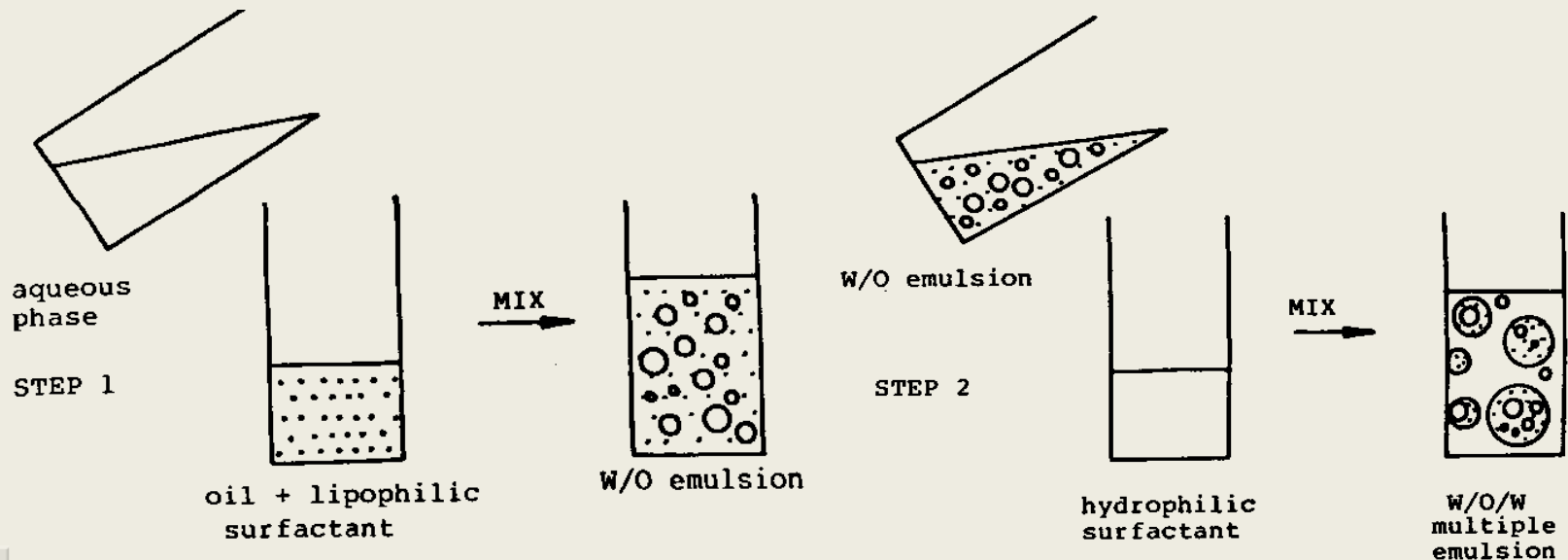
Oil-in-water (o/w)

Water-in-oil (w/o)

Oil-in-water-in-oil (o/w/o)

Water-in-oil-in-water (w/o/w)

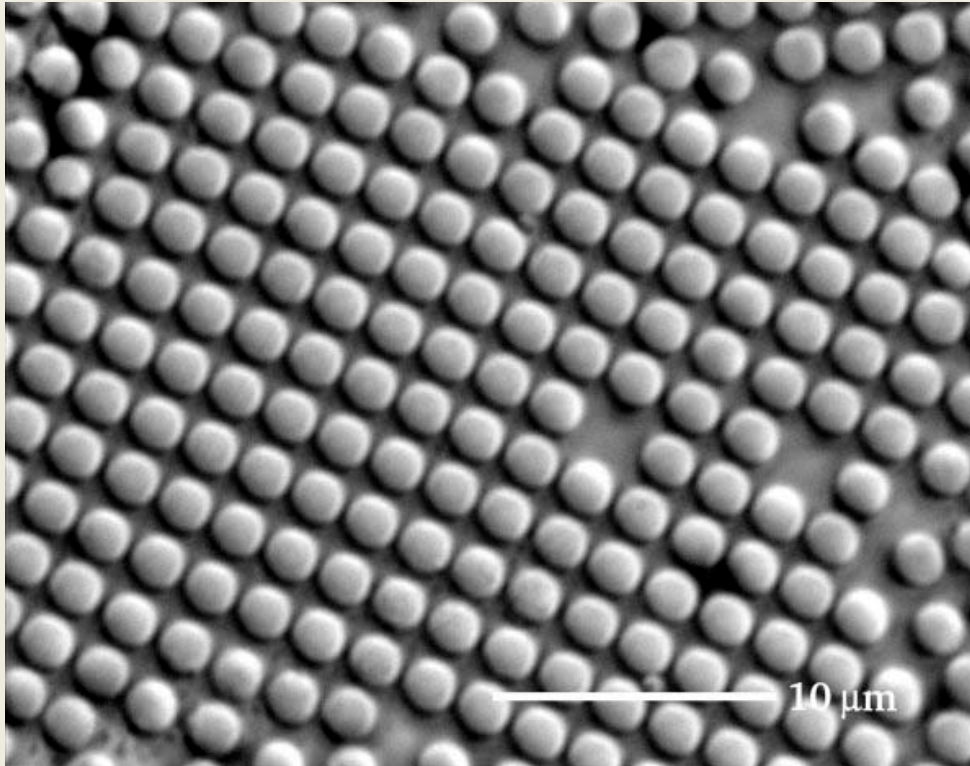
- Two-stage method of formulation of a W/O/W multiple emulsion



1. Introduction

1.2. Types of emulsion

▪ Monodisperse Emulsion



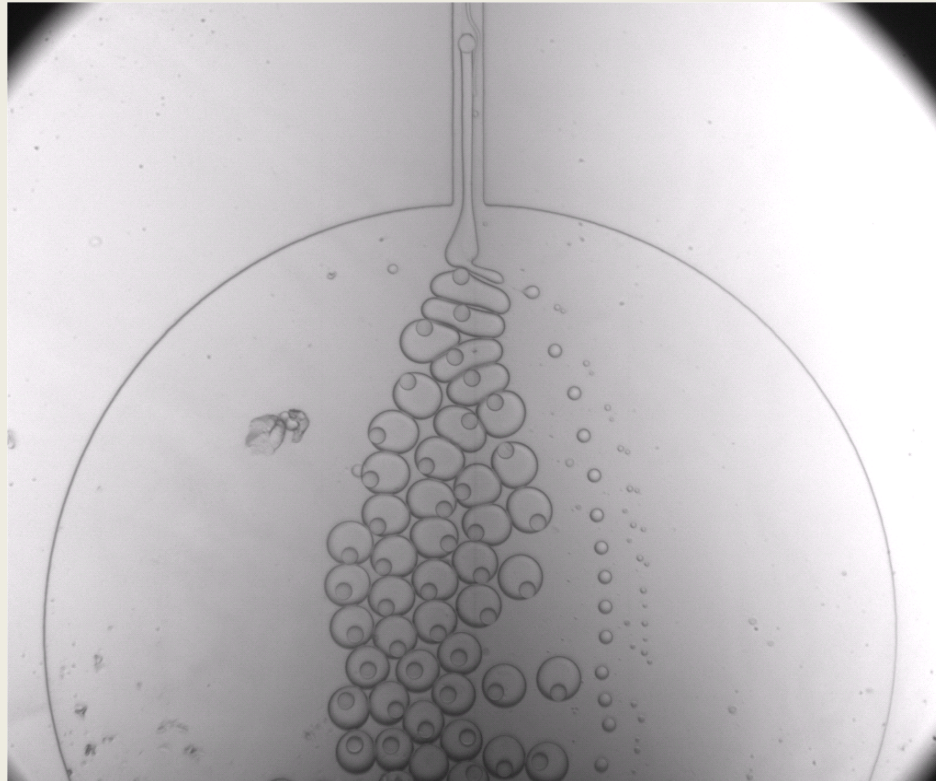
- Optical micrograph of monodisperse oil-in water emulsion.

V.N. Manoharan, A. Imhof, and D.J. Pine, "Photonic Crystals from Emulsion Templates", *Advanced Materials* **13** (6): 447–450 (2001)

1. Introduction

1.2. Types of emulsion

▪ Polydisperse Emulsion

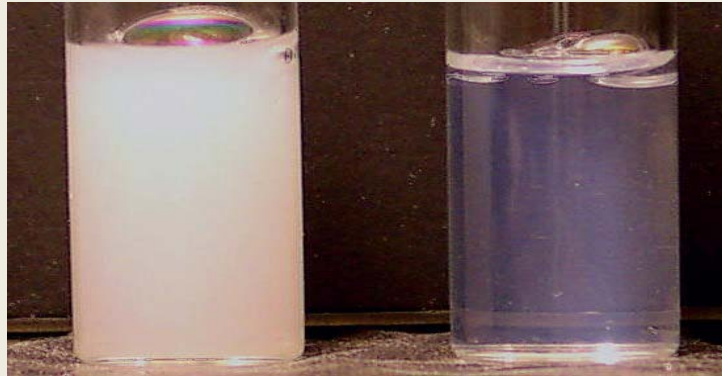


- Water/oil/water double emulsion made using a microfluidic device.
- The upper channel width is 50 micron. The inner drops are pure water, the outer drops are fluoro-carbon oil with fluorinated surfactants, and the outer phase is water with hydrophilic surfactants.

<http://www.seas.harvard.edu/weitzlab/coolpic03092005.html>

1. Introduction

1.3. What is microemulsion?



Macroemulsion	Microemulsion
Kinetically Stable	Thermodynamically Stable
1-10 μm (opaque)	Droplet size 10 - 100 nm (transparent)
Low surface area: 15 m^2/g	High surface area: 200 m^2/g
O/W IFT* 1-10 mN/m	Ultra Low O/W IFT ($10^{-2} - 10^{-3} \text{ mN/m}$)
W/O or O/W types	W/O , O/W and Bicontinuous types

*IFT : Interfacial Tension

1. Introduction

1.4. Surfactant

▪ What is surfactant?

: An abbreviation for **surface active agent**

: Be characterized by its tendency to absorb at surfaces and interfaces

▪ Interface : A boundary b/w any two immiscible phases

: 5 different interfaces exist

solid/vapor, solid/liquid, solid/solid, liquid/vapor, liquid/liquid
(vapor/vapor always miscible)

▪ Surface : One of the phases is a gas, usually air

▪ Interfaces involving a liquid phase

Interface	Type of system	Product
Solid-liquid	Suspension	Solvent-borne paint
Liquid-liquid	Emulsion	Milk, cream
Liquid-vapor	Foam	Shaving cream

1. Introduction

1.4. Surfactant

▪ Interfacial free energy (or interfacial tension: IFT)

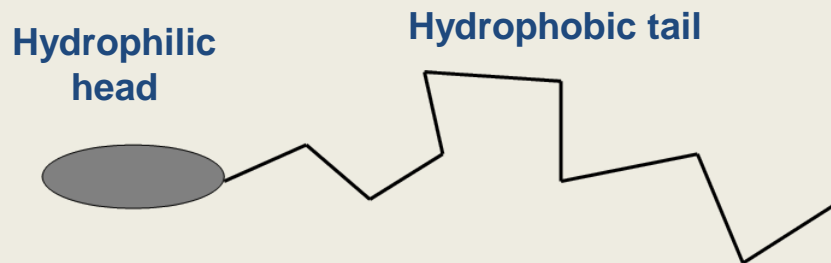
- A driving force for a surfactant to adsorb at an interface
- To lower the free energy of that phase boundary
- Representing the amount of work required to expand the interface
- When that boundary is covered by surfactant molecules, the surface tension is reduced → stabilizing the emulsion

▪ Nature of surfactant : amphiphilic (amphi-: both, -philic: -love)

Surfactant molecules = soluble part (lyophilic)

+ insoluble part (lyophobic) in a specific fluid

In water fluid, soluble part (hydrophilic) + insoluble (hydrophobic)



<Schematic illustration of a surfactant>

1. Introduction

1.4. Surfactant

▪ Surfactant aggregation in solution

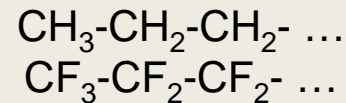
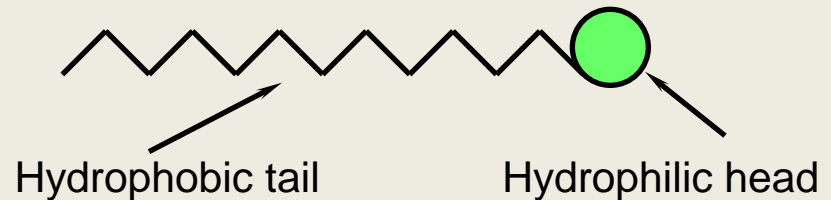
Oils and water do not mix!

Why?

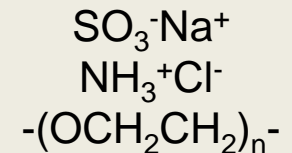
Water is a polar liquid, $\epsilon = 81$

Oils are non polar, $\epsilon \sim 2$
(ϵ - dielectric const.)

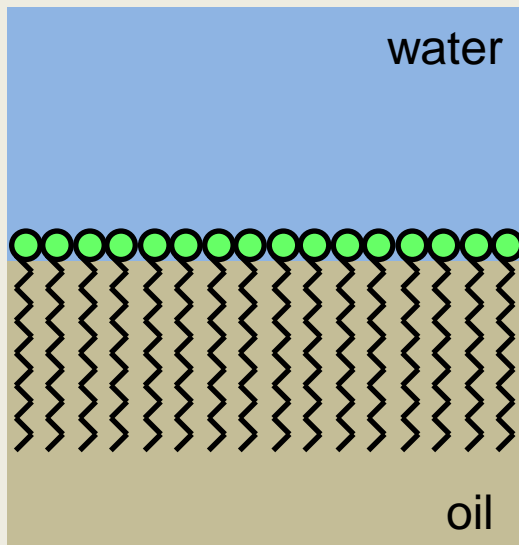
Surfactant molecule



strong interaction with oil



strong interaction with water



In solution, surfactant adsorbed on the surfaces
→ reduce the surface tension
→ form surfactant aggregation

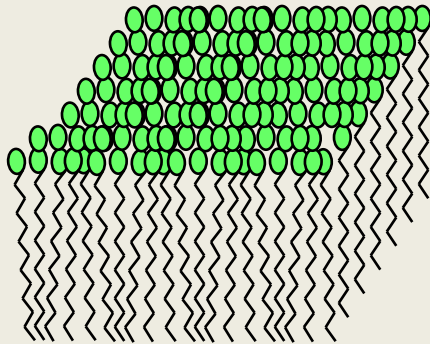
hydrophilic head - water
hydrophobic tail - oil

1. Introduction

1.4. Surfactant

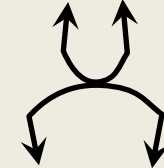
▪ Surfactant aggregation in solution

Surfactant film



Properties of the surfactant film:

- Interfacial tension
- Lateral elasticity
- Spontaneous curvature
- Bending elasticity
- Saddle splay elasticity



Properties of the surfactant film change with:

- Molecular structure
- Additives
- Ionic strength
- Co-surfactant
- Temperature, pressure etc.

1. Introduction

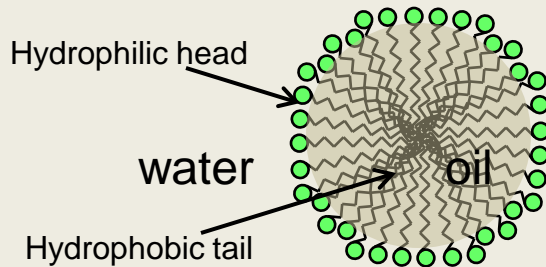
1.4. Surfactant

▪ Surfactant aggregation in solution

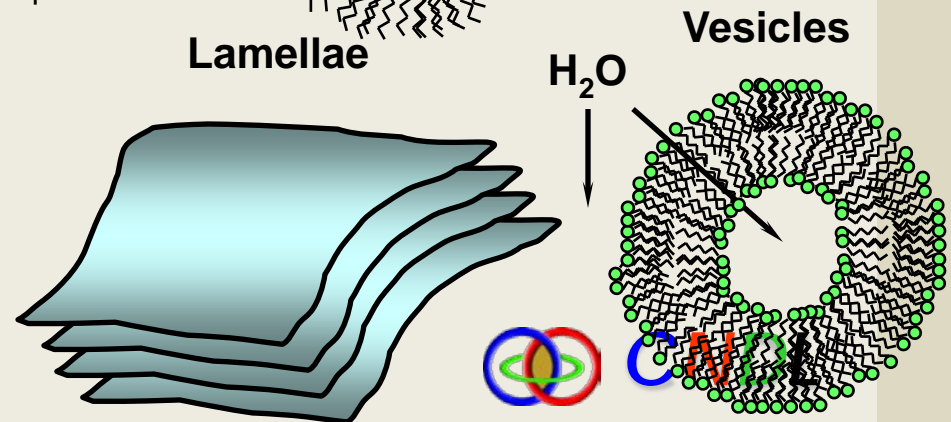
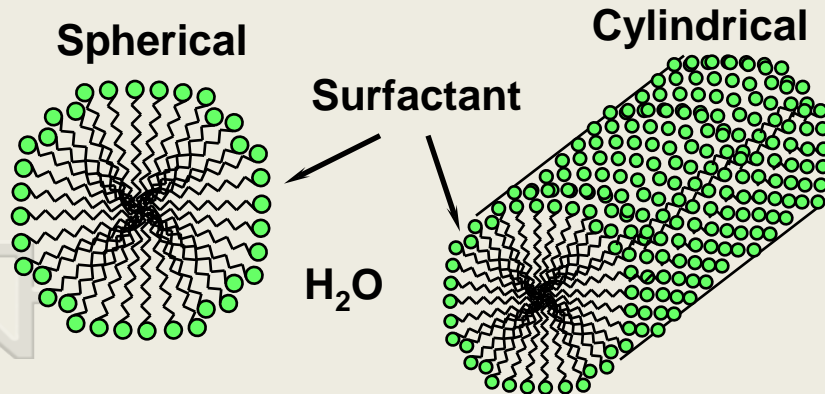
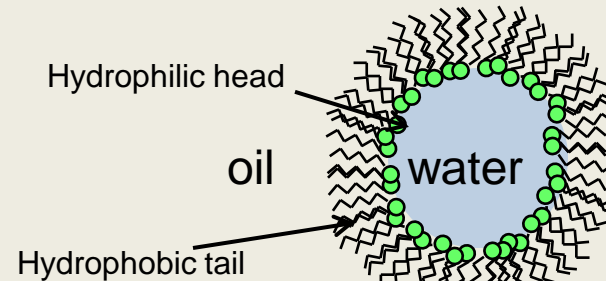
Micelle

- An aggregate of surfactant molecules dispersed in a liquid colloid
- The shape and size of a micelle is a function of the molecular geometry of its surfactant molecules and solution conditions such as surfactant concentration, temperature, pH, and ionic strength

Normal phase micelle (oil-in-water)

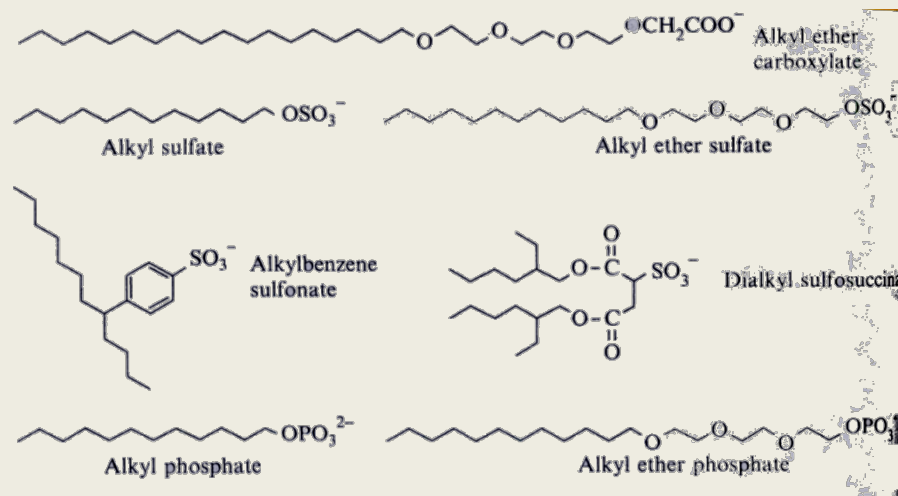


Inverse/reverse micelle (water-in-oil)

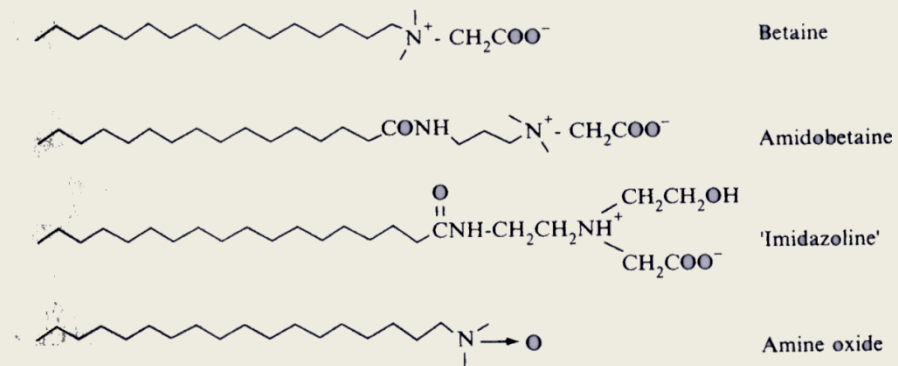


1. Introduction

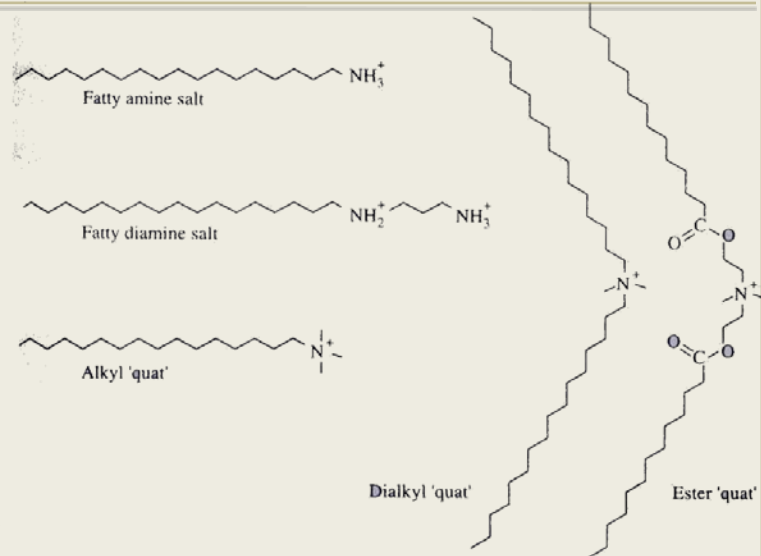
1.4. Surfactant



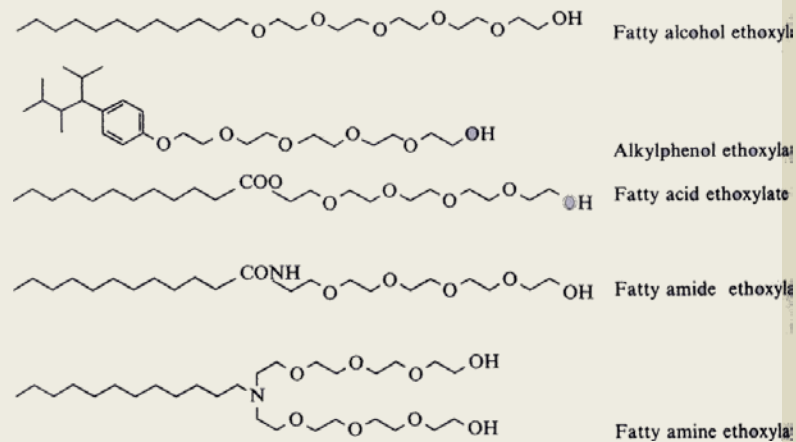
Anionic surfactants



Zwitterionic surfactants



cationic surfactants



Non-ionic surfactants

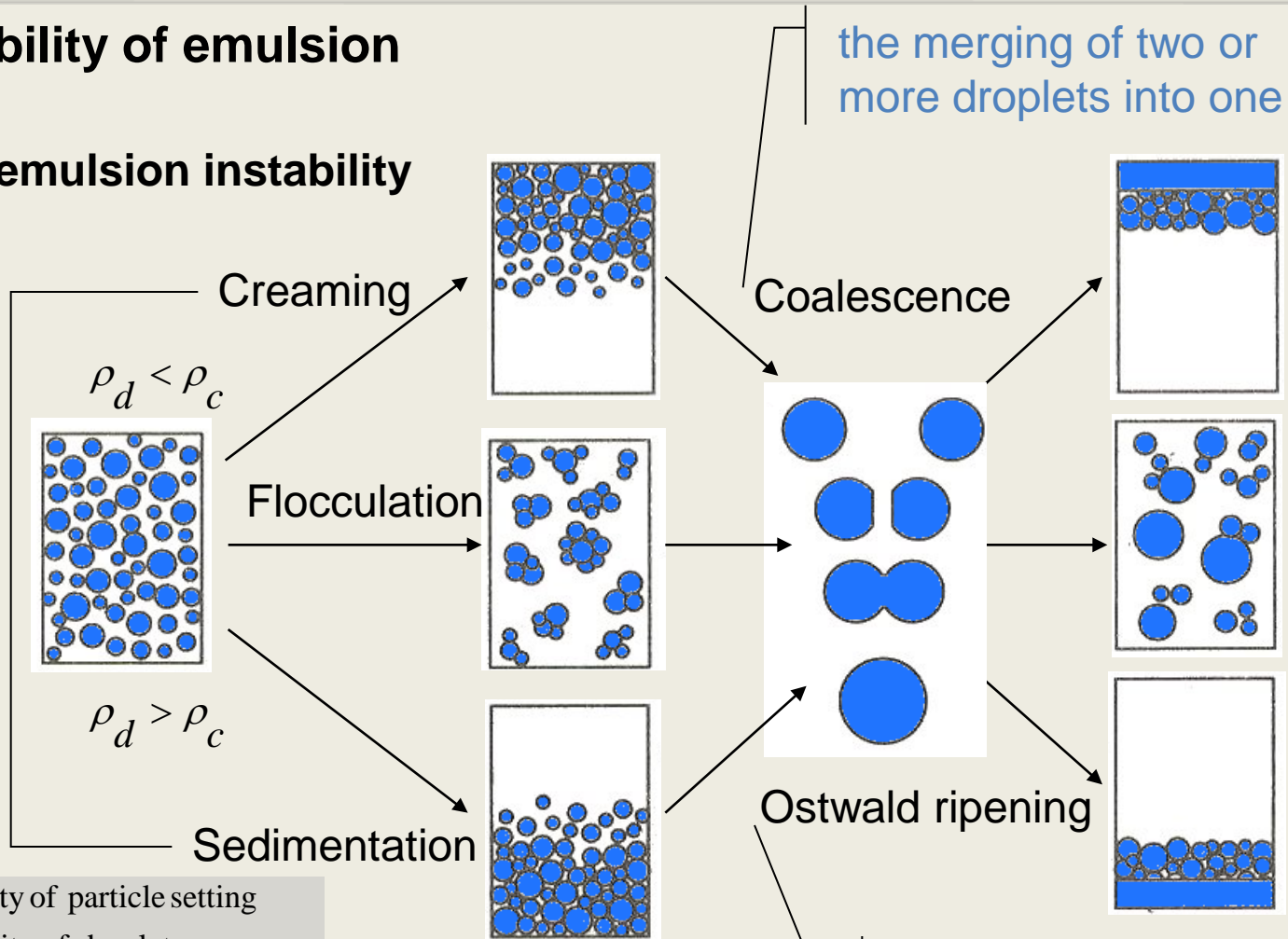
2. Stability of microemulsion

2.1. instability of emulsion

Types of emulsion instability

Stoke's law

$$v = -\frac{2gr^2(\rho_d - \rho_c)}{9\eta_c}$$



Appendix

v : velocity of particle setting
 ρ_d : density of droplets
 ρ_c : density of continuous liquid
 g : acceleration of gravity
 r : radius of droplets
 η_c : viscosity of continuous liquid

The big droplets will get bigger and the number of small droplets diminish

2. Stability of microemulsion

2.1. instability of emulsion

Effect of radius of droplet

Table. Calculated time for a droplet of variable sizes to move 5cm long in a vertical direction

r (μm)	100	10	1	0.1	0.01
t	11.5 s	10 min	32 h	133 d	36 yr

Radius of droplet $\downarrow \rightarrow$ velocity of particle setting \downarrow

Effect of stabilizer

- Increase the viscosity of the continuous phase, which makes it difficult for the droplets to move
- Protect the droplets by forming energy barrier between droplets

\rightarrow Deter flocculation and coalescence

2. Stability of microemulsion

2.2. Stability of microemulsion

Why are microemulsions thermodynamically stable?

$$\Delta G_M = \Delta G_1 + \Delta G_2 - T\Delta S_M$$

ΔG_M = free energy change for microemulsion formation

ΔG_1 = free energy change in the interfacial free energy

ΔG_2 = free energy change due to interaction between droplets

ΔS_M = increase in entropy due to dispersion of oil as droplets

$\Delta G_M < 0$: spontaneous formation of microemulsions

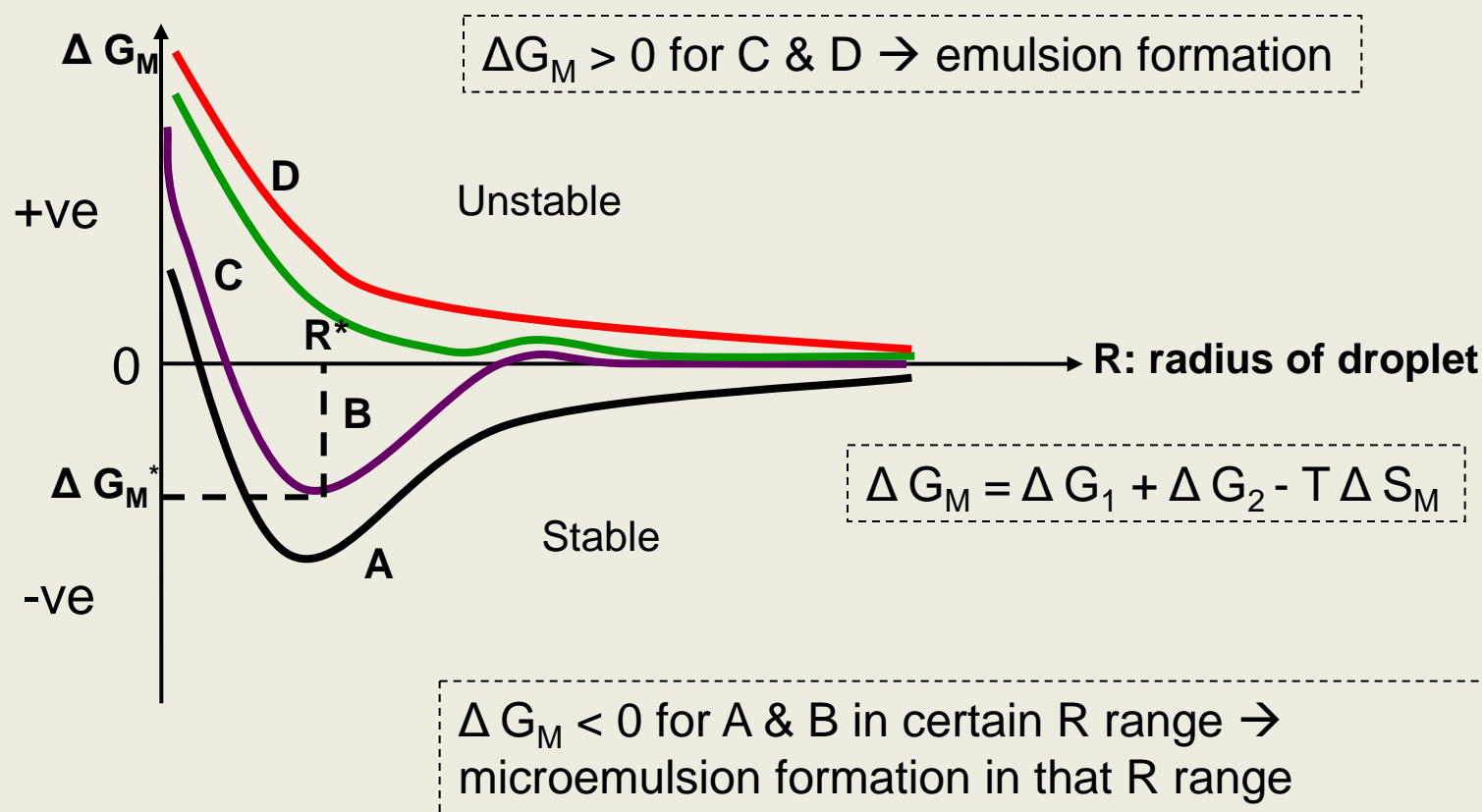
$\Delta G_M > 0$: only emulsion can be produced, which is thermodynamically
may be unstable



2. Stability of microemulsion

2.2. Stability of microemulsion

Why are microemulsions thermodynamically stable?



2. Stability of microemulsion

2.2. Stability of microemulsion

A. Interfacial free energy change

$$\Delta G_M = \Delta G_1 + \Delta G_2 - T \Delta S_M$$

If the droplets are assumed to be spherical, the increase in the free energy caused by the creation of interfacial area is given by

$$\Delta G_1 = 4\pi R^2 m (f_s + f_d)$$

R : radius of the droplets,

f_s : specific surface free energy of the uncharged surface,

f_d : specific surface free energy for the formation of the double layers,

m : total number of droplets

Appendix



2. Stability of microemulsion

2.2. Stability of microemulsion

$$\Delta G_M = \Delta G_1 + \Delta G_2 - T \Delta S_M$$

B. Energy of interaction among the droplets

- The pair potential between droplets at a distance r from centre to centre is denoted by $u(r)$.
- The probability of finding a particular droplet in a volume element, dV , at a distance r from the centre of a fixed droplet is $g(r)dV/V_c$.
- The number of droplets in a spherical shell of thickness dr :

$$\frac{m}{V_c} g(r) 4\pi r^2 dr$$

$$\left(\begin{array}{l} r : \text{distance between center of droplet} \\ m : \text{number of droplet} \\ g(r) : \text{radial distribution function} \\ V_c : \text{volume of the mixture which is taken as } 1\text{cm}^3 \end{array} \right)$$

- The interaction of a particular droplet with all other droplets is given by

$$U = \frac{m}{V_c} \int_{2R'}^{\infty} u(r) g(r) 4\pi r^2 dr \quad \left(\begin{array}{l} 2R' : \text{average distance b/w the centres of two nearest droplets} \\ \text{if the droplets are uniformly distributed} \end{array} \right)$$

- Since the volume fraction of closely-packed uniform spheres is 0.74

$$R' = R \left(\frac{0.74}{\phi_2} \right)^{\frac{1}{3}}$$

$$\therefore \Delta G_2 = \frac{m}{2} U$$



2. Stability of microemulsion

2.2. Stability of microemulsion

Microemulsions are formed because ...

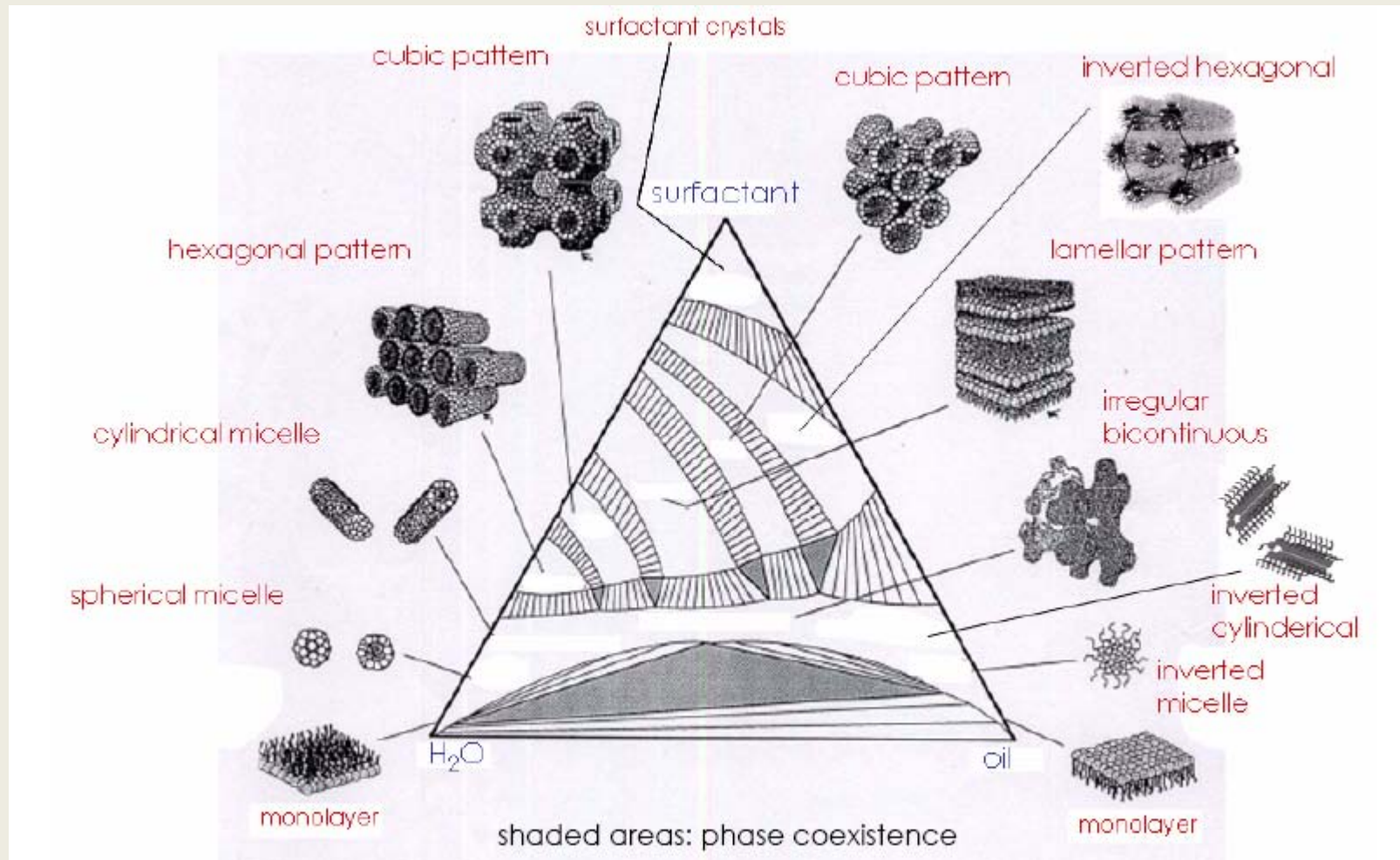
- The penalty for the apparent increase in free energy is compensated by the lowering of IFT to ultra low levels ($10^{-2} - 10^{-3}$ mN/m)
- The work done in lowering IFT is achieved through a gain in system entropy ΔS due to the creation of a large number of sub-micron sized droplets

All this occurs when at molecular levels, surfactants form the most condensed interfacial film between oil and water



3. Formation Mechanisms of Micelles and Microemulsions

Phase diagram: water + oil + surfactant



▪ How to explain?

3. Formation Mechanisms of Micelles and Microemulsions

3.1. Simple Geometric Factors

- The structures of micelle can be simply determined by the geometric factors of the surfactant at the interface.

▪ Critical packing parameter (CPP)

$$\frac{v}{a_0 l_c}$$

v : partial molecular volume of surfactant

a_0 : area of head group of surfactant

l_c : maximum chain length

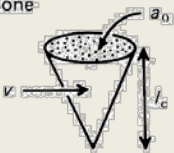
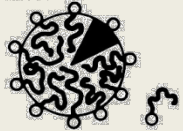

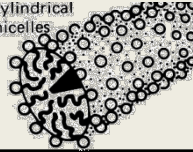

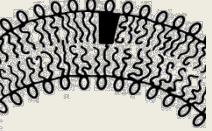

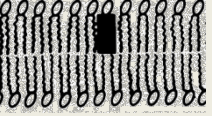

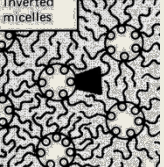
- (1) Spherical micelles : $\text{CPP} < 1/3$
- (2) Non-spherical micelles : $1/3 < \text{CPP} < 1/2$
- (3) Vesicles or bilayers : $1/2 < \text{CPP} < 1$
- (4) Inverted micelles : $1 < \text{CPP}$

- The change of environment (pH, temperature, ionic strength) will affect these parameters.



3. Formation Mechanisms of Micelles and Microemulsions

3.1. Simple Geometric Factors

Packing parameter	Critical packing shape	Structures formed
$<1/3$	Cone 	Spherical micelles 
$1/3-1/2$	Truncated cone 	Cylindrical micelles 
$1/2-1$	Truncated cone 	Flexible bilayers, vesicles 
~ 1	Cylinder 	Planar bilayers 
>1	Inverted truncated cone or wedge 	Inverted micelles 

-The relationship between aggregate type and geometry on the packing requirements of surfactant head group and chains

The most condensed interfacial film between oil and water is formed when maximum number of surfactants pack – Occurs when surfactants orient vertically !

Ref. Intermolecular and Surface Forces, Israelachvili, Jacob N.

3. Formation Mechanisms of Micelles and Microemulsions

3.1. Simple Geometric Factors

▪ Spherical micelles

- Usually formed by anionic surfactants
- For an o/w micelles, this can be done by adjusting the repulsion between head groups, resulting in large values for a_0 .

▪ Cylindrical micelles

- It is a quite common phenomenon that micelles grow as the preferred surface curvature decreases. Any change that reduces the effective head group area will lead to the growth of micelles.

- Basic three ways to form cylindrical micelles

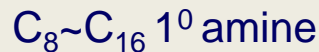
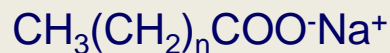
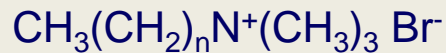
- ① addition of a cosurfactant with a very compact head group (i.e. n-alkanol)
- ② changing the counterion (i.e. changing Na^+ to Mg^{2+} reduce the effective volume of head groups.)
- ③ by electrolyte addition or temperature change (i.e. reduce the area of the head groups)



3. Formation Mechanisms of Micelles and Microemulsions

✓ However it is difficult to explain the mesophase formation transition by various conditions with only geometry

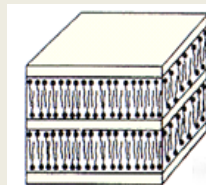
surfactant



hexagonal



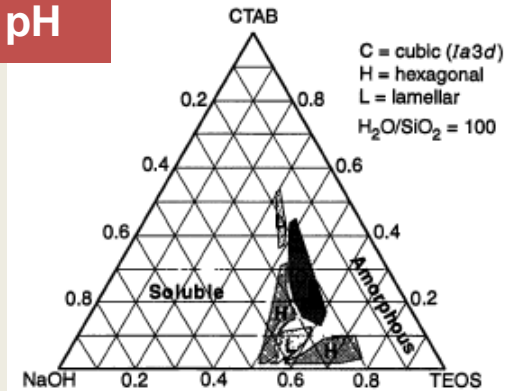
cubic



lamellar

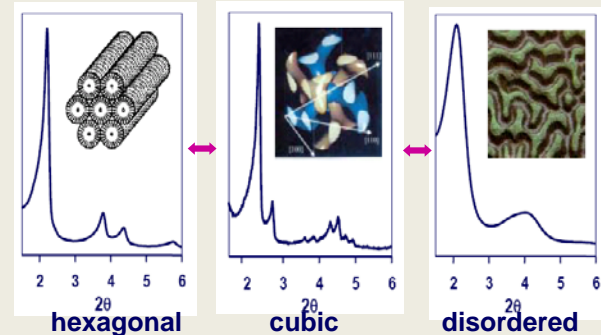
Chem.Mater.,8,1147,(1996)

pH



Science , 267,1138, (1995)

cosolvent



J.Phys.Chem.B., 107,10405 (2003)

3. Formation Mechanisms of Micelles and Microemulsions

3.2. Formulation of microemulsion – Bancroft's rules

▪ Bancroft's rules

- *“The liquid in which the stabilizer has a higher solubility forms the continuous phase.”*
W.D.Bancroft, *J.Phy.Chem.*16 (1912) 177
- What makes an emulsion oil-in-water or water-in-oil is not the relative percentages of oil or water, but which phase the emulsifier is more soluble in.
- The type of emulsion (i.e. o/w or w/o) is dictated by the emulsifier and that the emulsifier should be soluble in the continuous phase.
- The Hydrophilic-lipophilic balance (or HLB) of a surfactant can be used in order to determine whether it's a good choice for the desired emulsion or not.
- Low HLB emulsifiers are soluble in oil and give rise to w/o emulsions.



3. Formation Mechanisms of Micelles and Microemulsions

3.2. Formulation of microemulsion – Bancroft's rules

▪ HLB Concept

- In an attempt to extend it into some kind of quantitative relationship between surfactant hydrophilicity and function in solution, Griffin introduced the concept of the hydrophilic-lipophilic balance (HLB) of a surfactant.
- Griffin's HLB numbers were restricted to non-ionic surfactants.

Table. Use of Griffin's HLB number concept

HLB number range	Appearance of aqueous solution
1-4	No dispersibility
3-6	Poor dispersibility
6-8	Milky dispersion after agitation
8-10	Stable milky dispersion
10-13	From translucent to clear
13-20	Clear solution

HLB number range	Application
3-6	w/o Emulsifier
7-9	Wetting agent
8-14	o/w Emulsifier
9-13	Detergent
10-13	Solubilizer
12-17	Dispersant

An arbitrary scale of 0 to 20 :
: 0 ~ completely hydrophobic molecule
20 ~ completely hydrophilic molecule

3. Formation Mechanisms of Micelles and Microemulsions

3.2. Formulation of microemulsion – Bancroft's rules

▪ HLB Concept

- Griffin's HLB number concept was later extended by Davies, who introduced a scheme to assign HLB numbers to chemical groups which compose as surfactant.

Determination of HLB numbers according to Davies

$$\text{HLB} = 7 + \sum (\text{hydrophilic group numbers}) + \sum (\text{lipophilic group numbers})$$

Group	HLB number
<i>Hydrophilic</i>	
–SO ₄ Na	35.7
–CO ₂ K	21.1
–CO ₂ Na	19.1
–N (tertiary amine)	9.4
Ester (sorbitan ring)	6.3
Ester (free)	2.4
–CO ₂ H	2.1
–OH (free)	1.9
–O–	1.3
–OH (sorbitan ring)	0.5
<i>Lipophilic</i>	
–CF ₃	–0.870
–CF ₂ –	–0.870
–CH ₃	–0.475
–CH ₂ –	–0.475
–CH–	–0.475
–CH–	

Ref.) K.Holmberg, Surfactants and polymers in aqueous solution, 2nd Ed., John Wiley & Sons Ltd, England, 2003, p.460

J.T.Davies, Proceedings of the International Congress of Surface Activity, 1957, 426-438

3. Formation Mechanisms of Micelles and Microemulsions

3.2. Formulation of microemulsion – Bancroft's rules

▪ HLB Concept

“The HLB method of selecting an emulsifier is crude but simple.”

- Some general guidelines for the selection of surfactants as emulsifier
 - (1) The surfactant should have a strong tendency to migrate to the oil-water interface.
 - (2) Oil-soluble surfactants preferably form w/o emulsions, and vice versa.
 - (3) Good emulsions are often formed by using a mixture of one hydrophilic and one hydrophobic surfactant.
 - (4) The more polar the oil phase, then the more hydrophilic the emulsifier should be, and vice versa.

Table. The use of the HLB method in selecting an emulsifier.

Emulsification of a mixture of 20% paraffin oil (HLB=10) and 80% aromatic mineral oil (HLB=13) in water

HLB number of oil: $10 \times 0.20 + 13 \times 0.80 = 12.4$

A mixture of $C_{12}E_{24}$ with HLB = 17.0 and $C_{16}E_2$ with HLB = 5.3 is used.
A 60:40 mixture of the two gives a surfactant HLB number as follows:

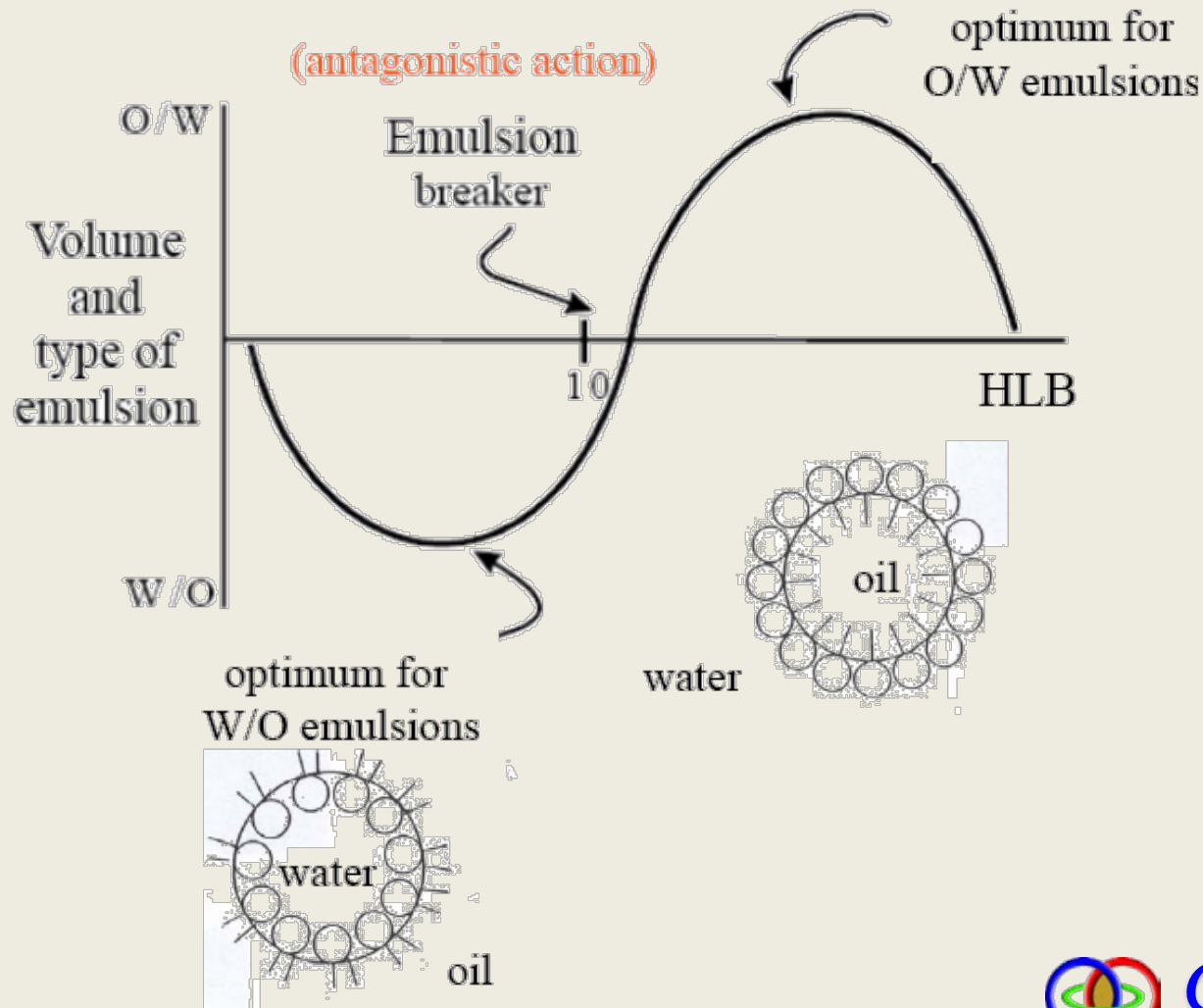
$17.0 \times 0.60 + 5.3 \times 0.40 = 12.3$

This surfactant combination is found to give excellent emulsion stability.

3. Formation Mechanisms of Micelles and Microemulsions

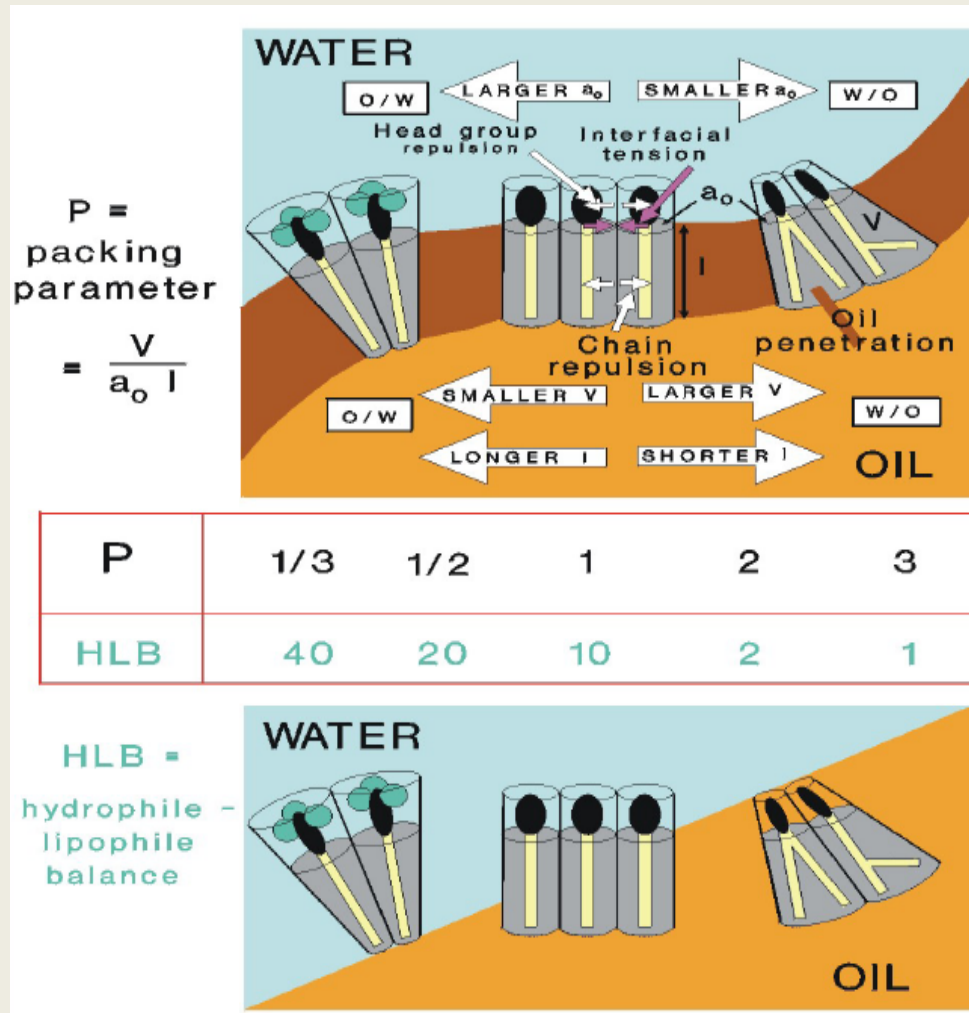
3.2. Formulation of microemulsion – Bancroft's rules

- HLB Concept



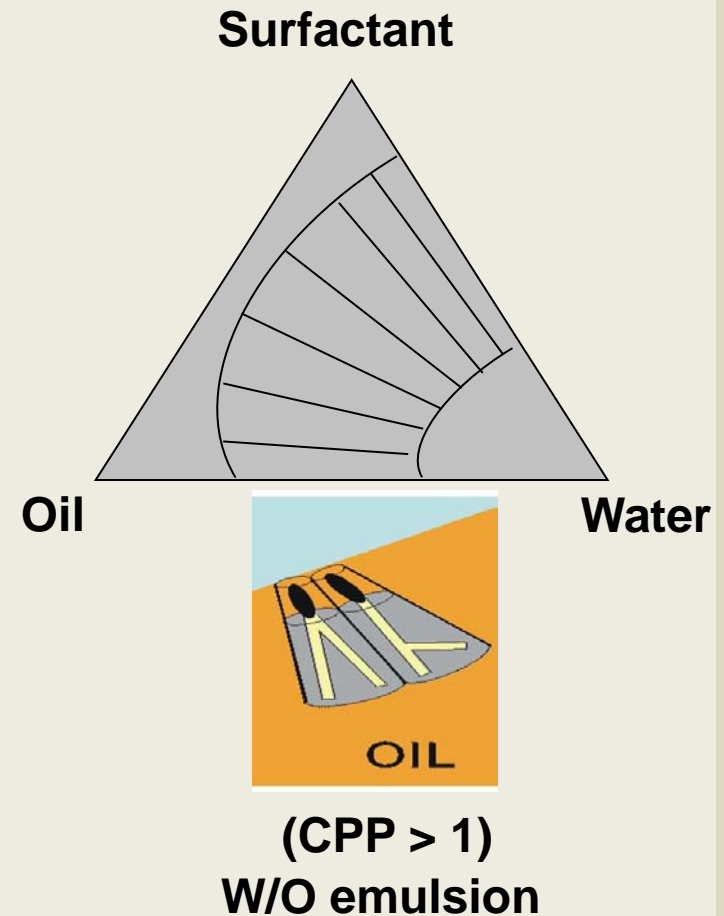
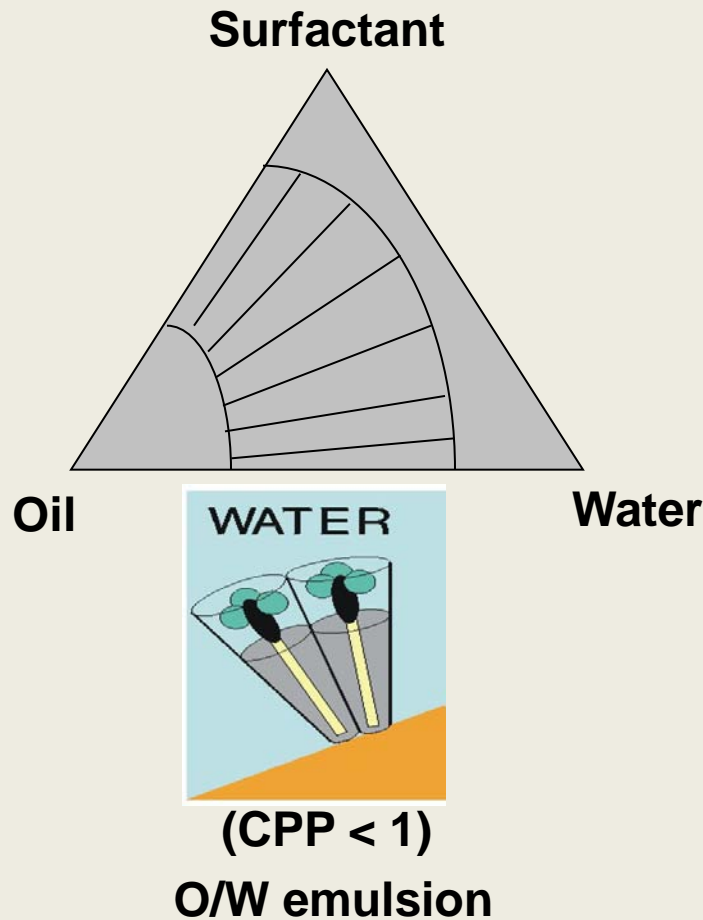
3. Formation Mechanisms of Micelles and Microemulsions

3.2. Formulation of microemulsion – Bancroft's rules



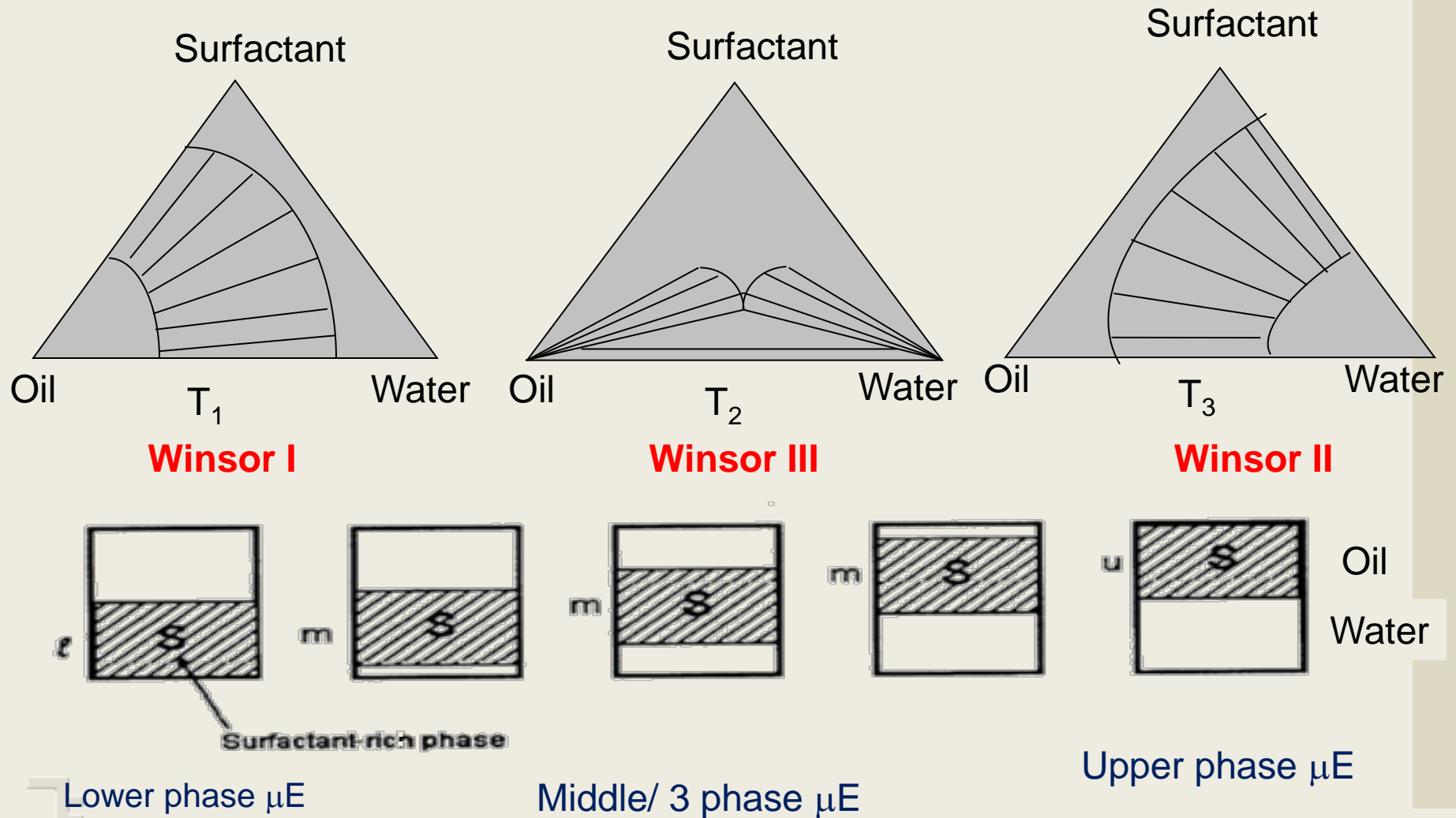
3. Formation Mechanisms of Micelles and Microemulsions

3.2. Formulation of microemulsion – Bancroft's rules



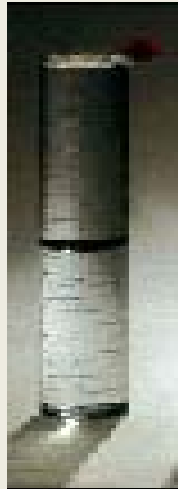
3. Formation Mechanisms of Micelles and Microemulsions

3.2. Formulation of microemulsion – Bancroft's rules



3. Formation Mechanisms of Micelles and Microemulsions

3.2. Formulation of microemulsion – Bancroft's rules



Winsor I



Winsor III



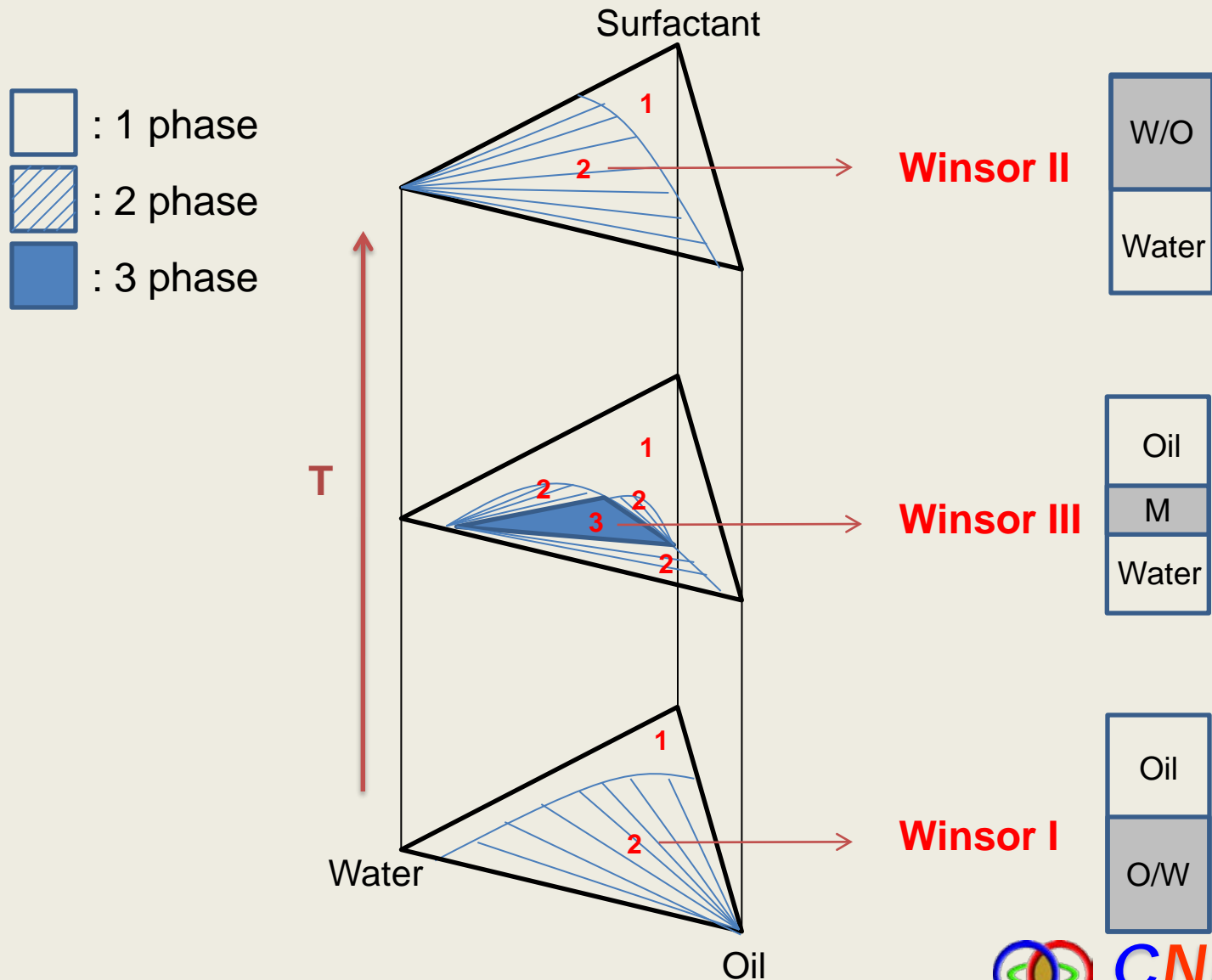
Winsor II

Variables to play with

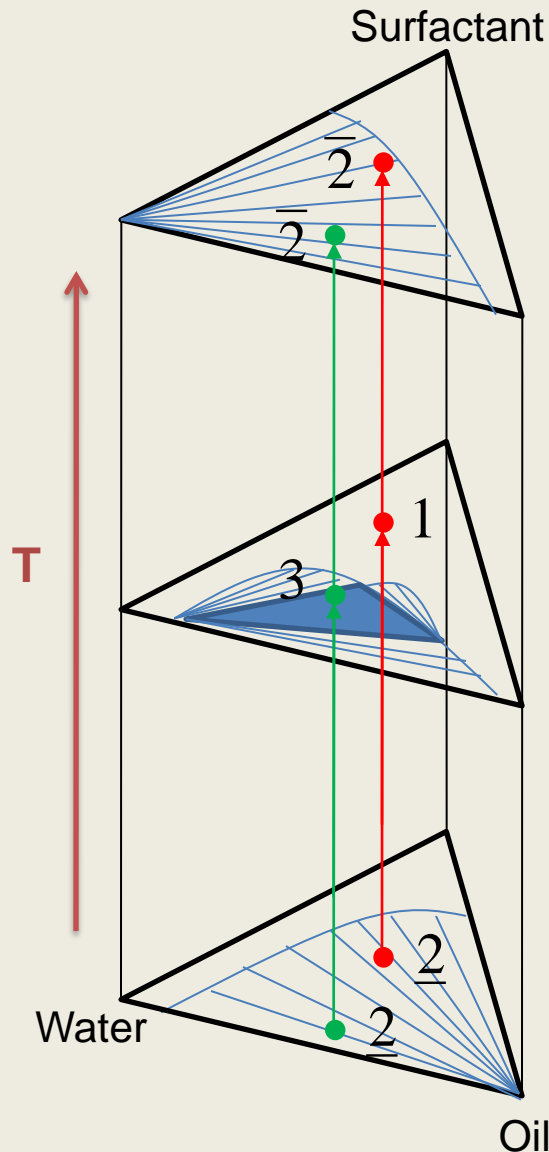
Salinity
Oil chain length
Alcohol conc.
Temperature




Total surfactant
water/oil ratio
surfactant/oil ratio
MW of surfactant

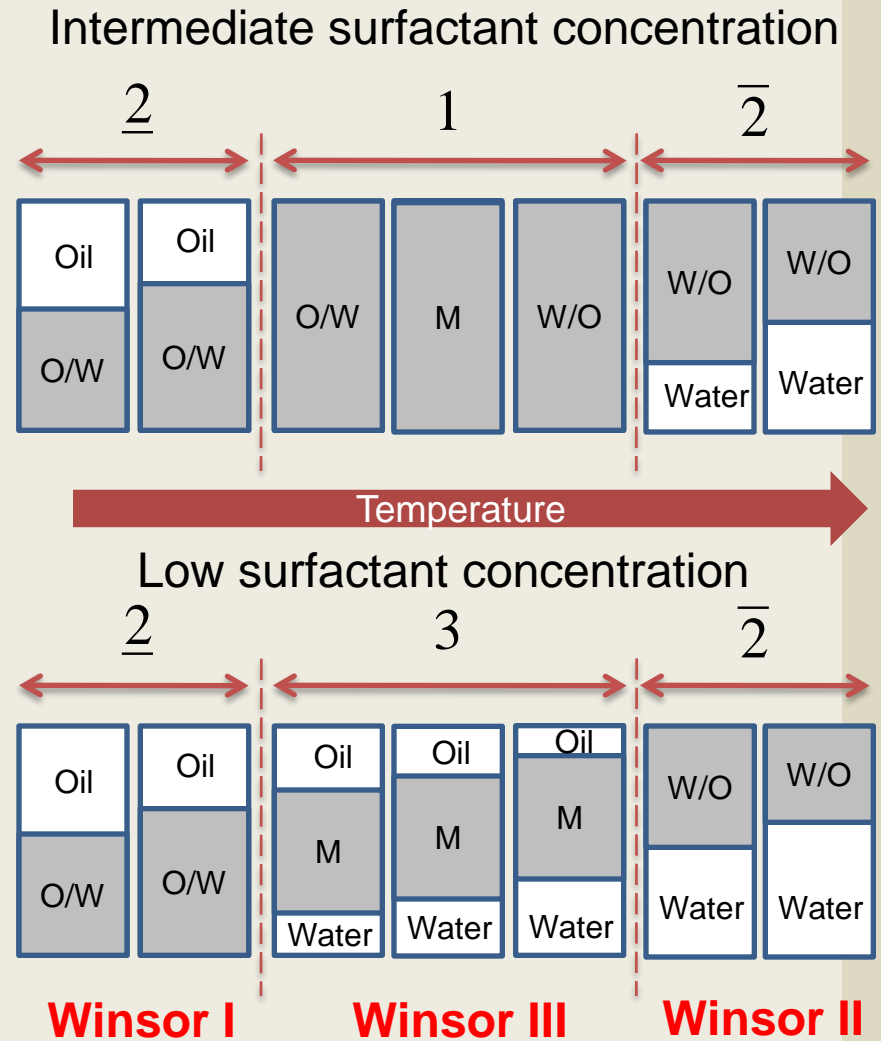
3. Formation Mechanisms of Micelles and Microemulsions



3. Formation Mechanisms of Micelles and Microemulsions

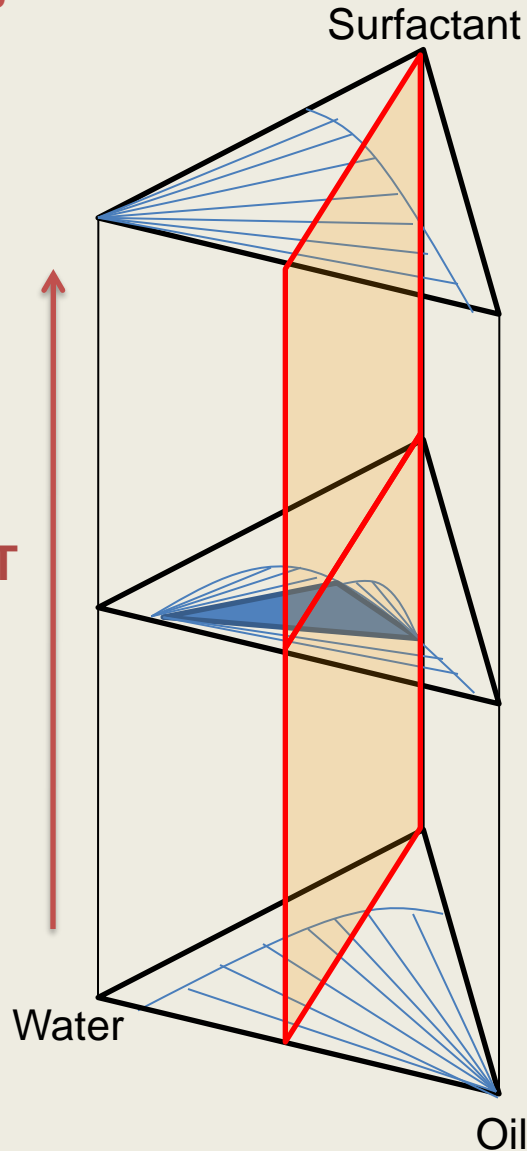





-  : 1 phase
-  : 2 phase
-  : 3 phase

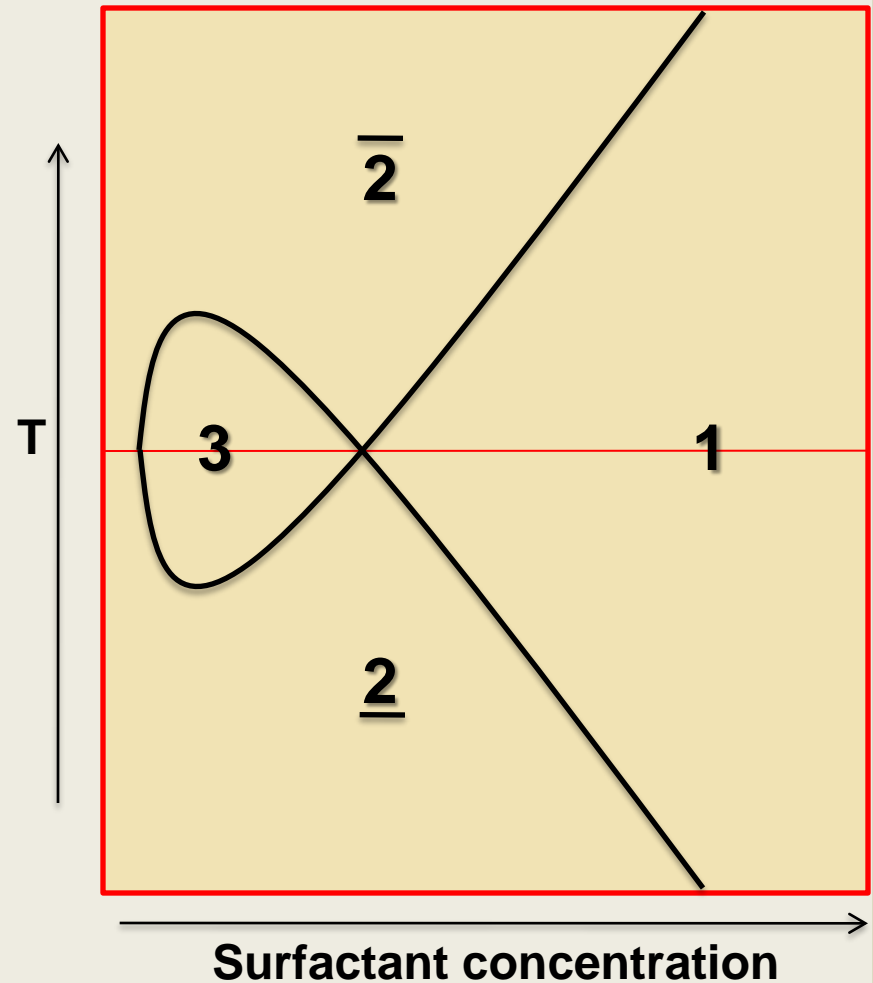


3. Formation Mechanisms of Micelles and Microemulsions

▪ “Fish” diagram

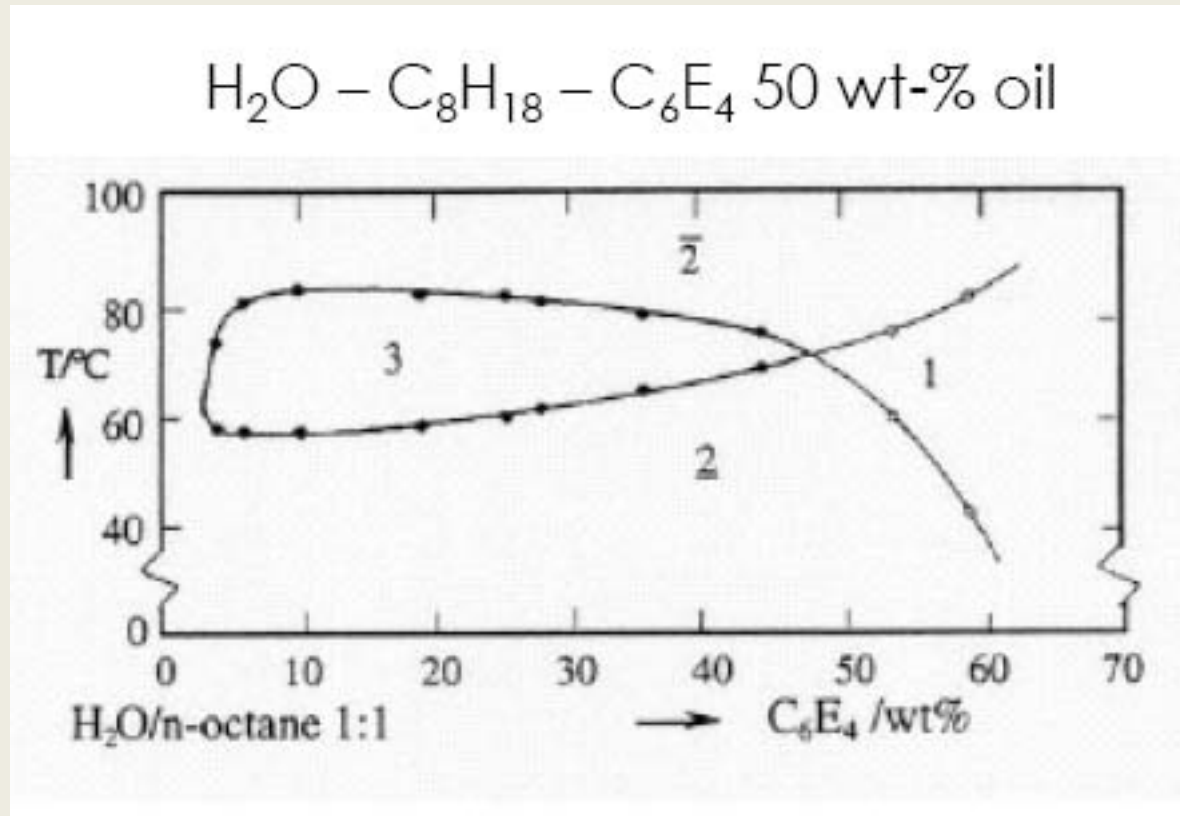


-  : 1 phase
-  : 2 phase
-  : 3 phase



3. Formation Mechanisms of Micelles and Microemulsions

- “Fish” diagram

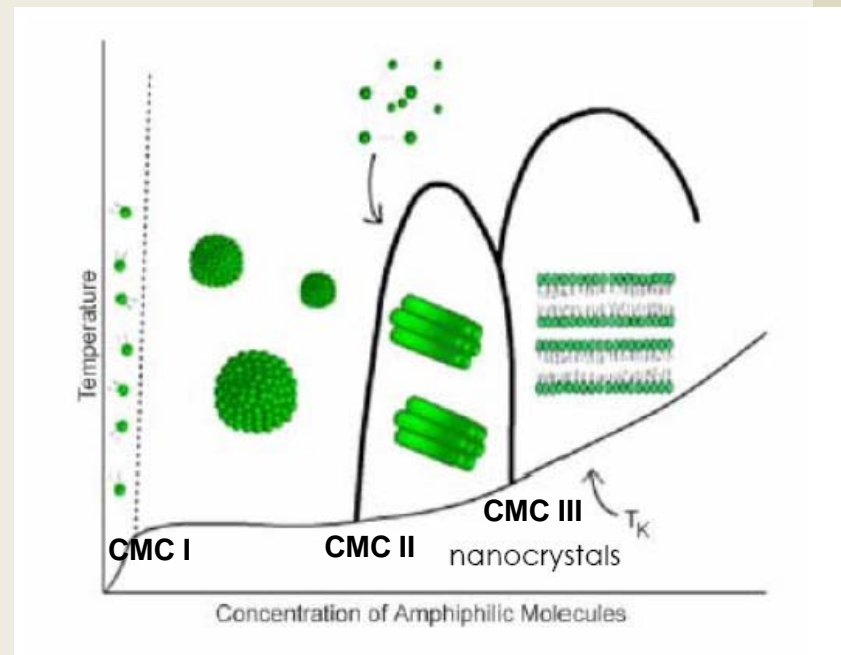
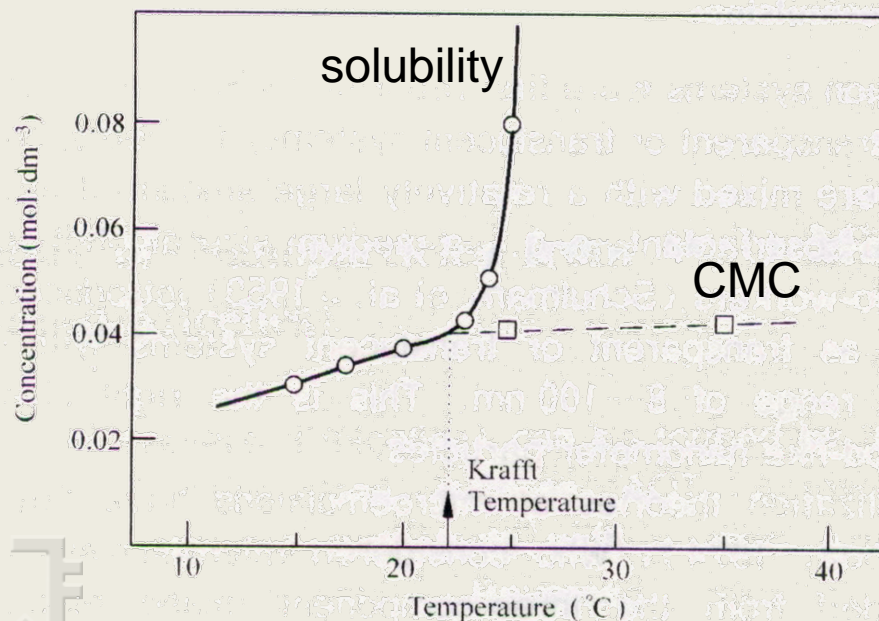


3. Formation Mechanisms of Micelles and Microemulsions

3.3. Solubilization and Formation of Microemulsions

▪ Solubilization of surfactant

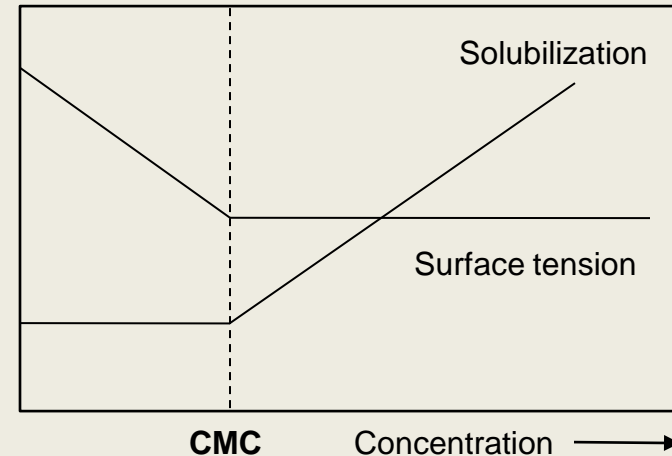
- The dissolution of hydrophobic (or hydrophilic) materials into water (or oil) to an extent greatly exceeding their normal solubilities in water (or oil)
- The solubility behavior of surfactants is anomalous as the temperature is increased to a value at which there is a sudden increase in solubility and the Material then becomes very highly soluble. (Krafft, 1899)



3. Formation Mechanisms of Micelles and Microemulsions

3.3. Solubilization and Formation of Microemulsions

- **CMC (Critical Micelle Concentration)**
- Surface tension decreases with surfactant concentration at low concentration.
- It takes on an approximately constant value at specific concentration. At this time, surfactants form spherical shape.
- We call such aggregates micelles, and the concentration where they start to form is known as the critical micelle concentration (CMC).



Surfactant	CMC
Dodecylammonium chloride	$1.47 \times 10^{-2} \text{ M}$
Dodecyltrimethylammonium chloride	$2.03 \times 10^{-2} \text{ M}$
Decyltrimethylammonium bromide	$6.5 \times 10^{-2} \text{ M}$
Dodecyltrimethylammonium bromide	$1.56 \times 10^{-2} \text{ M}$
Sodium dodecyl sulfate	$8.3 \times 10^{-3} \text{ M}$
Sodium decyl sulfate	$3.3 \times 10^{-2} \text{ M}$
Sodium octyl sulfate	$1.33 \times 10^{-1} \text{ M}$
Dimethyldodecylamineoxide	$2.1 \times 10^{-3} \text{ M}$
$\text{CH}_3(\text{CH}_2)_9(\text{OCH}_2\text{CH}_2)_6\text{OH}$	$9 \times 10^{-4} \text{ M}$
Potassium perfluorooctanoate	$2.88 \times 10^{-2} \text{ M}$

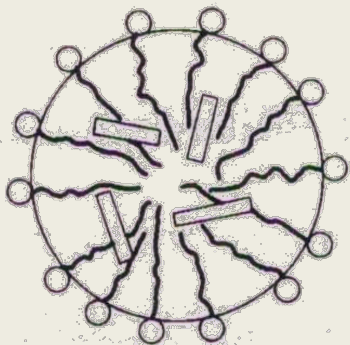
3. Formation Mechanisms of Micelles and Microemulsions

3.3. Solubilization and Formation of Microemulsions

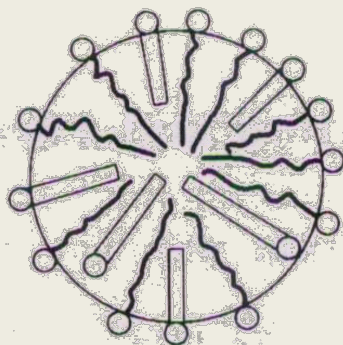
■ Addition of the third party component

- Four general possible regions

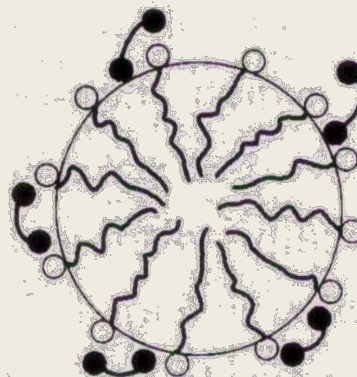
- (1) In the hydrocarbon of the micelle
- (2) Orientation in the micelle which could be deep or shallow
- (3) In the hydrophilic portion of the surfactant
- (4) Adsorption on the surface of the micelle



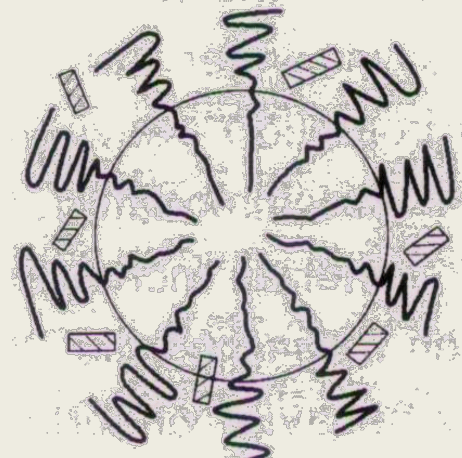
(1)



(2)



(3)



(4)



4. Synthesis of Organic Nanomaterials from O/W Microemulsion Polymerization

Case study #1

- First reported o/w microemulsion in polymerization of methylacrylate and methylmethacrylate. Polymer nanoparticles can be obtained. But, phase separation occurred.

Stoffer, Bone, *J. Polym. Sci., Polym. Chem.*, 1980, 18, 2641.

- First successful microemulsion polymerization was reported.

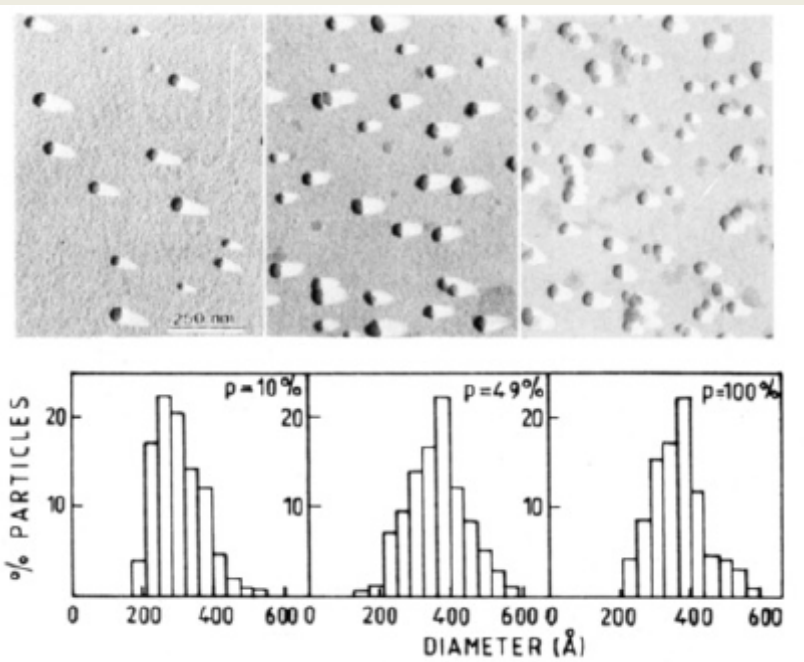
- CTAB/styrene/hexanol/water

- Monodisperse nanoparticles : 20, 35nm

Atik, Thomas, *J. Am. Chem. Soc.*, 1981, 103, 4279.

- First study of microemulsion polymerization using electron microscopy

Carver, *J. Phys. Chem.*, 1989, 93, 4867.

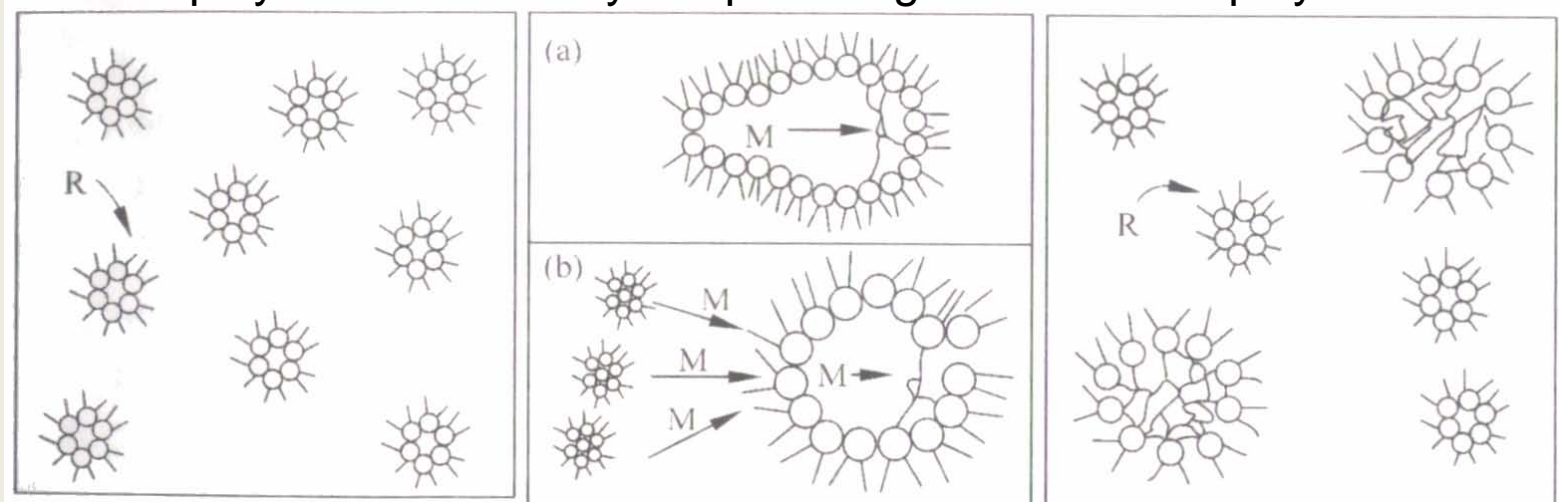


4. Synthesis of Organic Nanomaterials from O/W Microemulsion Polymerization

Case study #1

Schematic representation of synthesis of organic nanoparticles in o/w microemulsions

Before polymerization Polymer particle growth End of polymerization



(a) by collisions between particles

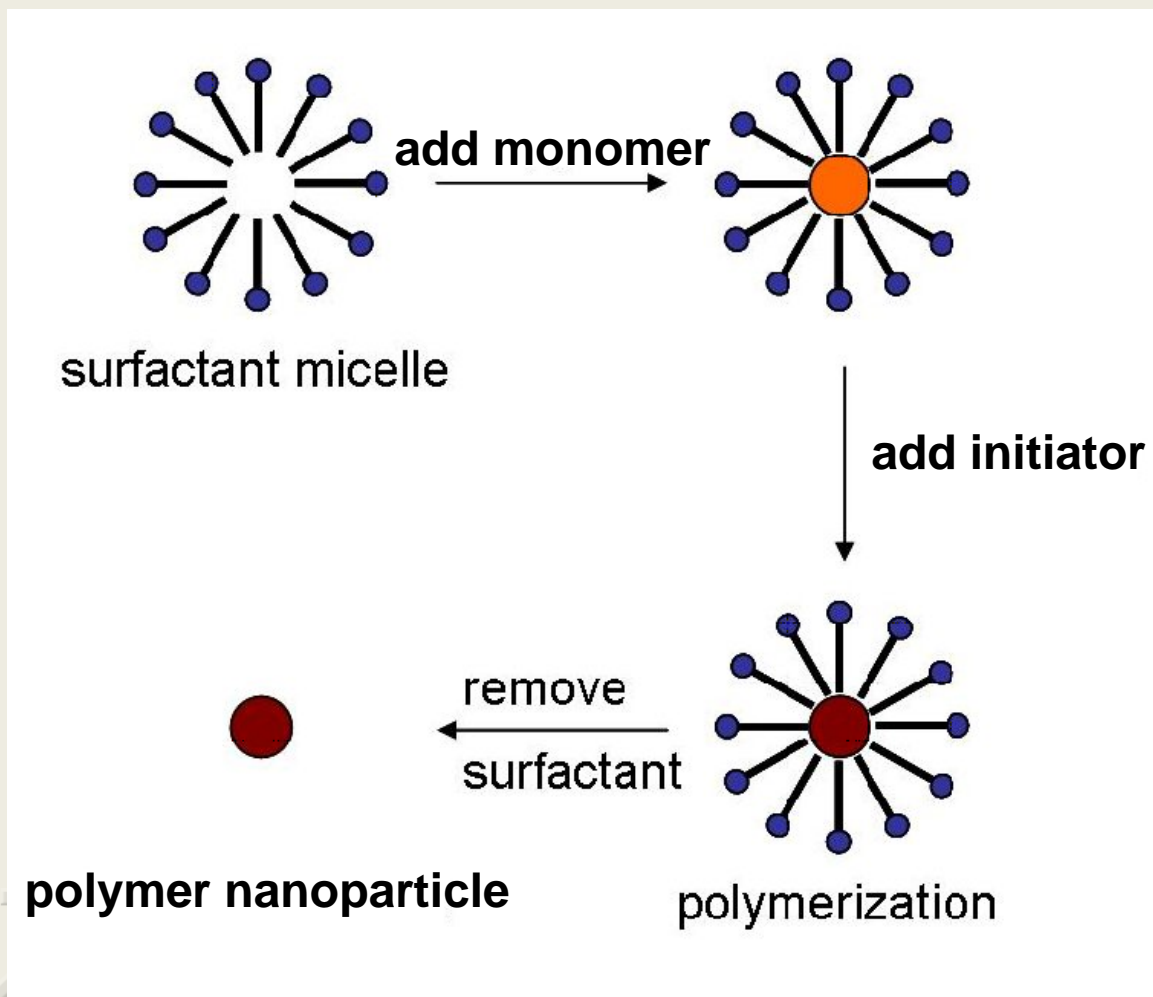
(b) by monomer diffusion through the oil phase

Candau, in Scientific Methods for the Study of Polymer Colloids and Their Application, Kluwer Academic Publ., 73 (1990)

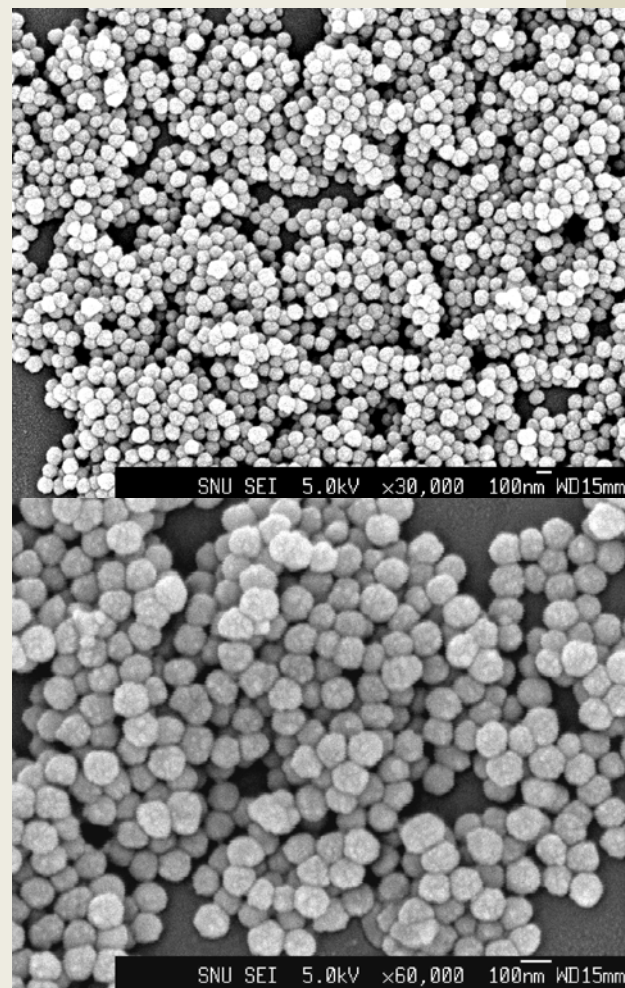
4. Synthesis of Organic Nanomaterials from O/W Microemulsion Polymerization

Case study #1

Schematics of conventional microemulsion polymerization method



SEM micrographs of Polypyrrole NPs (100nm)

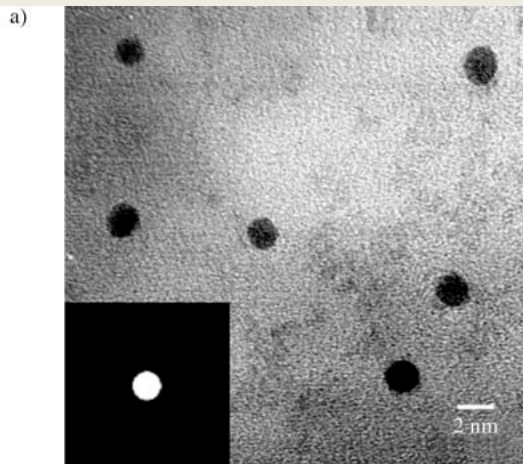


4. Synthesis of Organic Nanomaterials from O/W Microemulsion Polymerization

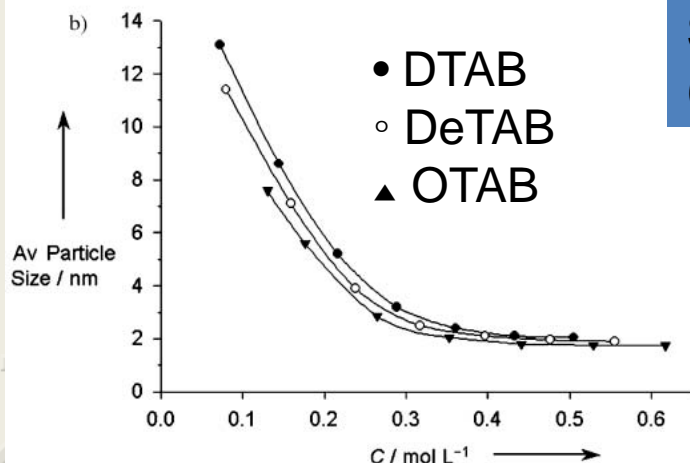
Case study #2

▪ Influence factors of polymer particle size in microemulsion method

(1) Surfactant concentration and alkyl chain length



- a) TEM image and nanobeam electron diffraction pattern of the PPy nanoparticles prepared using DeTAB
b) Average change in nanoparticle size as a function of surfactant concentration



Surfactant alkyl chain length $\uparrow \Rightarrow$ size \uparrow
(\because enhanced flexibility of longer spacers provides more free volume inside the micelle)

Surfactant concentration $\uparrow \Rightarrow$ size \downarrow
(\because number of micelle $\uparrow \Rightarrow$ dense packing)

octyltrimethylammonium bromide (OTAB),
decyltrimethylammonium bromide (DeTAB),
dodecyltrimethylammonium bromide (DTAB)

4. Synthesis of Organic Nanomaterials from O/W Microemulsion Polymerization

Case study #2

▪ Influence factors of polymer particle size in microemulsion method

(2) Temperature

Temperature (°C)	Particle size (nm)
3	2
25	12
70	53

As the polymerization temperature $\uparrow \Rightarrow$ size \uparrow
(\because increased mobility of surfactant chains)

Angew. Chem. Int. Ed., **2002**, 41, 4016.

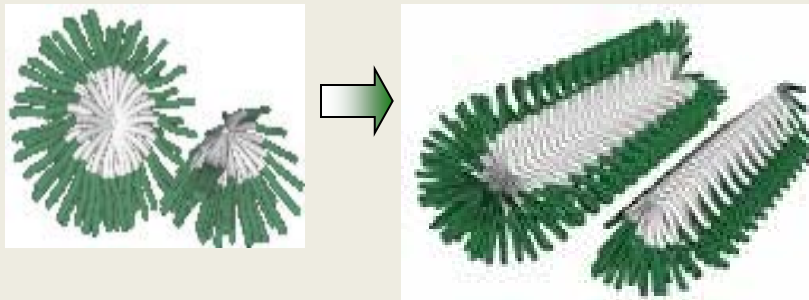


4. Synthesis of Organic Nanomaterials from O/W Microemulsion Polymerization

Case study #3

▪ Morphological transition – Sphere to rod transition

The spherical surfactant micelles undergo a transition to larger rodlike aggregates with the increase of surfactant concentration (CMC I \rightarrow CMC II)



The formation of rodlike micelles is enhanced by

1. the addition of electrolyte
2. decreasing the temperature
3. increasing the length of the surfactant hydrocarbon chain

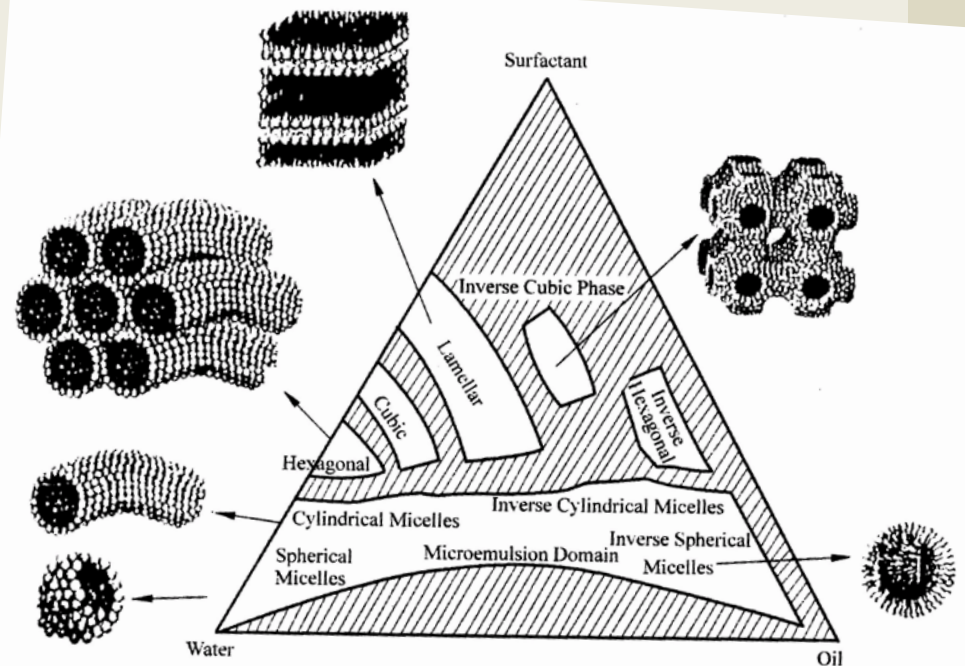


Figure 1.3 A schematic phase diagram of surfactant-oil-water systems showing a variety of self-assembled structures (After Liu, J., et al., 1996).

4. Synthesis of Organic Nanomaterials from O/W Microemulsion Polymerization

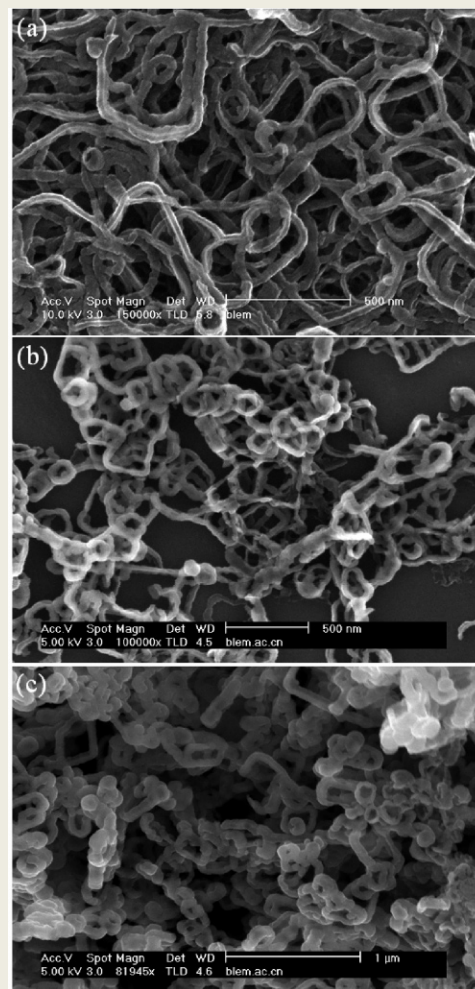
Case study #3

▪ Morphological transition – Sphere to rod transition

Polypyrrole
nanoparticles to rod
transition

Monomer : pyrrole
Surfactant : CTAB

Initiator :
ammonium
persulfate (APS)



12 cmc

6 cmc

2 cmc

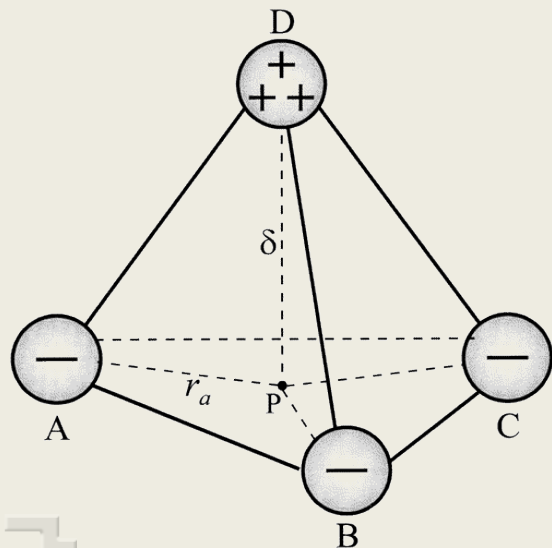
4. Synthesis of Organic Nanomaterials from O/W Microemulsion Polymerization

Case study #4

▪ Morphological transition – Sphere to rod transition : addition of electrolyte

- Increase of Cation Valence → affect the molecular structure
- CMC depends on total ionic strength(I_0)

$$I = 1/2 \sum C_i Q_i^2$$



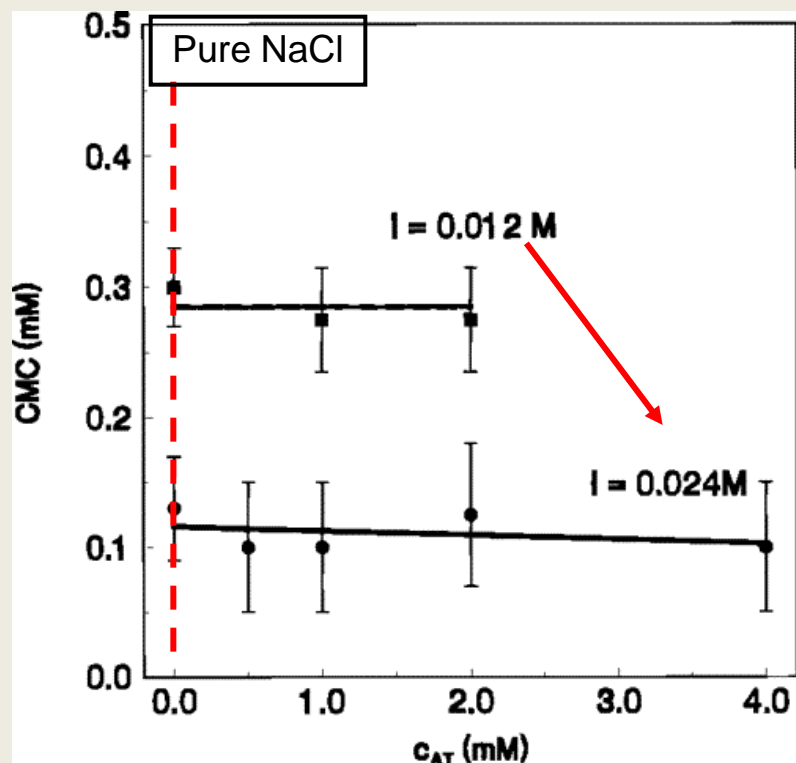
⇒ Al^{3+} can bind together three surfactant headgroups at the micelle surface, thus causing a decrease of the area per headgroup.

⇒ this will induce a transition from spherical to cylindrical micelle

4. Synthesis of Organic Nanomaterials from O/W Microemulsion Polymerization

Case study #4

- Morphological transition – Sphere to rod transition : addition of electrolyte



Critical micellization concentration (CMC) of SDP-2S, measured with static light scattering, vs the total Al³⁺ counterions concentration (c_{AT}),

The ionic strength is due to a mixture of NaCl and AlCl₃

$$I = \frac{1}{2} \sum C_i Q_i^2$$

In this studies on the growth of rod-like micelles of SDP-2S, they fixed the ionic strength of the added electrolyte, $I = 0.024 \text{ M}$, but varied the molar fractions of NaCl and AlCl₃