# Chapter 2. Nanomaterials based on Microemulsion physics

2.1. Introduction

2.2. Stability of microemulsions

2.3. Formation Mechanisms of micelles and microemulsions

2.4. Synthesis of inorganic nanomaterials from w/o microemulsions

2.5. Synthesis of organic nanomaterials from o/w microemulsions

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# 2.1. Introduction

## Template method to prepare the nanomaterials

**- Concept**

Add monomer

Removal of template

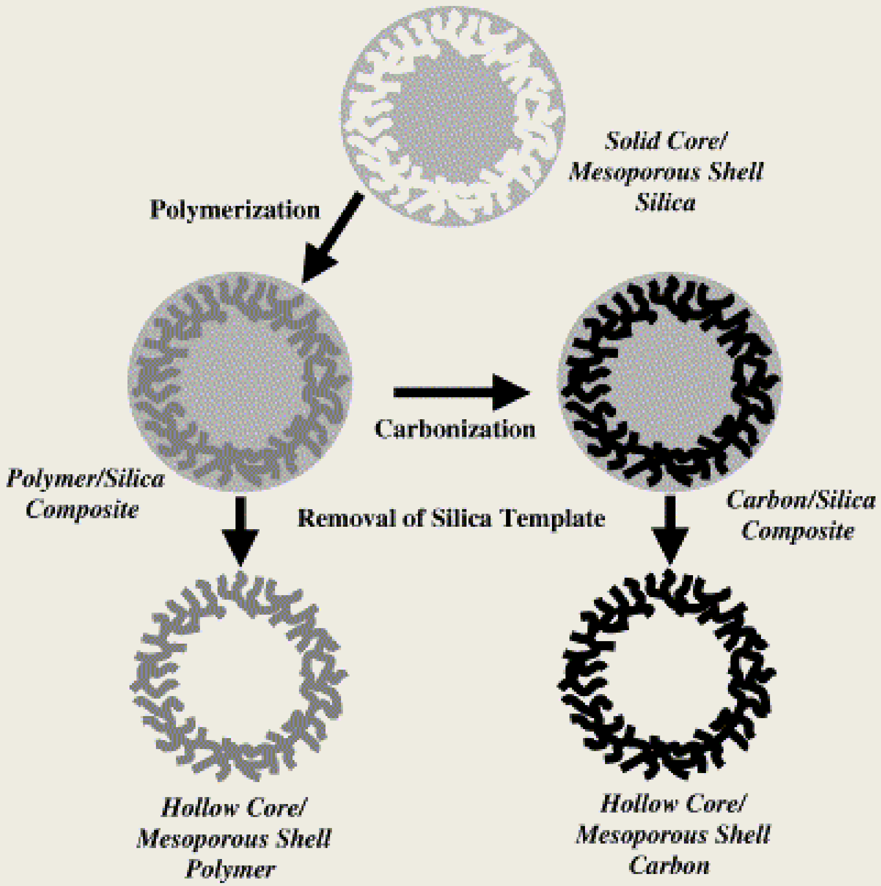
template

**- Kinds of template**

anodized aluminum oxide (AAO)
porous silicate
colloidal particle
polycarbonate membrane

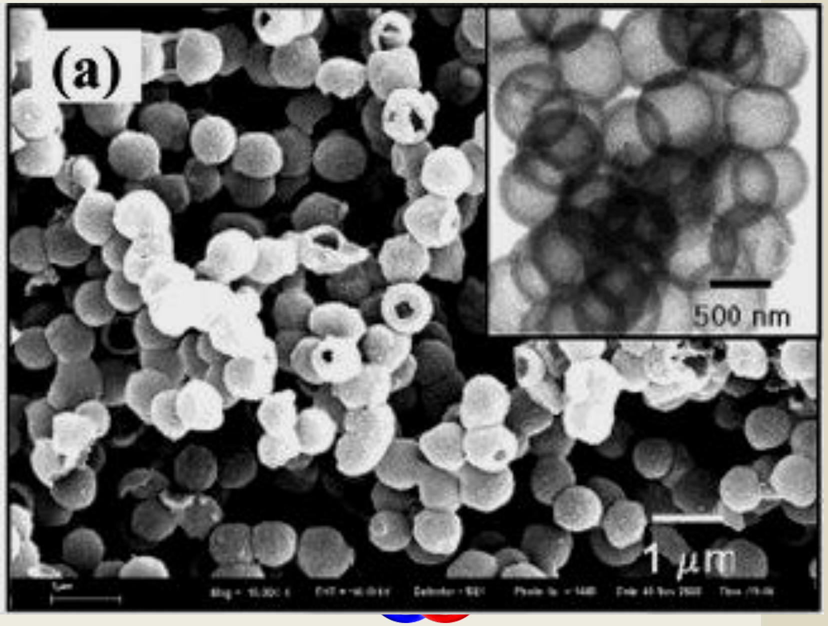
# 2.1. Introduction

## Examples of template method



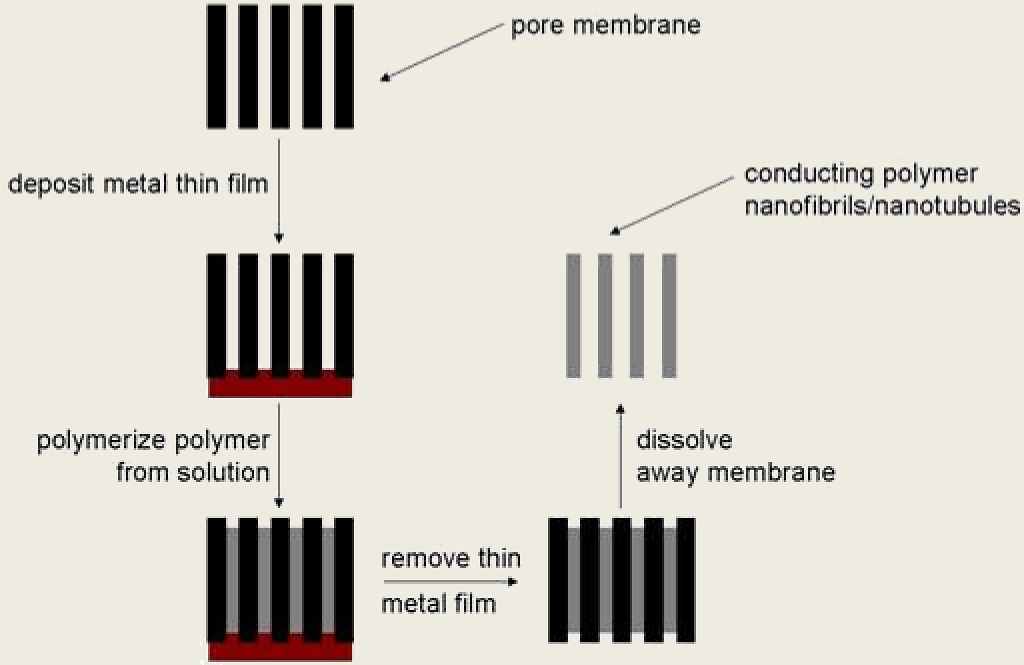
Hollow polymer and carbon spheres using silica template

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



# 2.1. Introduction

## Examples of template method



pore membrane

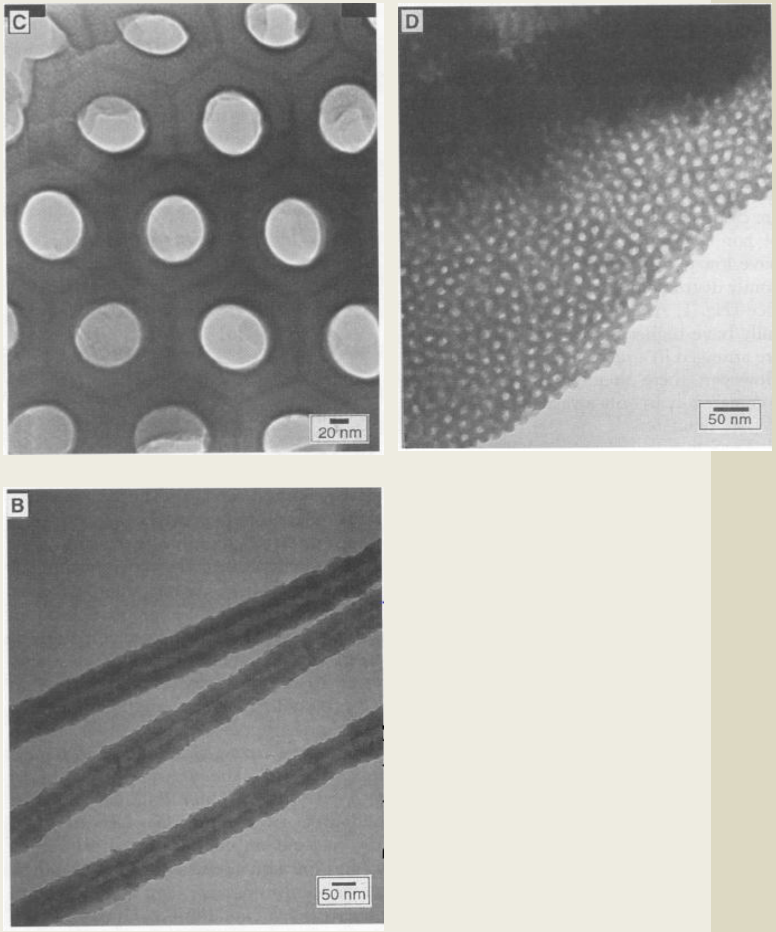
deposit metal thin film

conducting polymer nanofibrils/nanotubules

polymerize polymer from solution

dissolve away membrane

remove thin metal film

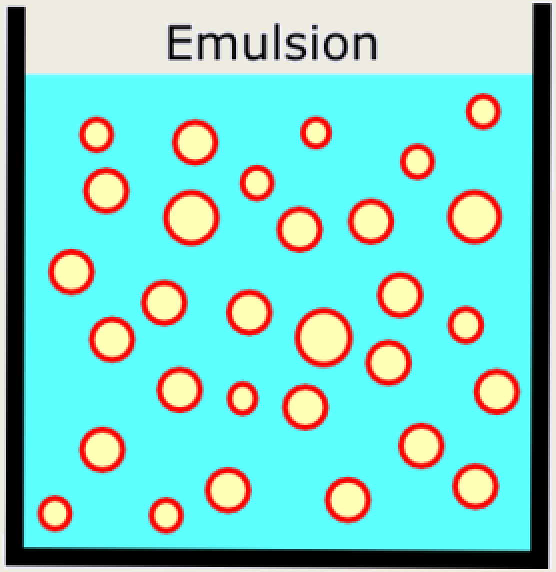


# 2.1. Introduction

## 2.1.1. 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

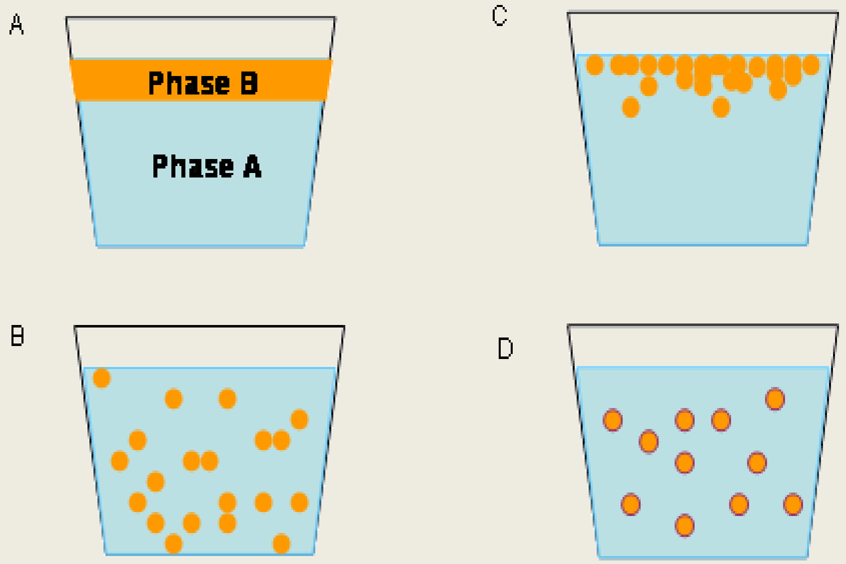
- An emulsion is a thermodynamically unstable system consisting of at least two immiscible liquid phases, one of which is dispersed as globules in the other liquid phase, stabilized by the presence of an emulsifying agent.

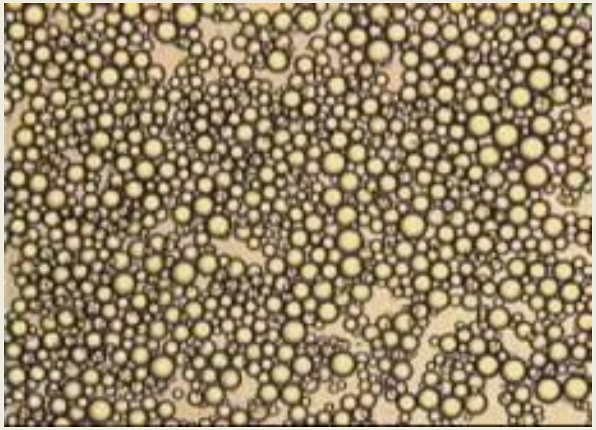


Ref. Wikipedia, the free encyclopedia

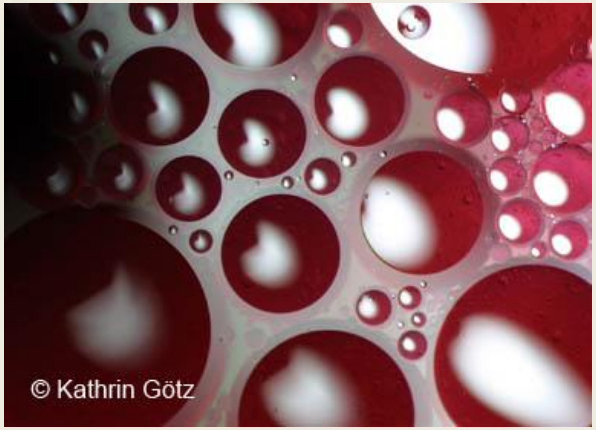
# 2.1. Introduction

## 2.1.1. What is emulsion?





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



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

A. Two immisicble 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

# 2.1. Introduction

## 2.1.1. 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

# 2.1. Introduction

## 2.1.1. 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<br>( Fog, mist ) | |
| | *Liquid* | Foam<br>(Whipped cream) | **Emulsion**<br>(mayonnaise, hand cream) | Sol or **Suspension**<br>(blood, pigmented ink) |
| | *Solid* | Solid Foam<br>( Aerogel, styrofoam, pumice ) | Gel<br>(Gelatin, jelly, cheese, opal) | Solid Sol<br>( ruby glass ) |

* All gases are soluble

# 2.1. Introduction

## 2.1.2. Types of emulsion

- “dispersed phase” in “continuous phase”

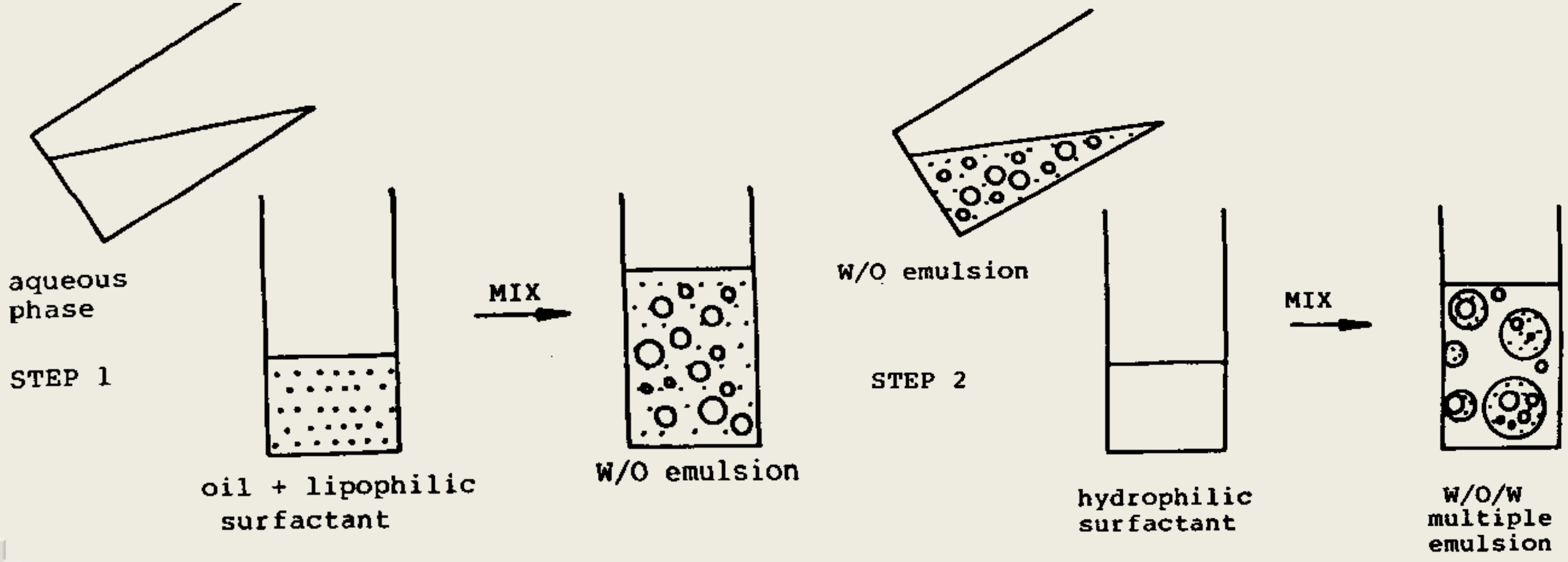
  Oil-in-water (o/w)

  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



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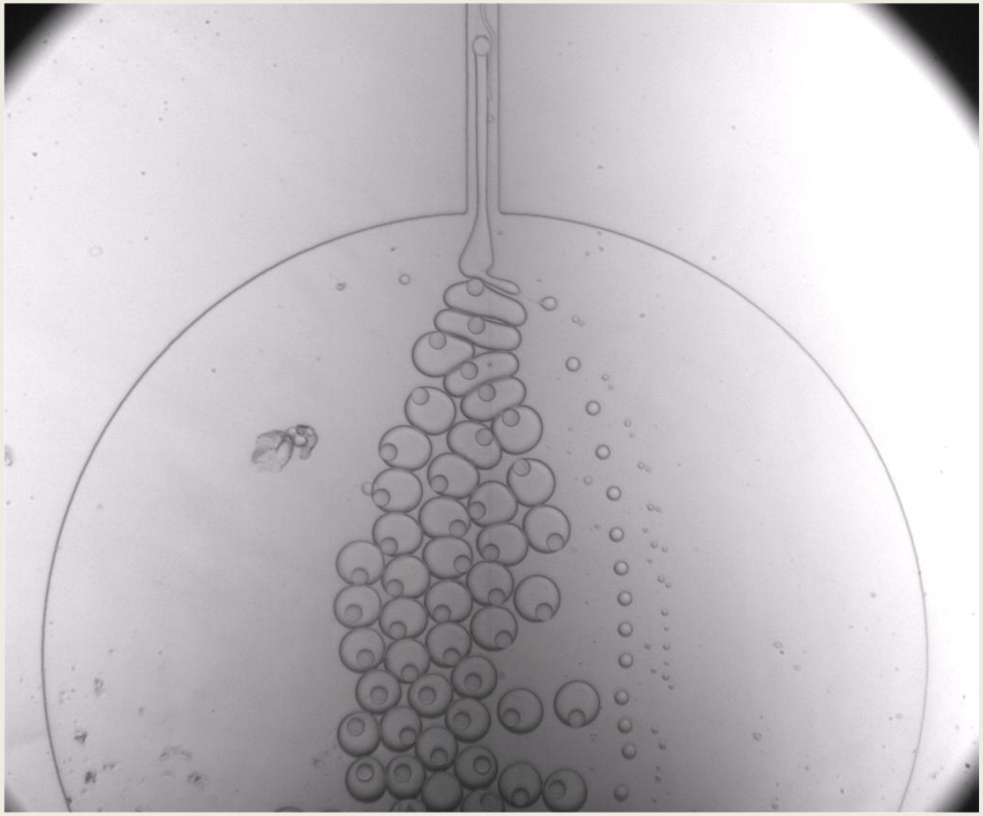
# 2.1. Introduction

## 2.1.2. Types of emulsion

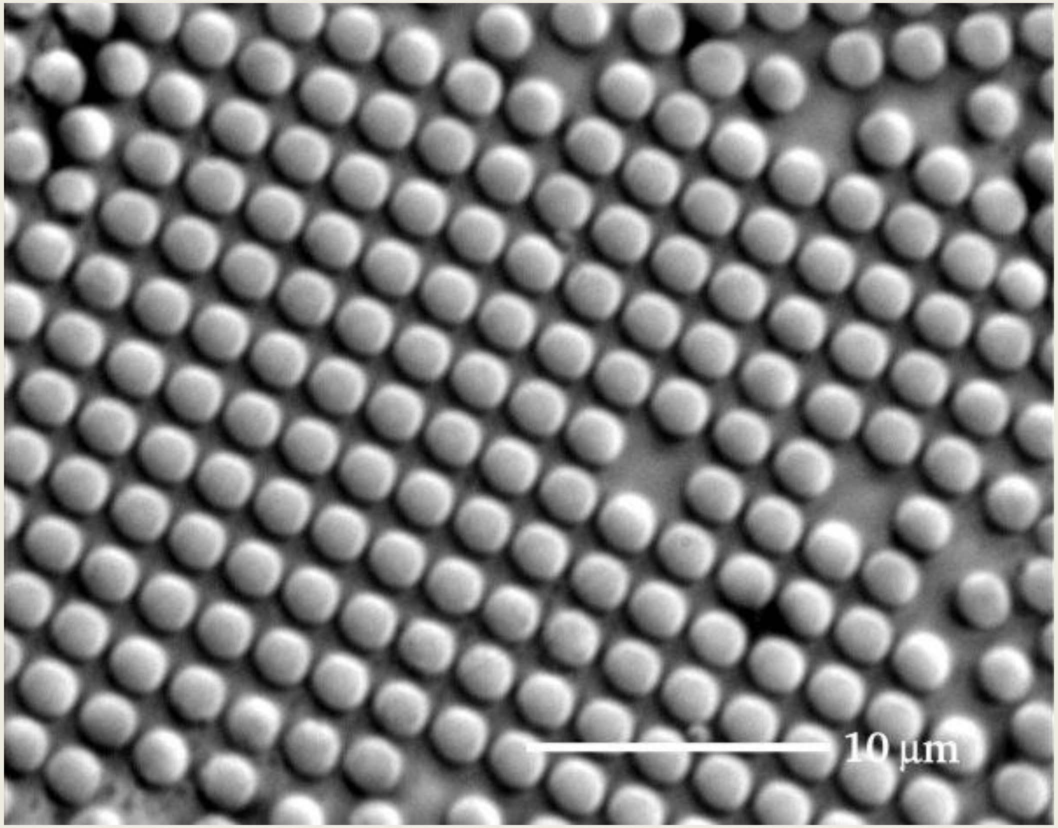


- Water/oil/water double emulsion made using a microfluidic device.
- The upper channel width is 50 micron. The inner drops are pure water, the outer drops are fluoro-carbon oil with fluorinated surfactants, and the outer phase is water with hydrophilic surfactants.

# 2.1. Introduction

## 2.1.2. Types of emulsion

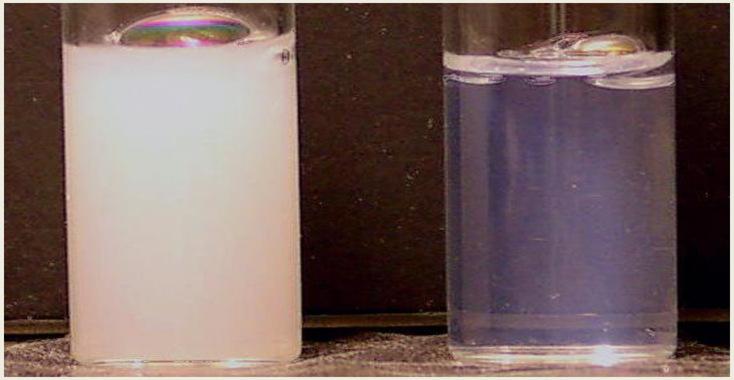
- **Monodisperse Emulsion Droplet**



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

# 2.1. Introduction

## 2.1.3. 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 ($10^{-2}$ – $10^{-3}$ mN/m) |
| W/O or O/W types | W/O , O/W and Bicontinuous types |

*IFT : Interfacial Tension

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# 2.1. Introduction

## 2.1.4. 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

- **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 |

# 2.1. Introduction

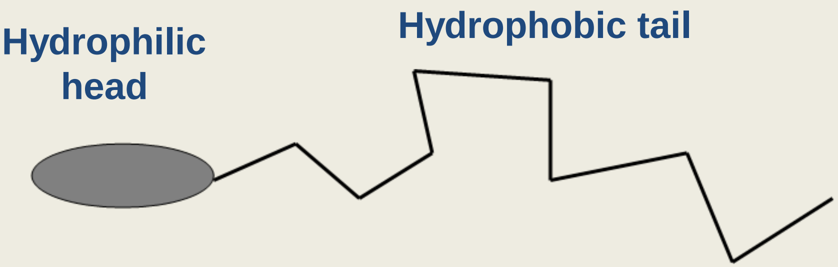
## 2.1.4. Surfactant

- **Interfacial free energy (or interfacial tension)**
  - 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

- **Nature of surfactant** : amphiphilic

  Surfactant molecules = soluble part (lyophilic)
  + insoluble part (lyophobic) in a specific fluid

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



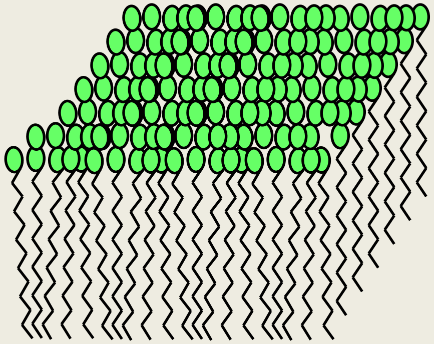
<Schematic illustration of a surfactant>

# 2.1. Introduction

## 2.1.4. Surfactant

- **Properties of the surfactant film**

**Surfactant film**



**Properties of the surfactant film change with:**

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

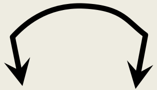
**Properties of the surfactant film:**

- Interfacial tension

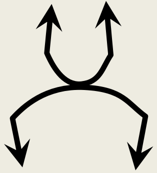
- Lateral elasticity

- Spontaneous curvature

- Bending elasticity



- Saddle splay elasticity



# 2.1. Introduction

## 2.1.4. Surfactant

- Surfactant aggregation in solution

Oils and water do not mix!
Why?
Water is a polar liquid, $\varepsilon = 81$
Oils are non polar, $\varepsilon \sim 2$
($\varepsilon$ - dielectric const.)

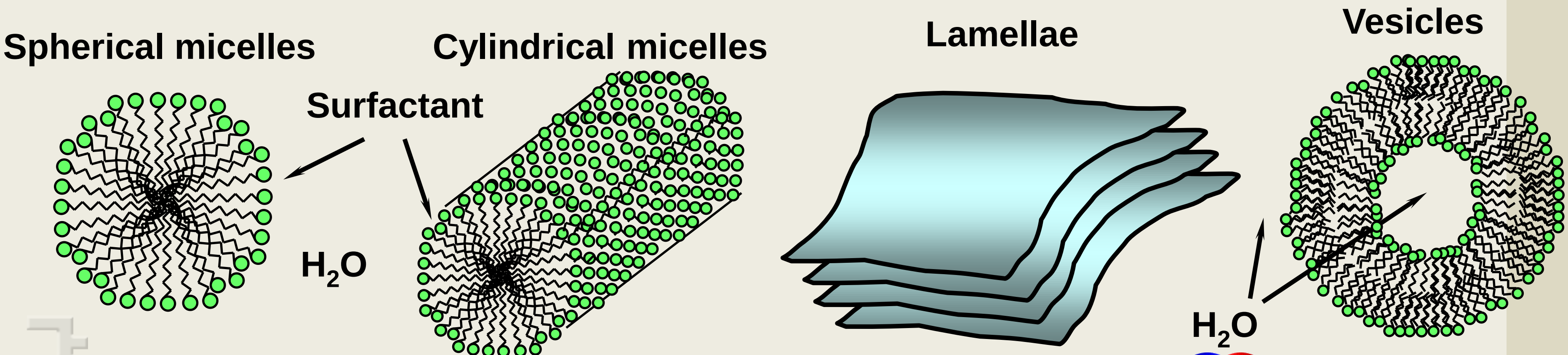
**Surfactant molecule**

Hydrophobic tail
$CH_3$-$CH_2$-$CH_2$- …
$CF_3$-$CF_2$-$CF_2$- …

Hydrophilic head
$SO_3^-Na^+$
$NH_3^+Cl^-$
-$(OCH_2CH_2)_n$-

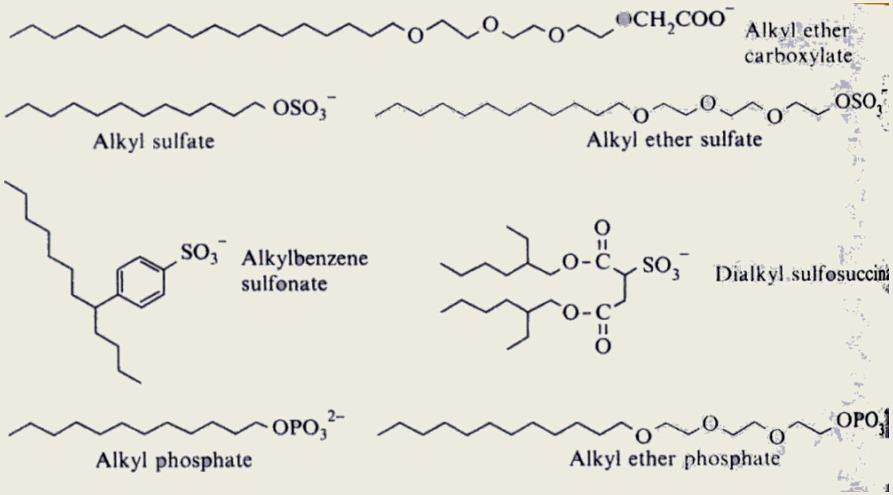
**When surfactants are dissolved in water, they:**

- reduce the surface tension because they are adsorbed on the surfaces
- form variety of aggregates – micelles, lamellae, bicelles, vesicles, etc

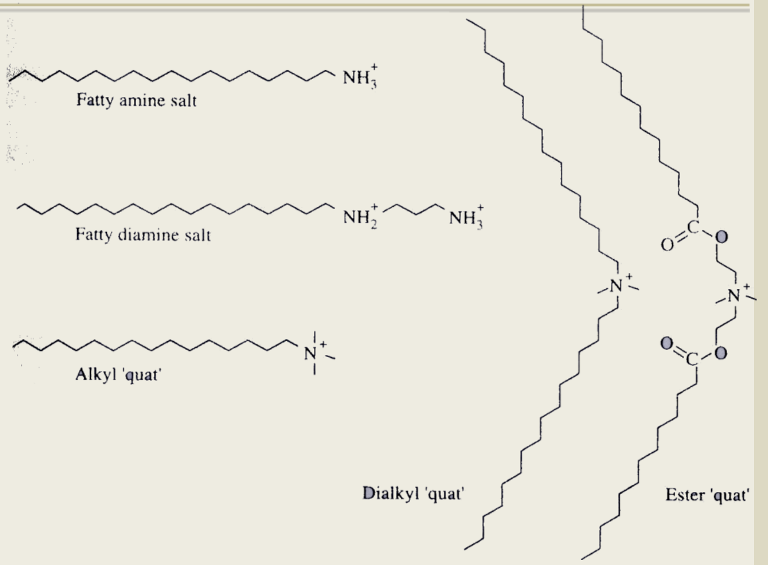


# 2.1. Introduction

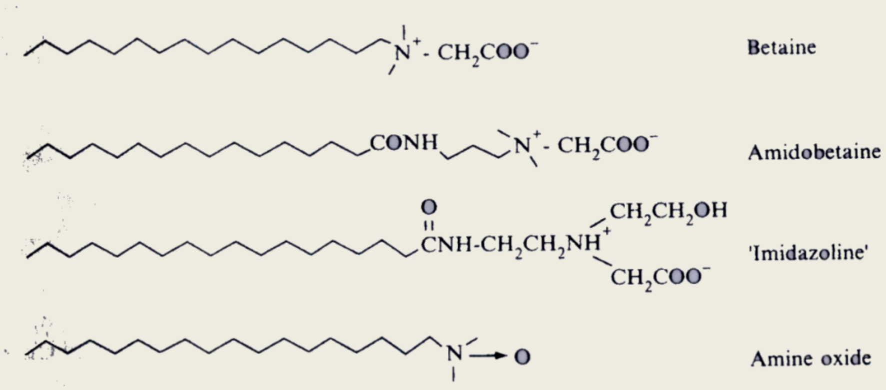
## 2.1.4. Surfactant



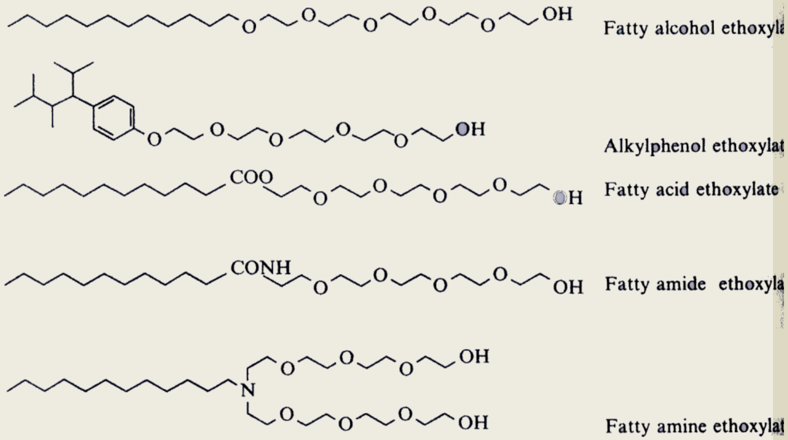
Anionic surfactants



cationic surfactants



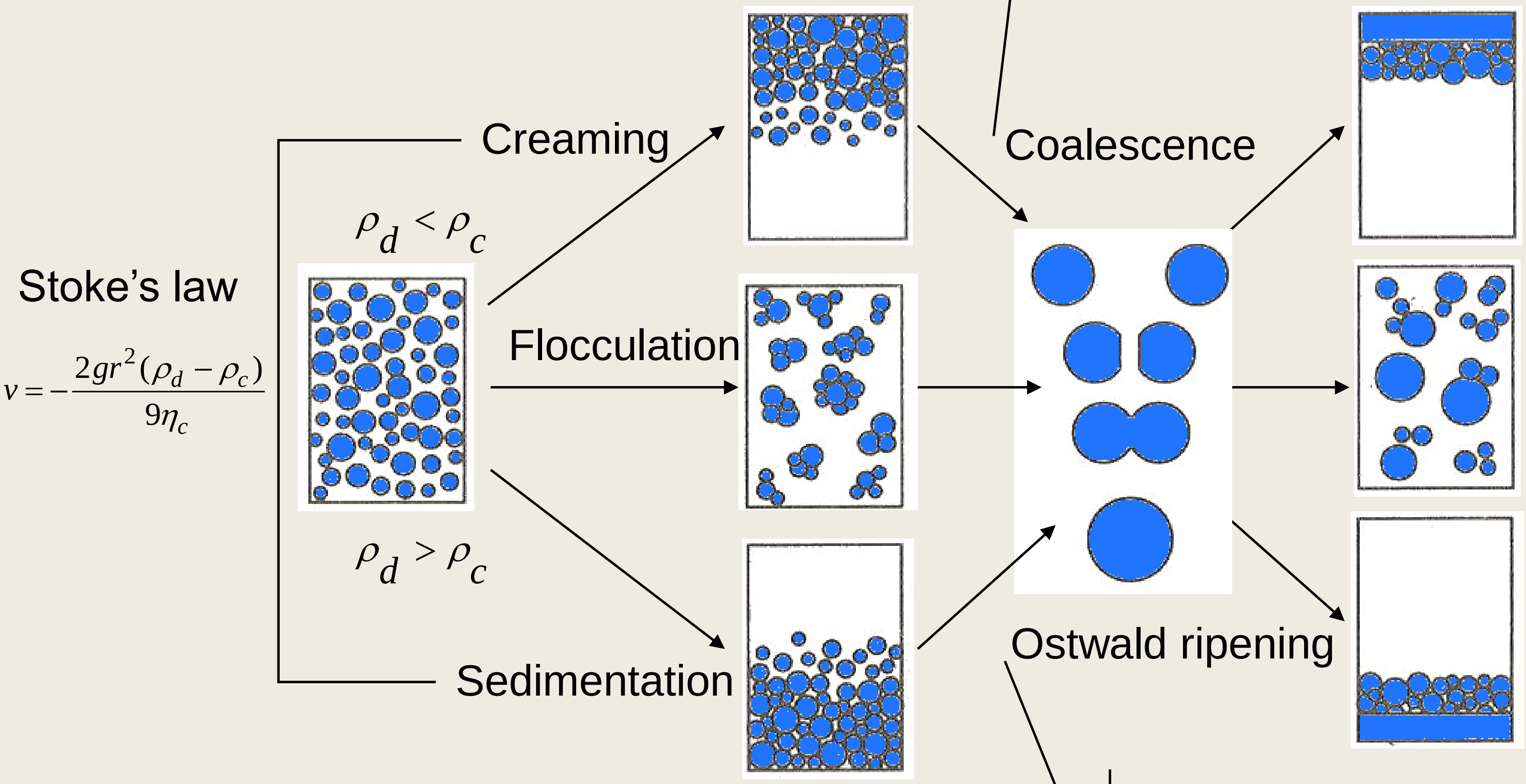
Zwitterionic surfactants



Non-ionic surfactants

# 2.2. Stability of microemulsion

## 2.2.1. Instability of emulsion



Stoke's law

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

$\rho_d < \rho_c$

$\rho_d > \rho_c$

Creaming

Flocculation

Sedimentation

Coalescence

Ostwald ripening

the merging of two or more droplets into one

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

# 2.2. Stability of microemulsion

## 2.2.1. Instability of emulsion

**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 |

Addition of stabilizer deters flocculation and coalescence because it increases the viscosity of the continuous phase, which makes it difficult for the droplets to move, and protect the droplets by forming energy barrier between droplets

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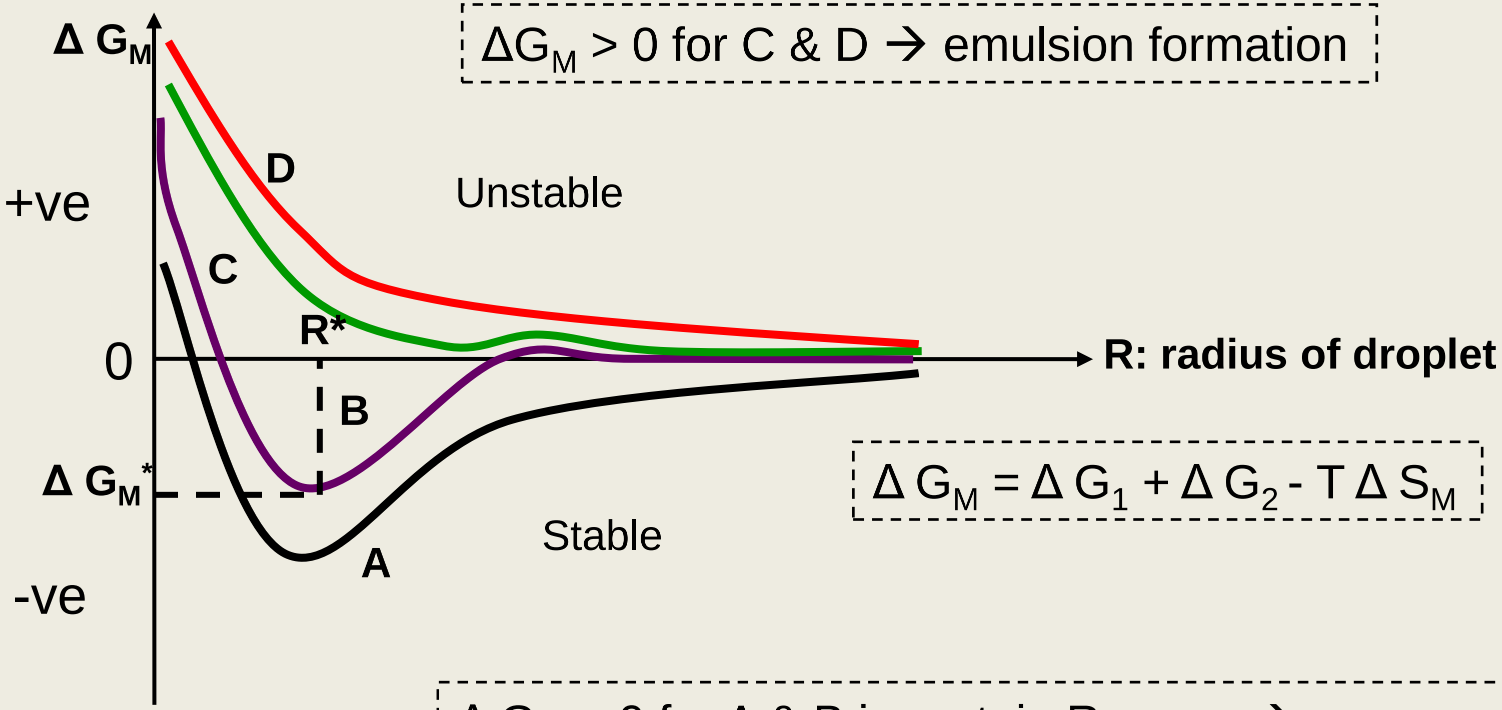
# 2.2. Stability of microemulsion

## 2.2.2. Stability of emulsion

**Why are microemulsions thermodynamically stable?**



$\Delta G_M > 0$ for C & D → emulsion formation

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

$\Delta G_M < 0$ for A & B in certain R range → microemulsion formation in that R range

* Ruckenstein, E, Chi, J. C., *Faraday Trans. II* 71 (1975) 1690.

# 2.2. Stability of microemulsion

## 2.2.2. Stability of emulsion

### Why are microemulsions thermodynamically stable?

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

$\Delta G_M$ = free energy change for microemulsion formation
$\Delta G_1$ = free energy change in the interfacial free energy
$\Delta G_2$ = free energy change due to interaction between droplets
$\Delta S_M$ = 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**

[*] **Ruckenstein, E, Chi, J. C., *Faraday Trans. II* 71 (1975) 1690.**

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# 2.2. Stability of microemulsion

## 2.2.2. Stability of emulsion

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

### A. Interfacial free energy change

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

Note that
$f_s$ equal to the surface tension for a single component system
Using the Debye-Hückel approximation,

$$f_d = -\frac{\psi_0{}^2}{8\pi R}\{\varepsilon_1(1+K_1R)+\varepsilon_2(K_2R\,ctnh K_2R-1)\}$$

The number of droplets, m ~ the volume of the dispersed phase, $\Phi_2$

$$m = \phi_2 / v \qquad (v = \frac{4}{3}\pi R^3)$$

# 2.2. Stability of microemulsion

## 2.2.2. Stability of emulsion

$$\boxed{\Delta G_M = \Delta G_1 + \Delta G_2 - T\Delta S_M}$$

### 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 :

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

g(r) : radial distribution function

$V_c$ : volume of the mixture which is taken as 1cm$^3$

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

$$U = \frac{m}{V_c}\int_{2R'}^{\infty} u(r) g(r) 4\pi r^2 \mathrm{d}r$$

2R' : average distance b/w the centres of two nearest droplets
if the droplets are uniformly distributed

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

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

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

# 2.2. Stability of microemulsion

## 2.2.2. Stability of emulsion

### 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 $\Delta S$ 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

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# 2.3. Formation Mechanisms of Micelles and Microemulsions

## 2.3.1. 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)**

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

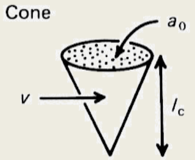
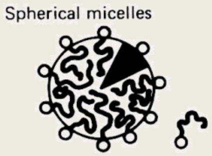
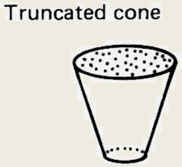
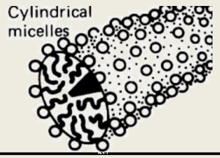
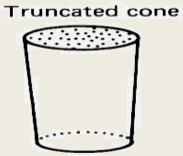
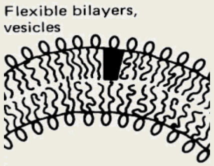
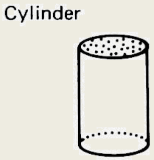
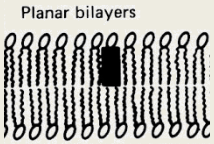
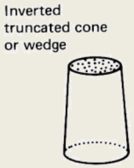
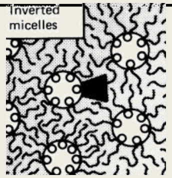
v : partial molecular volume of surfactant
$a_o$ : area of head group of surfactant
$l_c$ : maximum chain length

(1) Spherical micelles : CPP < 1/3
(2) Non-spherical micelles : 1/3 < CPP < 1/2
(3) Vesicles or bilayers : 1/2 < CPP < 1
(4) Inverted micelles : 1< CPP

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

# 2.3. Formation Mechanisms of Micelles and Microemulsions

## 2.3.1. Simple Geometric Factors

| Packing parameter | Critical packing shape | Structures formed |
|---|---|---|
| <1/3 |  |  |
| 1/3-1/2 |  |  |
| 1/2-1 |  |  |
| ~1 |  |  |
| >1 |  |  |

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

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

# 2.3. Formation Mechanisms of Micelles and Microemulsions

## 2.3.1. Simple Geometric Factors

### (1) 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 $a_0$.

### (2) 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

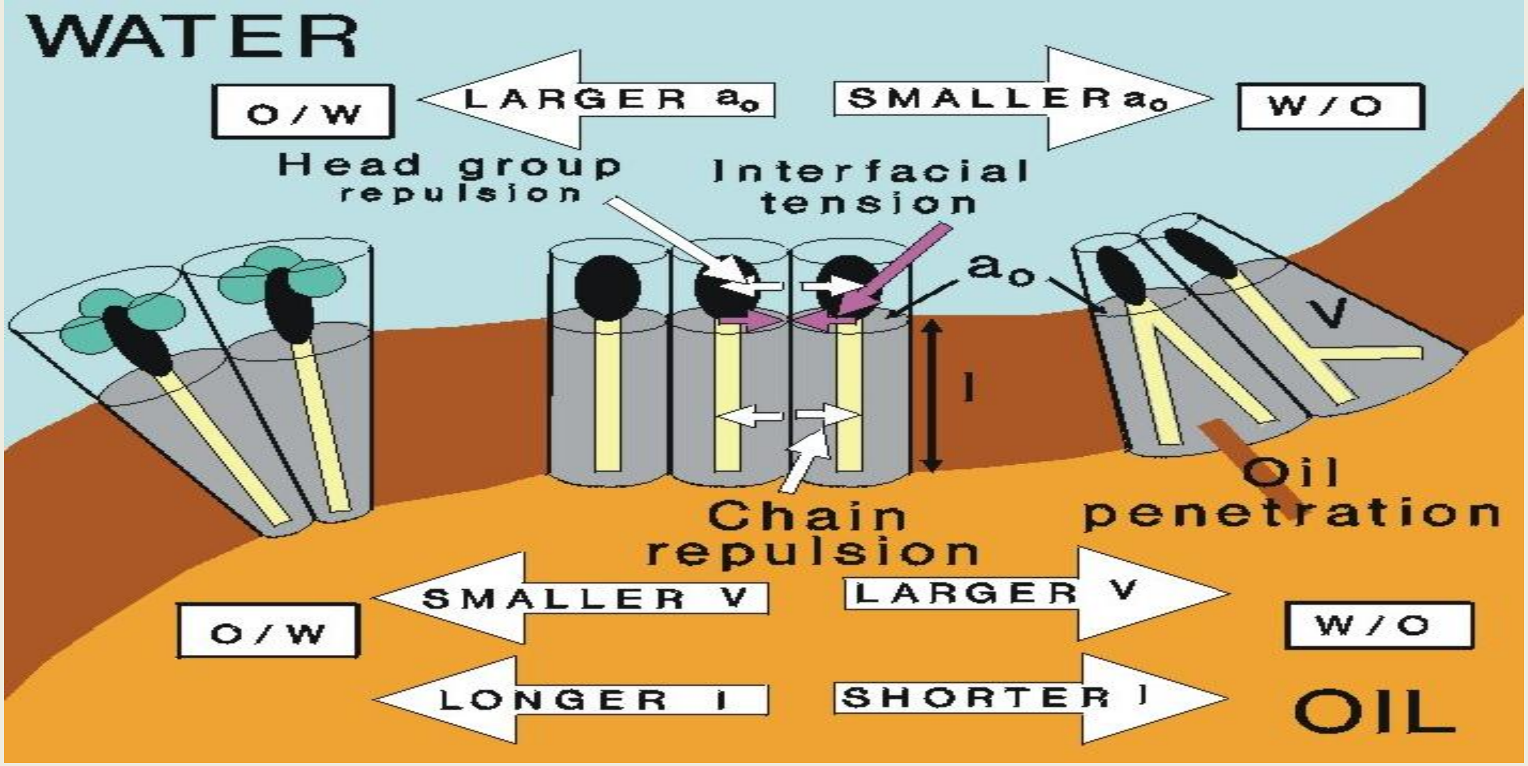
① addition of a cosurfactant with a very compact head group
(i.e. n-alkanol)

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)

# 2.3. Formation Mechanisms of Micelles and Microemulsions

## 2.3.1. Simple Geometric Factors



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

# 2.3. Formation Mechanisms of Micelles and Microemulsions

## 2.3.1. Simple Geometric Factors

### ※ 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

- 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.
- Low HLB emulsifiers are soluble in oil and give rise to w/o emulsions

### ※ Solubility and HLB

| Solubility | HLB Range |
|---|---|
| No dispersability in water | 1-4 |
| Poor Dispersion in water | 3-6 |
| Milky appearance | 6-8 |
| Stable milky appearance | 8-10 |
| Tanslucent to clear dispersion | 10-13 |
| Clear solution | 13- |

# 2.3. Formation Mechanisms of Micelles and Microemulsions

## 2.3.1. Simple Geometric Factors

### ※HLB Concept

- Bancroft's rule is entirely qualitative.
- 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.

HLB = 7 + ∑ (hydrophilic group HLB numbers) + ∑ (lipophilic group HLB numbers)

### ※ Use of Griffin's HLB number concept

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

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

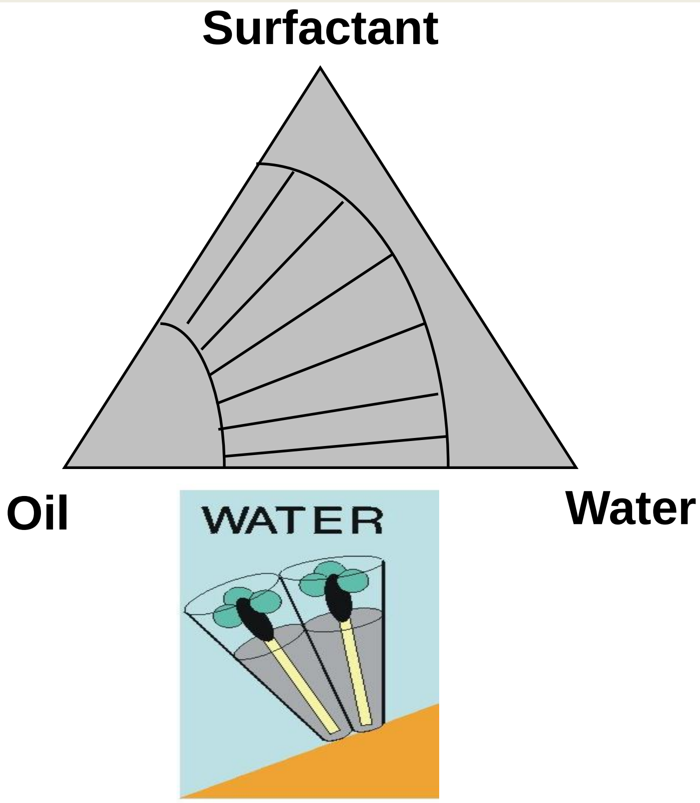
Ref.

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

M.J.Rosen, Surfactants and interfacial phenomena, 2nd Ed., Wiley, New York, 1989, p.327

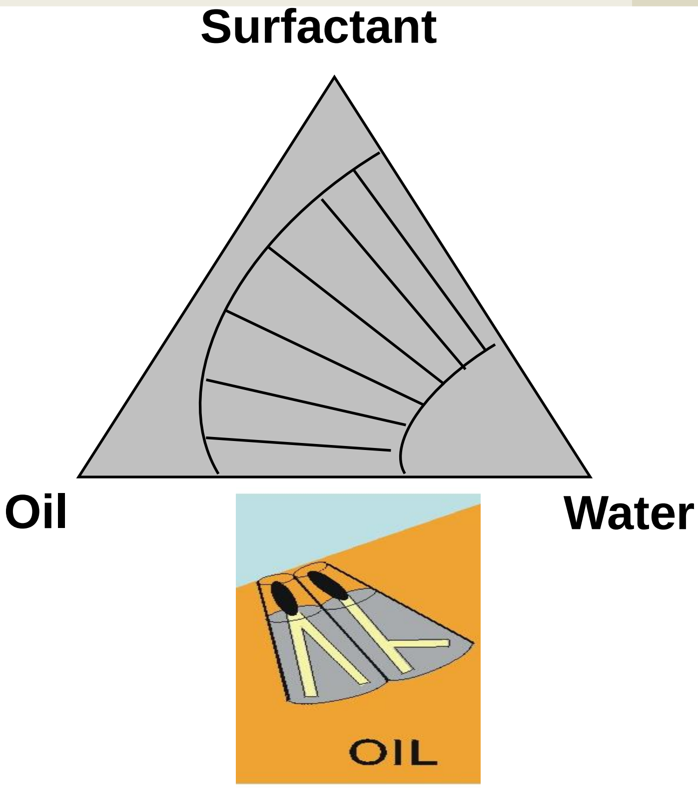
# 2.3. Formation Mechanisms of Micelles and Microemulsions

## 2.3.2. Formulation of microemulsion – Bancroft's rules



(CPP < 1)

O/W emulsion



(CPP > 1)

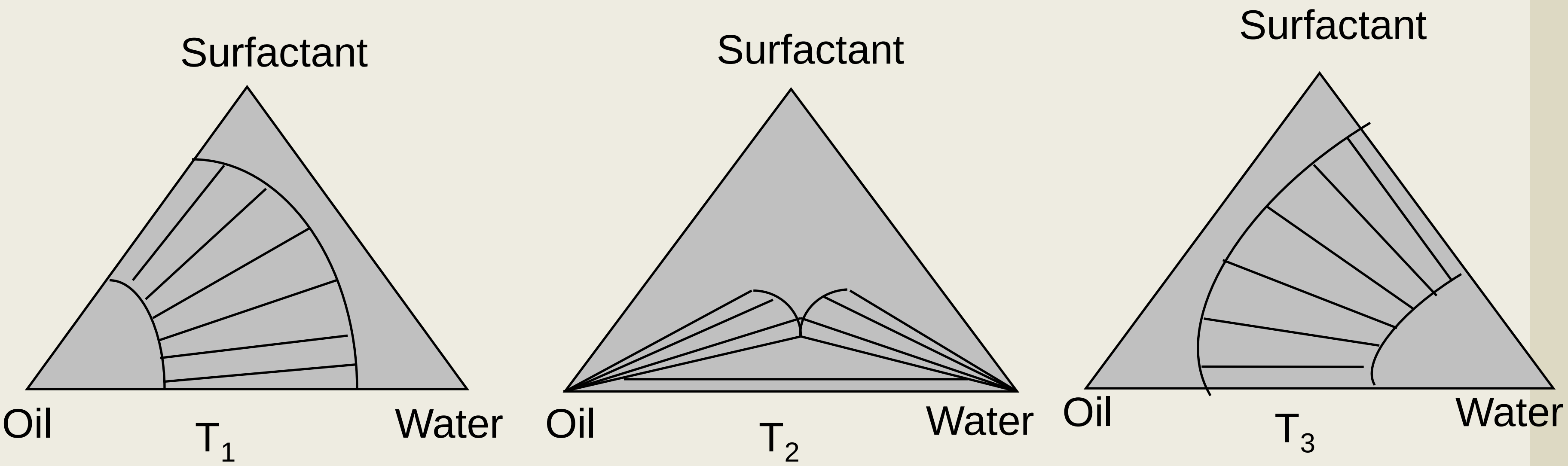
W/O emulsion

→

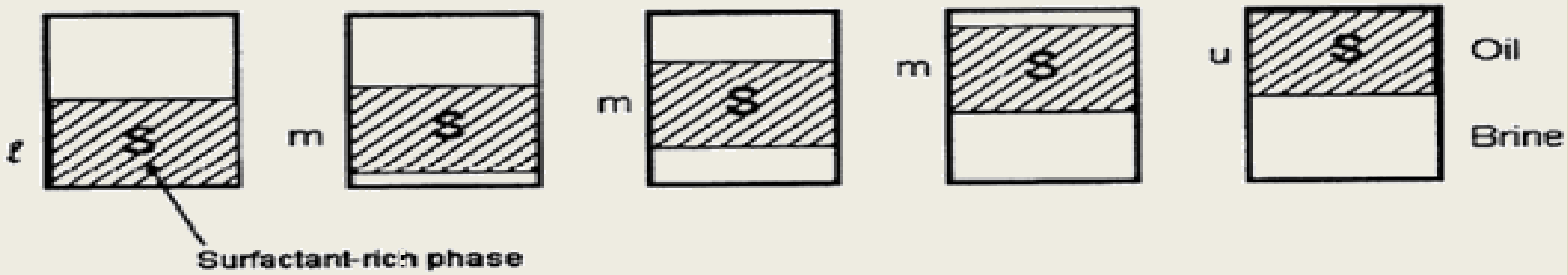
Change in variables (T, Salting out electrolyte etc.)

# 2.3. Formation Mechanisms of Micelles and Microemulsions

## 2.3.2. Formulation of microemulsion – Bancroft's rules



**Winsor I** **Winsor III** **Winsor II**



Lower phase μE

Middle/ 3 phase μE

Upper phase μE

# 2.3. Formation Mechanisms of Micelles and Microemulsions

## 2.3.2. Formulation of microemulsion – Bancroft's rules

**Variables to play with**

Salinity

Oil chain length

Alcohol conc.

Temperature

Total surfactant

brine/oil ratio

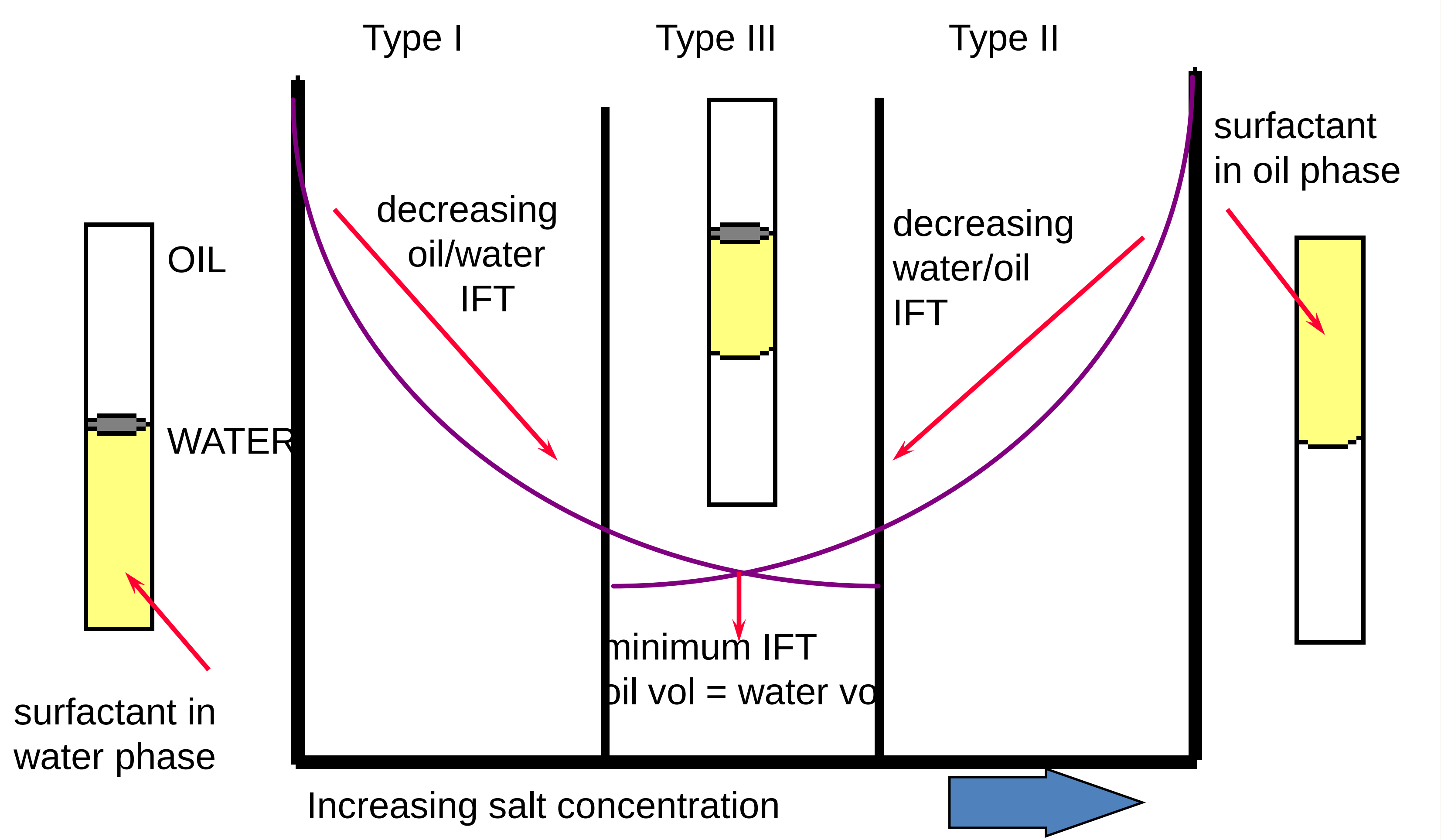
surfactant/oil ratio

M Wt. of surfactant

# 2.3. Formation Mechanisms of Micelles and Microemulsions

## 2.3.2. Formulation of microemulsion – Bancroft's rules

### ※ The Winsor Scan Diagram

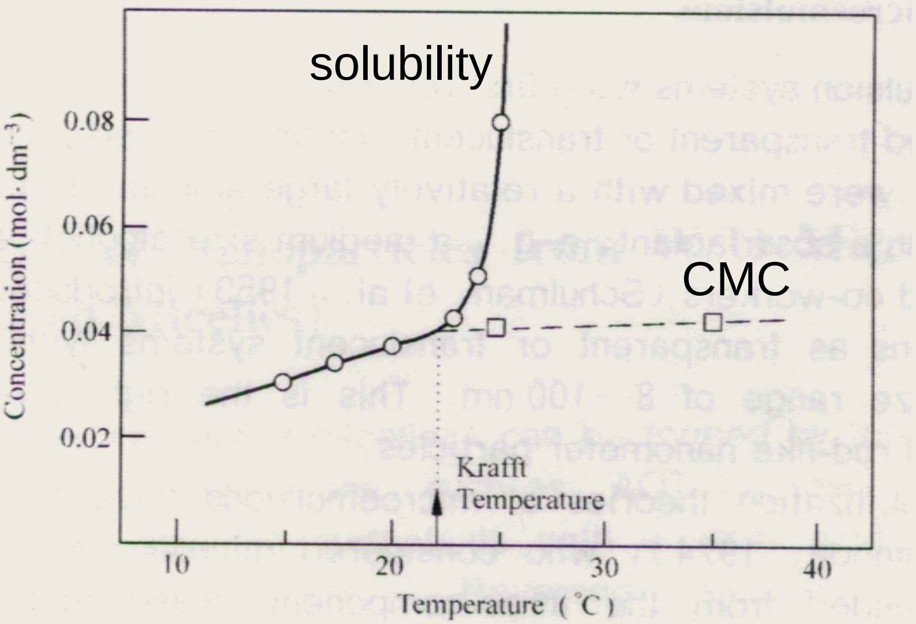


## 2.3.3. Solubilization and Formation of Microemulsions

**※ 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)



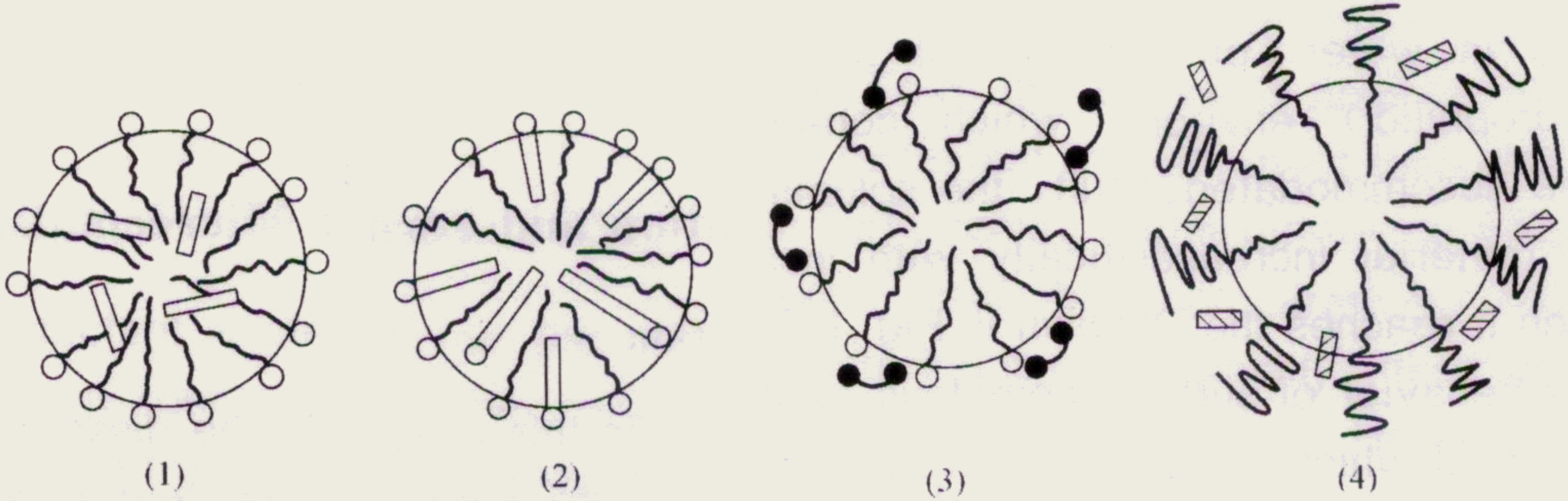
# 2.3. Formation Mechanisms of Micelles and Microemulsions

## 2.3.3. Solubilization and Formation of Microemulsions

**※Solubilization of the third party component**

- Four general possible ways for the incorporation of the solubilization

(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

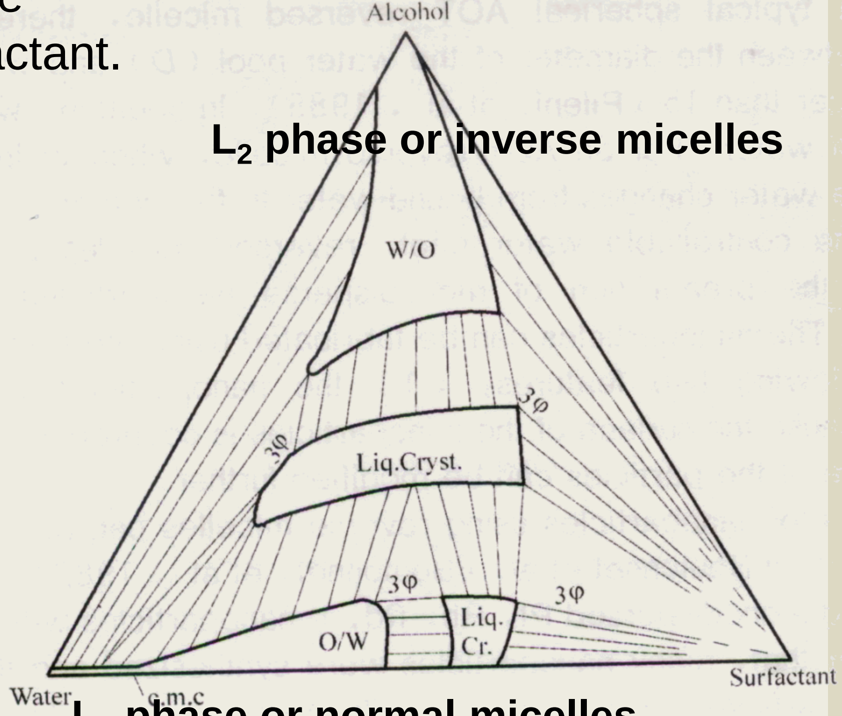


CNDL

# 2.3. Formation Mechanisms of Micelles and Microemulsions

## 2.3.3. Solubilization and Formation of Microemulsions

The solubilization theories of microemulsions
: first proposed by Shinoda,
: considered microemulsions as solubilized systems extended from the three-component phase diagrams of water-surfactant and co-surfactant.



**$L_2$ phase or inverse micelles**

**$L_1$ phase or normal micelles**

# 2.3. Formation Mechanisms of Micelles and Microemulsions

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

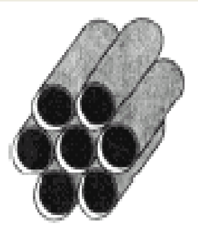
**surfactant**

$CH_3(CH_2)_nN^+(CH_3)_3\ Br^-$

$CH_3(CH_2)_nCOO^-Na^+$

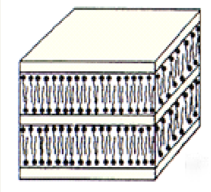
$C_8{\sim}C_{16}\ 1^0$ amine

$(EO)_n\text{-}(PO)_m\text{-}(EO)_n$



**hexagonal**

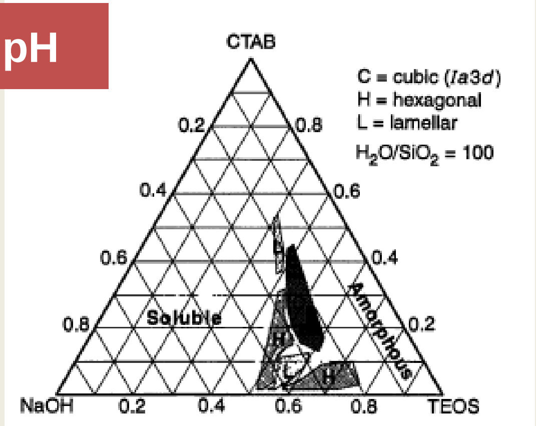
**cubic**



**lamellar**

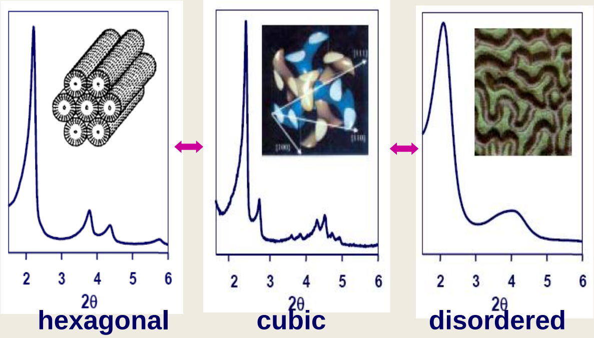
***Chem.Mater.***,8,1147,(1996)

**pH**



***Science*** **,** 267,1138, (1995)

**cosolvent**



**hexagonal** **cubic** **disordered**

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

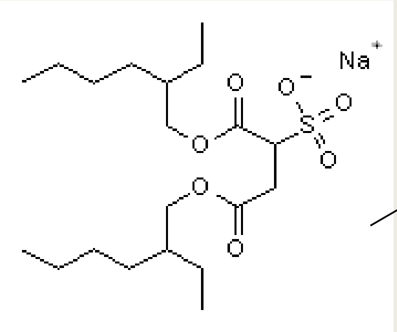
# 2.4 Synthesis of Inorganic nanomaterials from W/O Microemulsions (Reversed Micelles)

- Formed by ionic surfactants with double long alkyl chains such as AOT or by a mixture of ionic and nonionic surfactants.

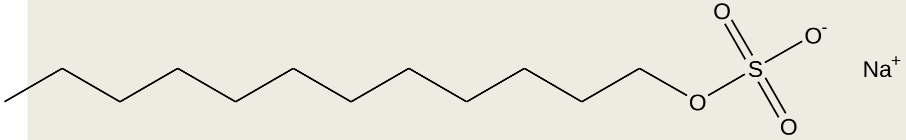
- Thermodynamically stable mixtures of four components
  : surfactant, co-surfactant, organic solvent and water

- Surfactants : AOT (aerosol OT: sodium dioctyl sulfosuccinate), SDS (sodium dodecyl sulfate), CTAB (cetyltrimethyl ammonium bromide), and Triton-X

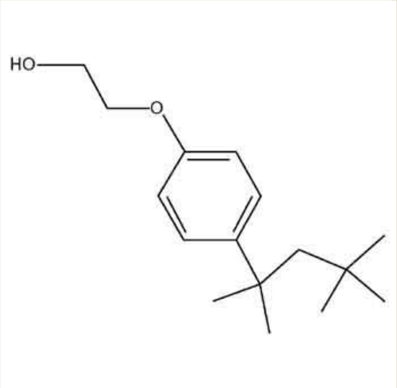
- Co-surfactants : aliphatic alcohols with a chain length of C6-C8



**AOT**

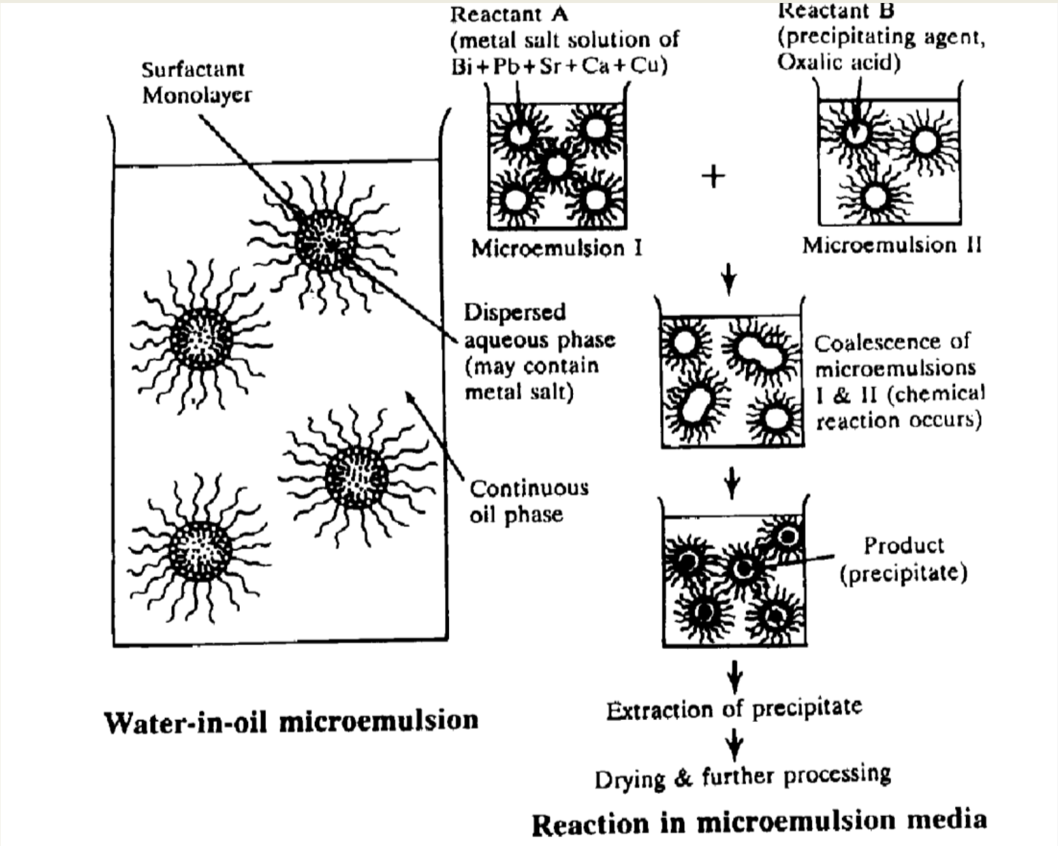


**SDS**



**Triton-X**

# 2.4 Synthesis of Inorganic nanomaterials from W/O Microemulsions (Reversed Micelles)



Schematic of W/O microemulsion and the reaction mechanism

# 2.4 Synthesis of Inorganic nanomaterials from W/O Microemulsions (Reversed Micelles)

## ※ Influence Factors on Synthesis

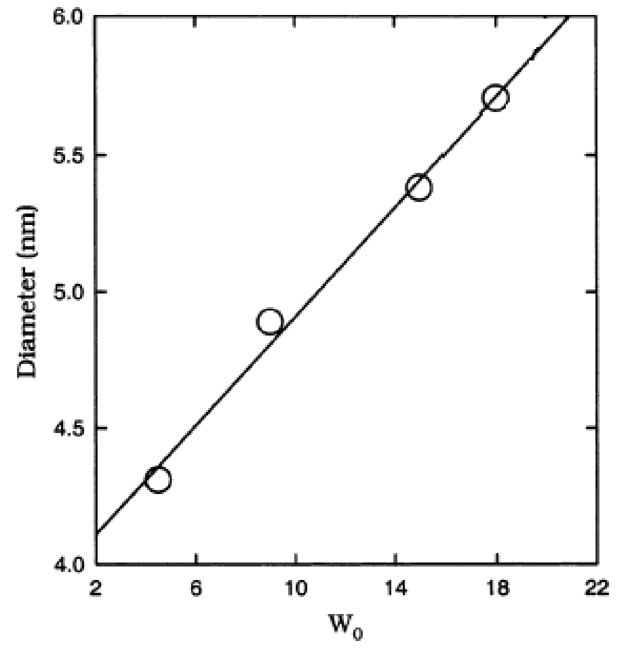
**(1) Water/surfactant ratio**

- **$w$ = [$H_2O$] / [surfactant]**
- **An important parameter in determining the size of the reversed micelles and the structure of water.**
- **For typical spherical AOT reversed micelle, water pool diameter D, D = 0.3 $w$**
- **Possible to prepare monodisperse nanoparticles with various sizes, due to the controllable water pool**

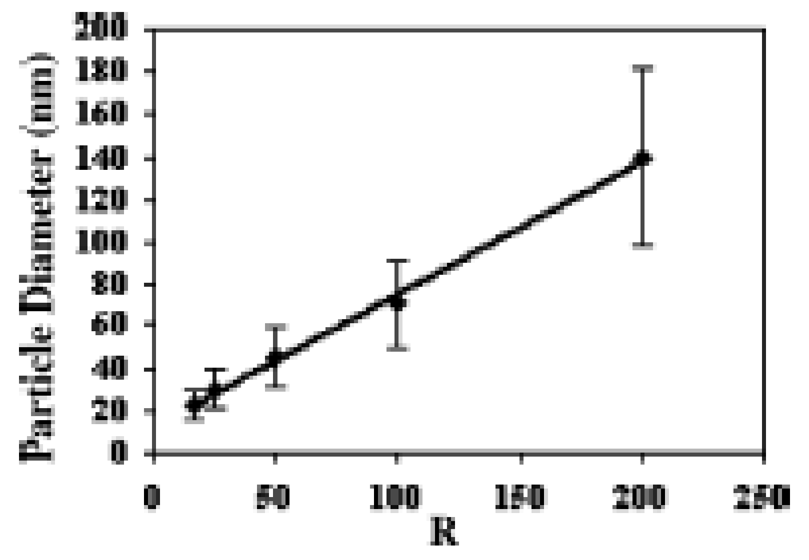
**(2) Surfactant and organic solvents**

# 2.4 Synthesis of Inorganic nanomaterials from W/O Microemulsions (Reversed Micelles)

## (1) water/surfactant (*W*o; R) ∝ diameter of droplets



Relationship between the average size of the $TiO_2$ nanoparticles and the *W*o value (water, AOT, cyclohexane, titanium isopropoxide in 1-hexanol)
J. Am. Chem. Soc. 2002, 124, 11514-11518



Plot of the Au cluster size in diameter as a function of *R*.
(AOT, n-heptane, water, HF, $KAuCl_4$)

J. Am. Chem. Soc. 2005, 127, 4574-4575

# 2.4 Synthesis of Inorganic nanomaterials from W/O Microemulsions (Reversed Micelles)

## (2) Surfactants and organic solvents

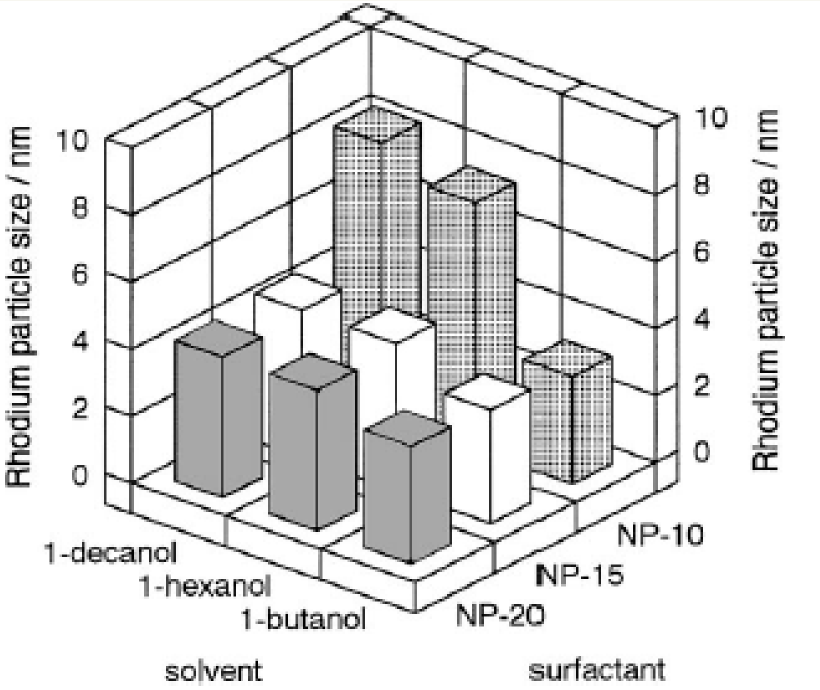


Fig. 8. Change in the rhodium particle size with the structure of surfactants and *n*-alcohols. Polyoxyethylene nonylphenylether/*n*-alcohol system, rhodium content: 2.0 wt.%.

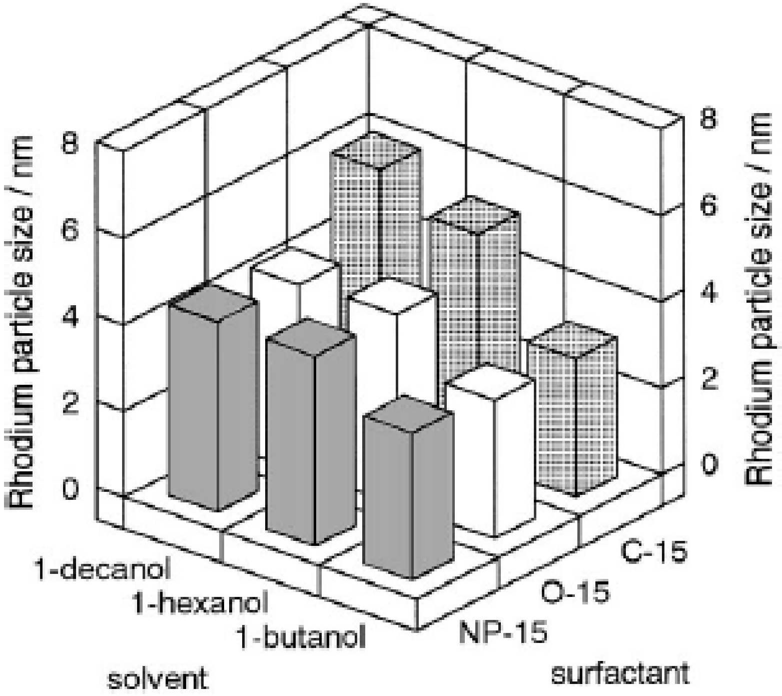


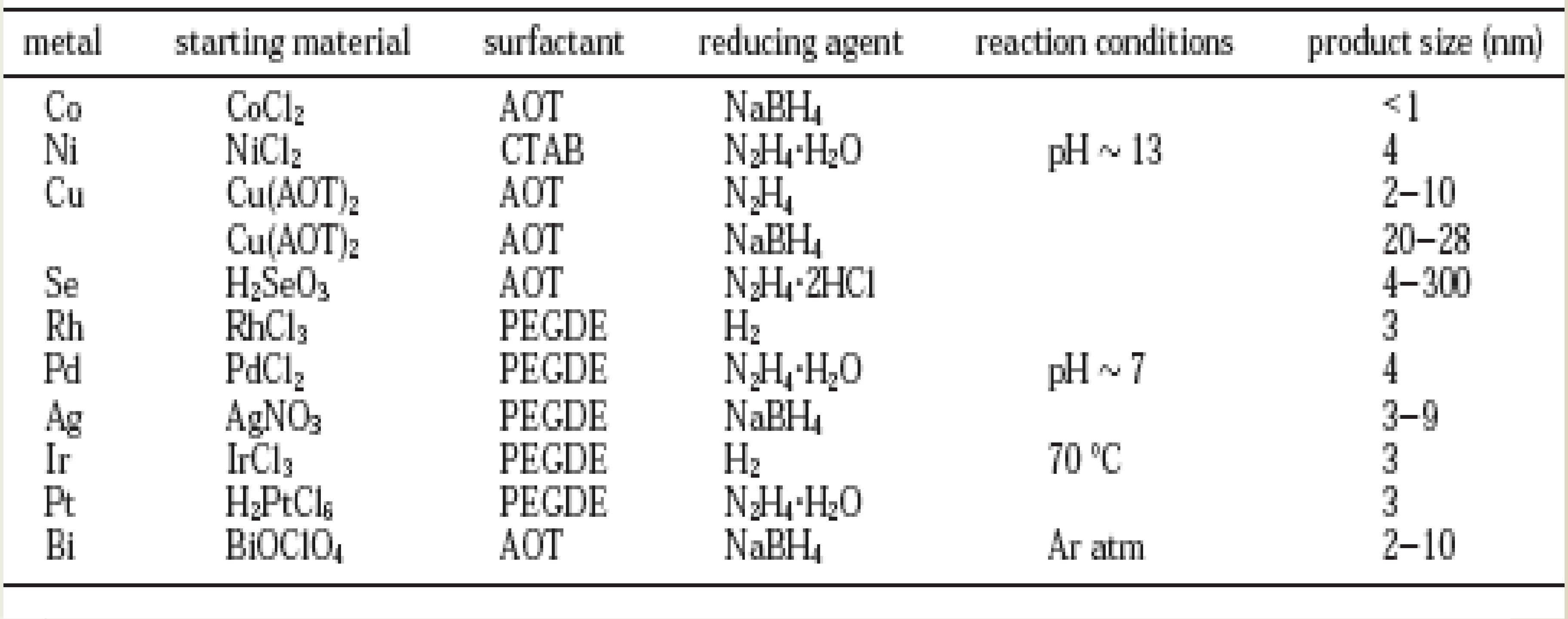
Fig. 9. Effect of the structure of hydrophobic groups on the rhodium particle size.

Applied Catalysis A: General, 190, 2000, 291–296

# 2.4 Synthesis of Inorganic nanomaterials from W/O Microemulsions (Reversed Micelles)

## 2.4.1 Metallic nanomaterials

**Representative Examples Of Metal Nanoparticles Prepared by Microemulsion**



| metal | starting material | surfactant | reducing agent | reaction conditions | product size (nm) |
|---|---|---|---|---|---|
| Co | $CoCl_2$ | AOT | $NaBH_4$ |  | < 1 |
| Ni | $NiCl_2$ | CTAB | $N_2H_4 \cdot H_2O$ | pH ~ 13 | 4 |
| Cu | $Cu(AOT)_2$ | AOT | $N_2H_4$ |  | 2–10 |
|  | $Cu(AOT)_2$ | AOT | $NaBH_4$ |  | 20–28 |
| Se | $H_2SeO_3$ | AOT | $N_2H_4 \cdot 2HCl$ |  | 4–300 |
| Rh | $RhCl_3$ | PEGDE | $H_2$ |  | 3 |
| Pd | $PdCl_2$ | PEGDE | $N_2H_4 \cdot H_2O$ | pH ~ 7 | 4 |
| Ag | $AgNO_3$ | PEGDE | $NaBH_4$ |  | 3–9 |
| Ir | $IrCl_3$ | PEGDE | $H_2$ | 70 °C | 3 |
| Pt | $H_2PtCl_6$ | PEGDE | $N_2H_4 \cdot H_2O$ |  | 3 |
| Bi | $BiOClO_4$ | AOT | $NaBH_4$ | Ar atm | 2–10 |

# 2.4 Synthesis of Metallic nanomaterials from W/O Microemulsions (Reversed Micelles)

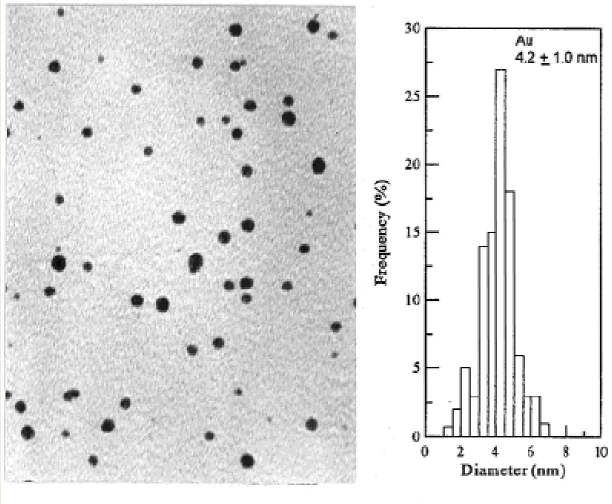
## 2.4.1 Metallic nanomaterials

### Synthesis Pd, Au, Au/Pd nanoparticles

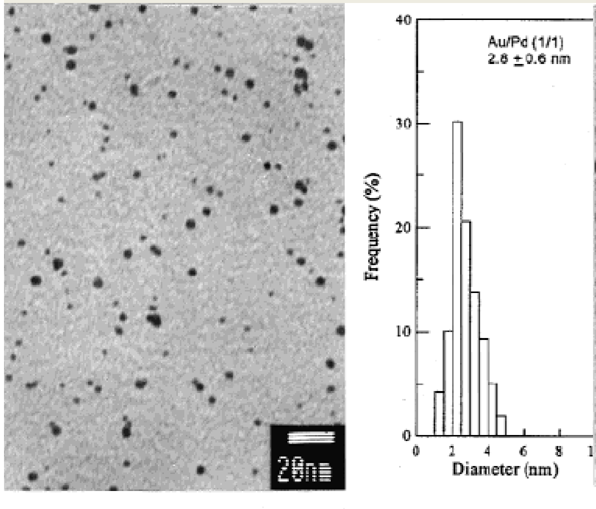
$$2H_2PdCl_4 + N_2H_5OH \rightarrow 2Pd + 8HCl + N_2 + H_2O$$

$$4HAuCl_4 + 3N_2H_5OH \rightarrow 4Au + 16HCl + 3N_2 + 3H_2O$$

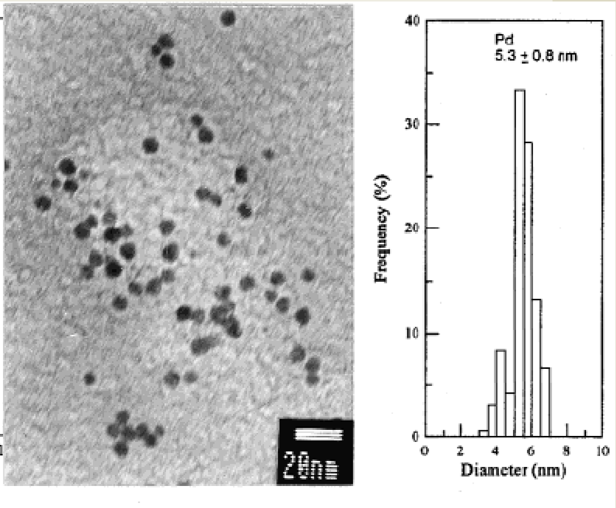
AOT/isooctane



(a)



(c)



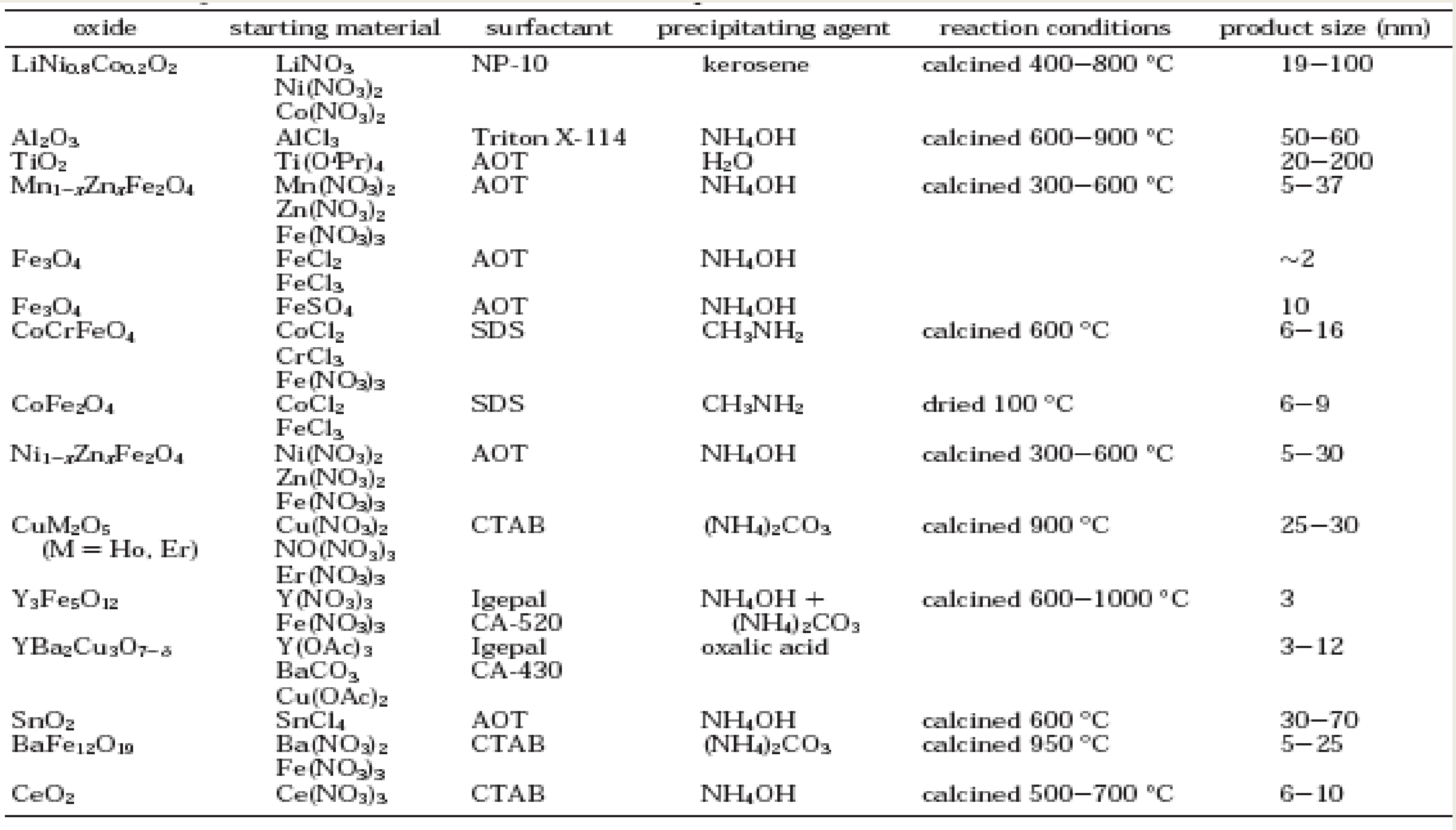
(e)

Langmuir, 2001, 17, 3877-3883

# 2.4 Synthesis of Metallic nanomaterials from W/O Microemulsions (Reversed Micelles)

## 2.4.2 Metal Oxide nanomaterials

### Survey from the Literature of Oxides Prepared from Microemulsions



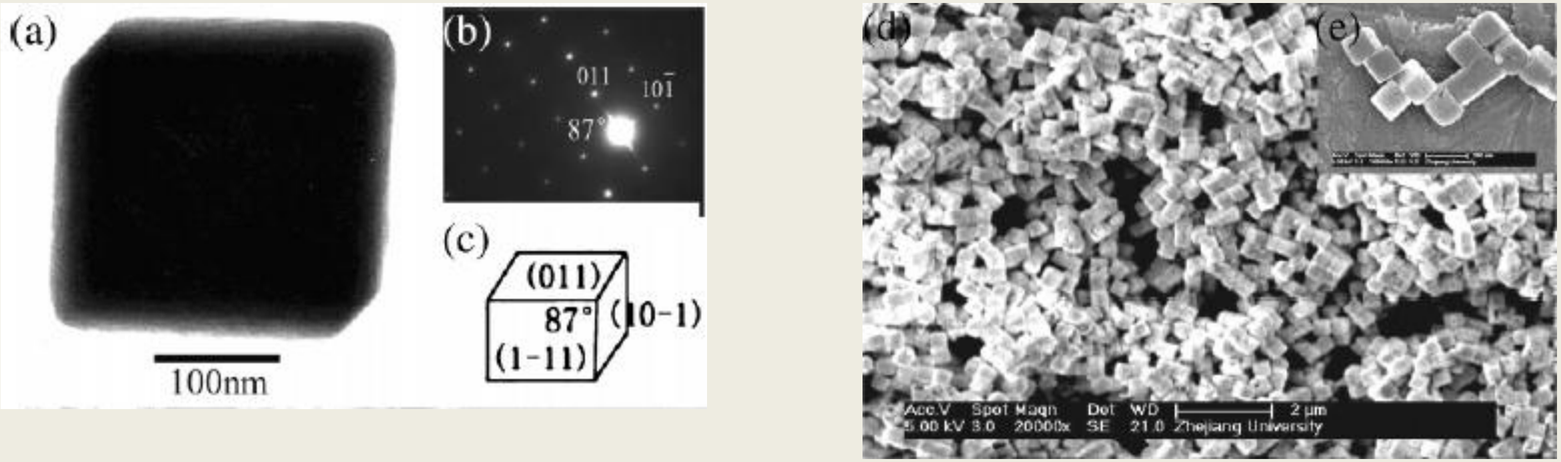
| oxide | starting material | surfactant | precipitating agent | reaction conditions | product size (nm) |
|---|---|---|---|---|---|
| $LiNi_{0.8}Co_{0.2}O_2$ | $LiNO_3$<br>$Ni(NO_3)_2$<br>$Co(NO_3)_2$ | NP-10 | kerosene | calcined 400–800 °C | 19–100 |
| $Al_2O_3$ | $AlCl_3$ | Triton X-114 | $NH_4OH$ | calcined 600–900 °C | 50–60 |
| $TiO_2$ | $Ti(O^iPr)_4$ | AOT | $H_2O$ |  | 20–200 |
| $Mn_{1-x}Zn_xFe_2O_4$ | $Mn(NO_3)_2$<br>$Zn(NO_3)_2$<br>$Fe(NO_3)_3$ | AOT | $NH_4OH$ | calcined 300–600 °C | 5–37 |
| $Fe_3O_4$ | $FeCl_2$<br>$FeCl_3$ | AOT | $NH_4OH$ |  | ~2 |
| $Fe_3O_4$ | $FeSO_4$ | AOT | $NH_4OH$ |  | 10 |
| $CoCrFeO_4$ | $CoCl_2$<br>$CrCl_3$<br>$Fe(NO_3)_3$ | SDS | $CH_3NH_2$ | calcined 600 °C | 6–16 |
| $CoFe_2O_4$ | $CoCl_2$<br>$FeCl_3$ | SDS | $CH_3NH_2$ | dried 100 °C | 6–9 |
| $Ni_{1-x}Zn_xFe_2O_4$ | $Ni(NO_3)_2$<br>$Zn(NO_3)_2$<br>$Fe(NO_3)_3$ | AOT | $NH_4OH$ | calcined 300–600 °C | 5–30 |
| $CuM_2O_5$ (M = Ho, Er) | $Cu(NO_3)_2$<br>$NO(NO_3)_3$<br>$Er(NO_3)_3$ | CTAB | $(NH_4)_2CO_3$ | calcined 900 °C | 25–30 |
| $Y_3Fe_5O_{12}$ | $Y(NO_3)_3$<br>$Fe(NO_3)_3$ | Igepal CA-520 | $NH_4OH$ + $(NH_4)_2CO_3$ | calcined 600–1000 °C | 3 |
| $YBa_2Cu_3O_{7-\delta}$ | $Y(OAc)_3$<br>$BaCO_3$<br>$Cu(OAc)_2$ | Igepal CA-430 | oxalic acid |  | 3–12 |
| $SnO_2$ | $SnCl_4$ | AOT | $NH_4OH$ | calcined 600 °C | 30–70 |
| $BaFe_{12}O_{19}$ | $Ba(NO_3)_2$<br>$Fe(NO_3)_3$ | CTAB | $(NH_4)_2CO_3$ | calcined 950 °C | 5–25 |
| $CeO_2$ | $Ce(NO_3)_3$ | CTAB | $NH_4OH$ | calcined 500–700 °C | 6–10 |

# 2.4 Synthesis of Metallic nanomaterials from W/O Microemulsions (Reversed Micelles)

## 2.4.2 Metal Oxide nanomaterials

### Preparation of Monodisperse $GeO_2$ Nanocubes in a Reverse Micelle System

$GeCl_4$, heptane (or octane), CTAB



(a) TEM image of a single $GeO_2$ cube. (b) SAED pattern of the particle in a; (c) illustration of the cubelike shape of the single crystal in a; (d) and (e) SEM images at different magnifications. Scale bar in e is 500 nm.

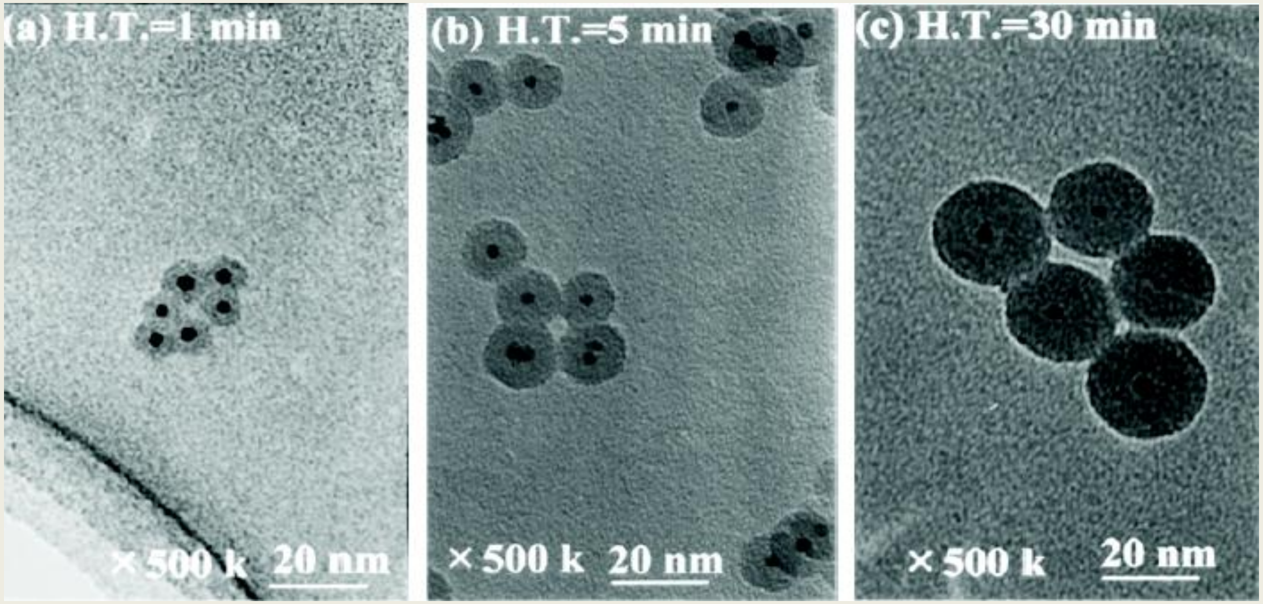
Chem. Mater. 2006, 18, 1817-1820

# 2.4 Synthesis of Metallic nanomaterials from W/O Microemulsions (Reversed Micelles)

## 2.4.3 Inorganic composites nanomaterials

**Synthesis Rh/SiO$_2$ nanoparticles**

polyoxyethylene (15) cetyl ether (C-15), cyclohexane and water.(tetraethylorthosilicate, TEOS)

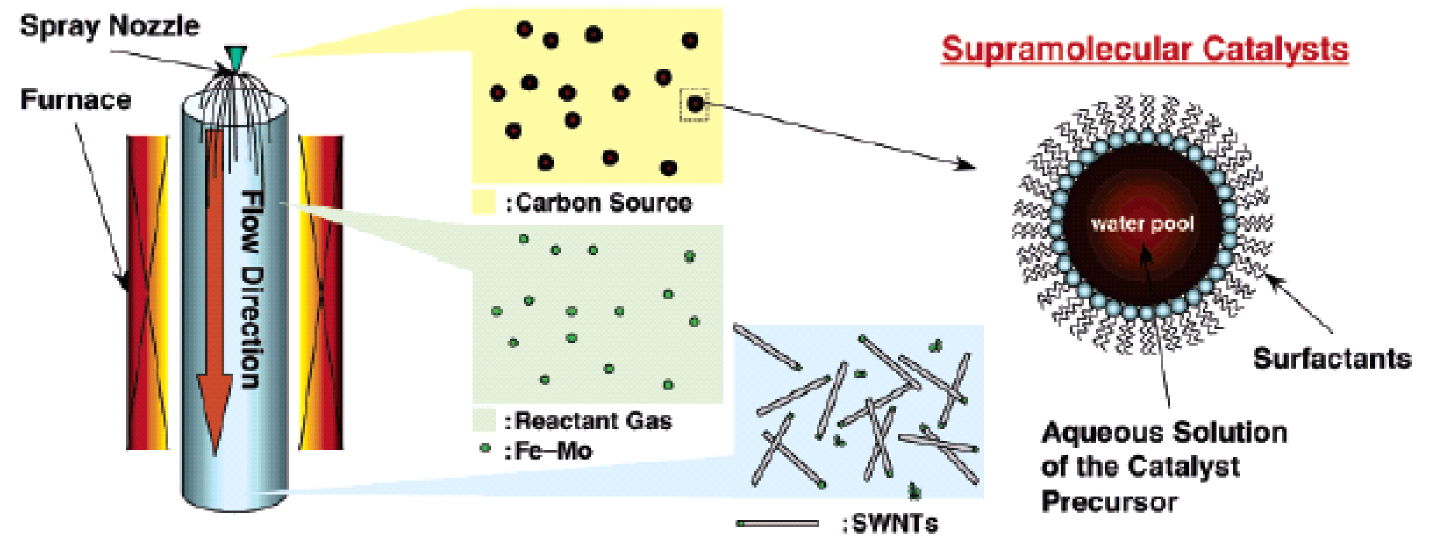


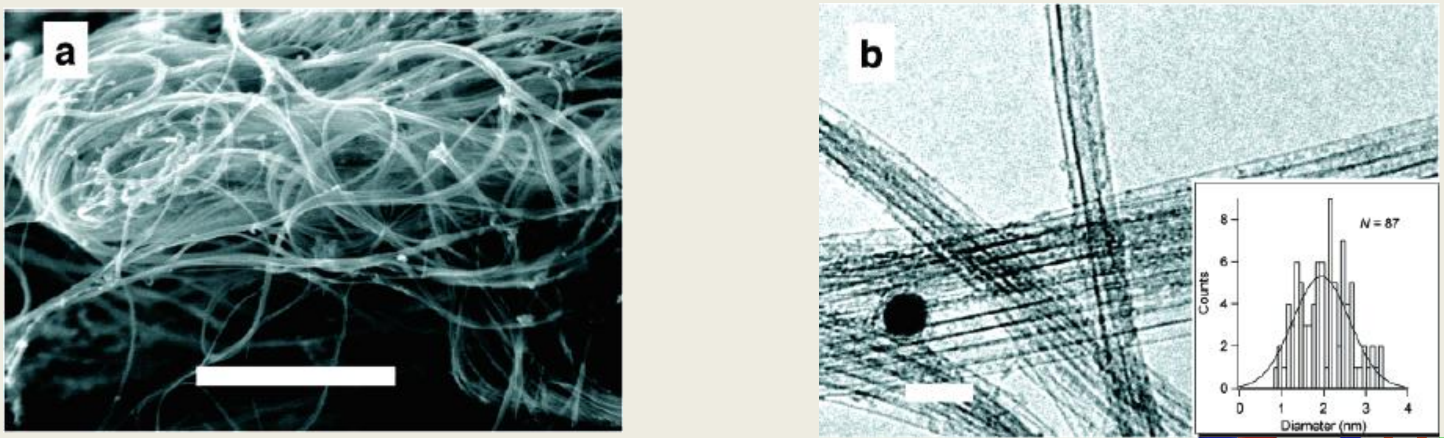
TEM photographs of SiO$_2$-coated Rh nanoparticles prepared with hydrolysis times of (a) 1, (b) 5 and (c) 30 minutes.

Journal of Materials Science, 37, 2002, 977 – 982

# Supramolecular Catalysts for the Gas-phase Synthesis of Single-walled Carbon Nanotubes

(dimethyldioctylammonium bromide, toluene, MoCl$_3$, FeCl$_3$, water)





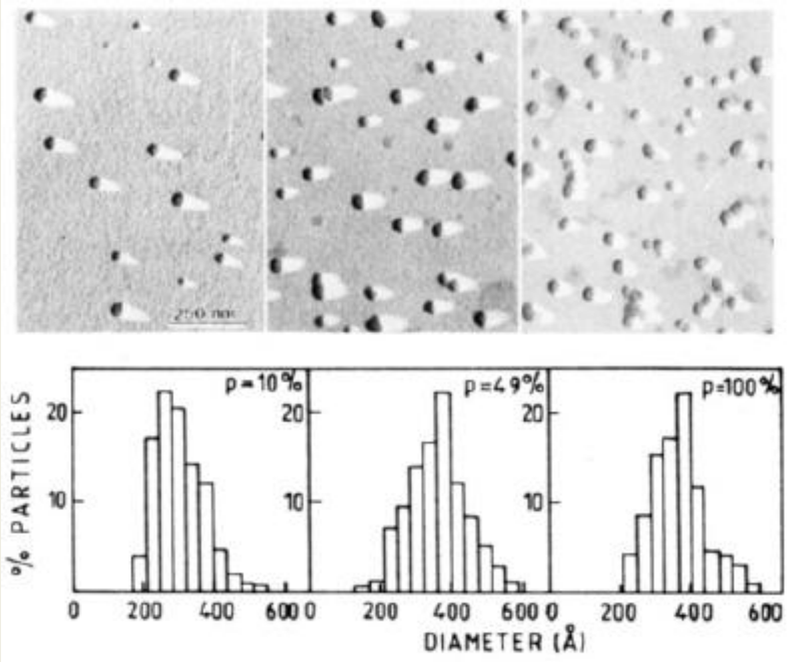
S. Iijima, et al. J. Phys. Chem. B. 2006, 110, 5849-5853

# 2.5. Synthesis of Organic nanomaterials from O/W Microemulsions polymerization

- 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., 18, 2641 (1980)**

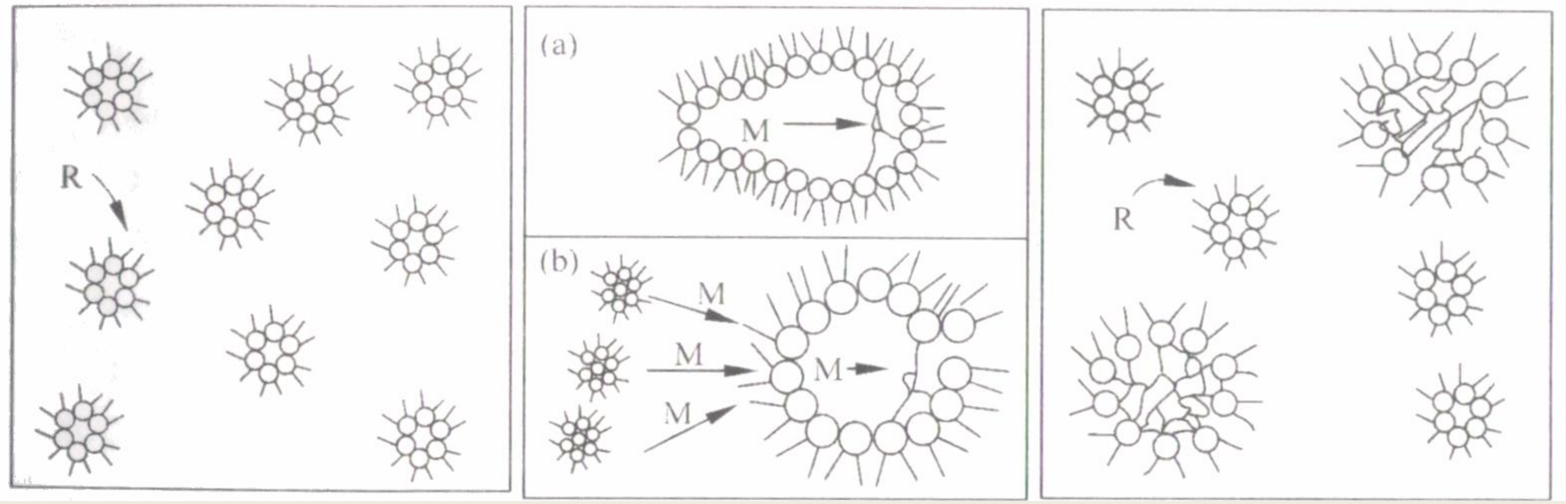
- First successful microemulsion polymerization was reported.
- CTAB/styrene/hexanal/water
- Monodisperse nanoparticles : 20, 35nm
**Atik, Thomas, JACS., 103, 4279 (1981)**

- First study of microemulsion polymerization using electron microscopy
**Carver, J. Phys. Chem., 93, 4867 (1989)**



# 2.5. Synthesis of Organic nanomaterials from O/W Microemulsions polymerization

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



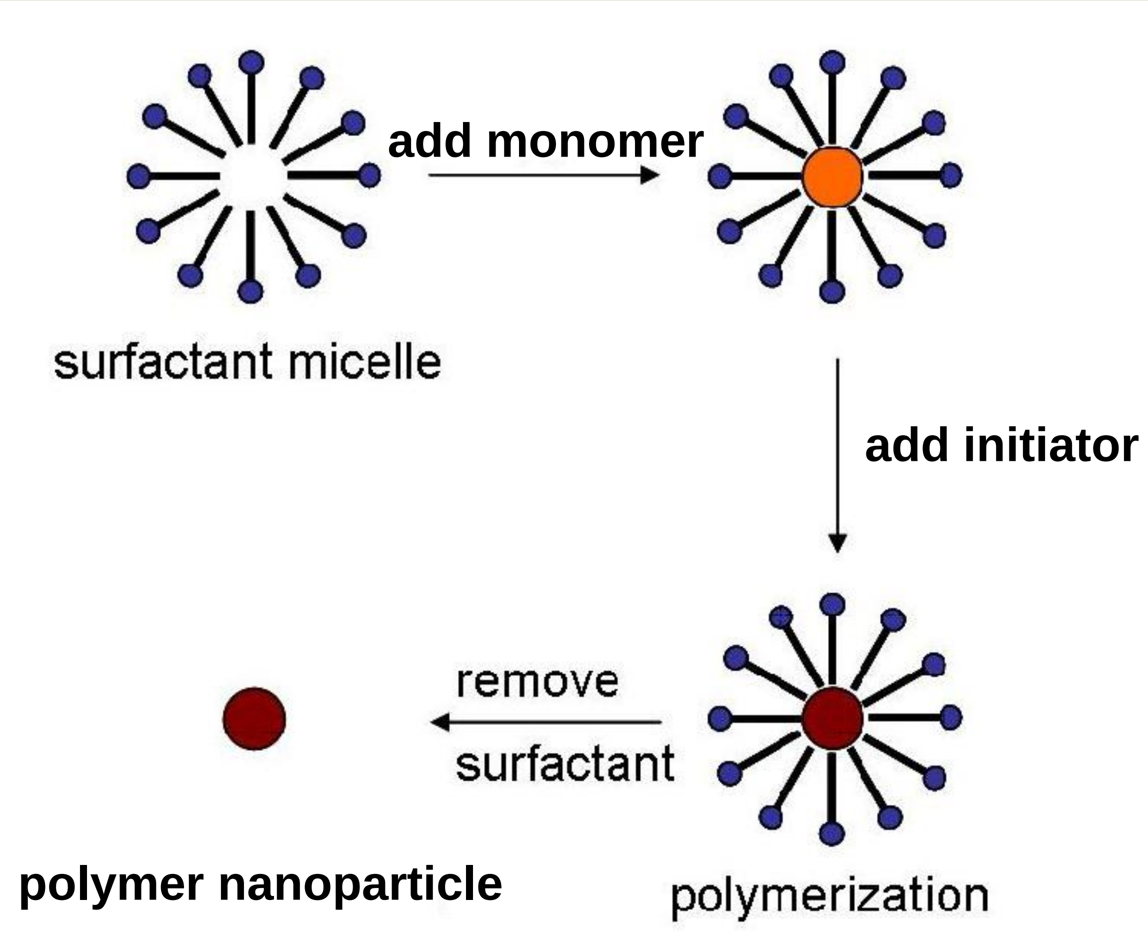
Before polymerization Polymer particle growth End of polymerization

(a) by collisions between particles
(b) by monomer diffusion through the oil phase

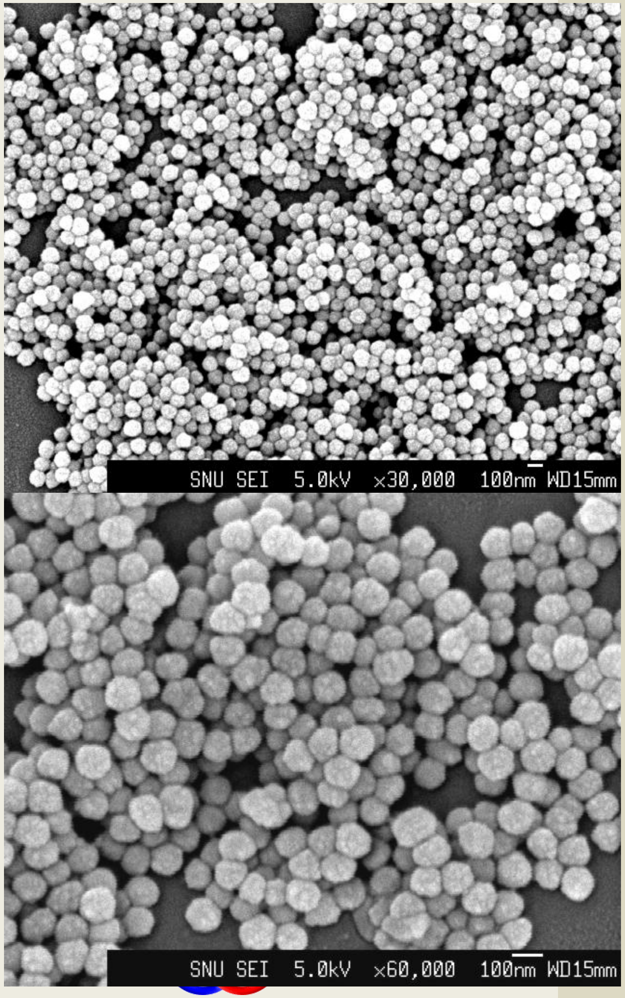
Candau, in Scientific Methods for the Study of Polymer Colloids and Their Application, Kluwer Academic Publ., 73 (1990)

# 2.5. Synthesis of Organic nanomaterials from O/W Microemulsions polymerization

Schematics of conventional microemulsion polymerization method



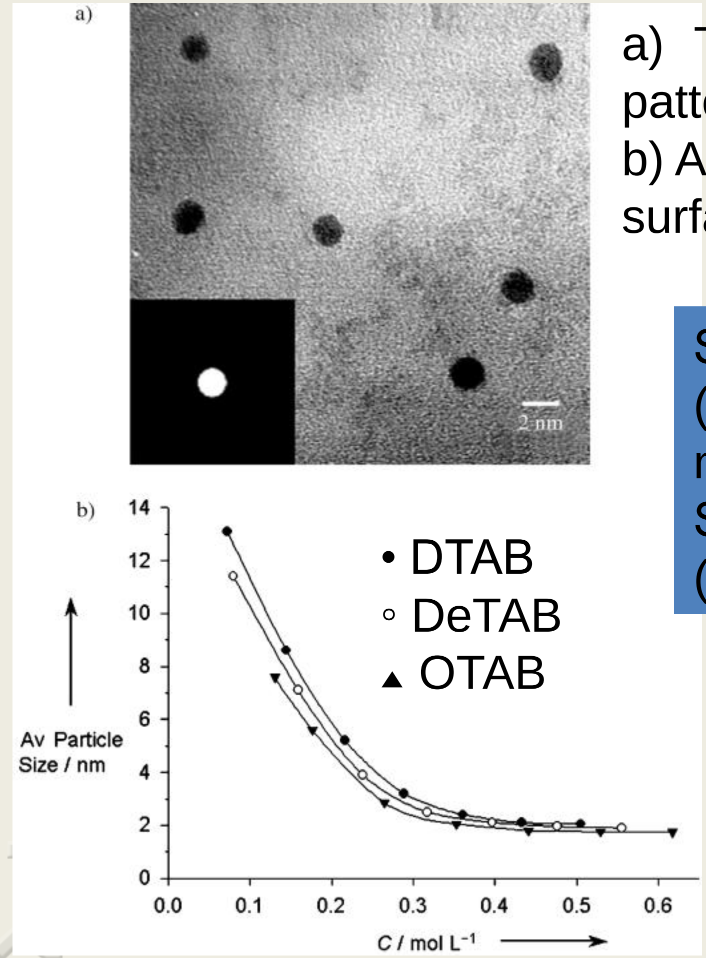
SEM micrographs of Polypyrrole NPs (100nm)



# 2.5. Synthesis of Organic nanomaterials from O/W Microemulsions polymerization

## ※ 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 ↑ ⇒ size ↑
(∵ enhanced flexibility of longer spacers provides more free volume inside the micelle)
Surfactant concentration ↑ ⇒ size ↓
(∵ number of micelle ↑ ⇒ dense packing)

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

Angew. Chem. Int. Ed. 41, 4016 (2002)

# 2.5. Synthesis of Organic nanomaterials from O/W Microemulsions polymerization

※ **Influence factors of polymer particle size in microemulsion method**

**(2) Temperature**

| Temperature (℃) | Particle size (nm) |
|---|---|
| 3 | 2 |
| 25 | 12 |
| 70 | 53 |

As the polymerization temperature ↑ ⇒ size ↑
(∵ increased mobility of surfactant chains)

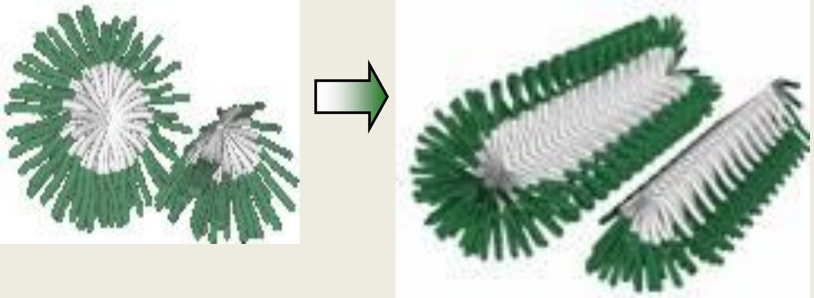
Angew. Chem. Int. Ed. 41, 4016 (2002)

CNDL

# 2.5. Synthesis of Organic nanomaterials from O/W Microemulsions polymerization

## ※ Morphological transition – Sphere to rod transition

The spherical surfactant micelles undergo a transition to larger rodlike aggregates with the increase of surfactant concentration (CMCⅠ→CMCⅡ)



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

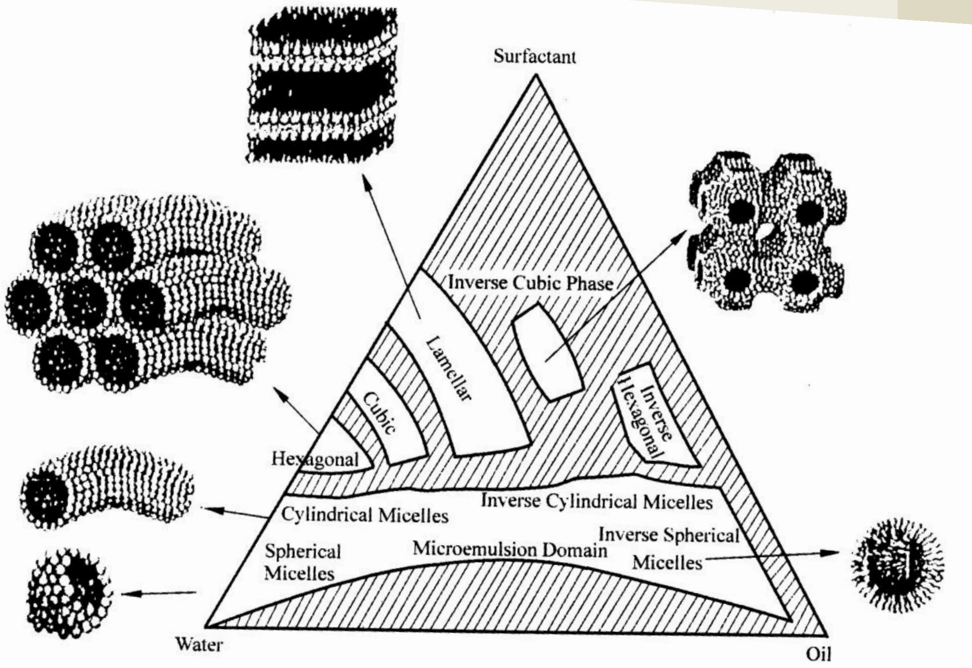


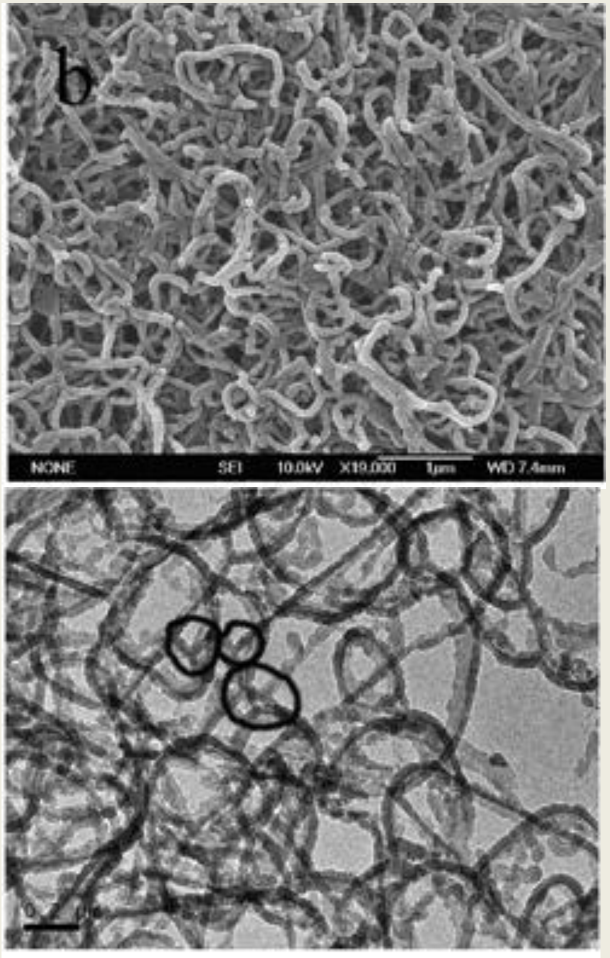
**Figure 1. 3** A schematic phase diagram of surfactant-oil-water systems showing a variety of self-assembled structures (After Liu, J. ,et al. ,1996).

# 2.5. Synthesis of Organic nanomaterials from O/W Microemulsions polymerization

## ※ Morphological transition – Sphere to rod transition

High-Yield Synthesis of Superhydrophilic Polypyrrole Nanowire

Monomer : pyrrole
Surfactant : hexadecyltrimethylammonium bromide (HTAB)
Initiator : ammonium persulfate (APS)



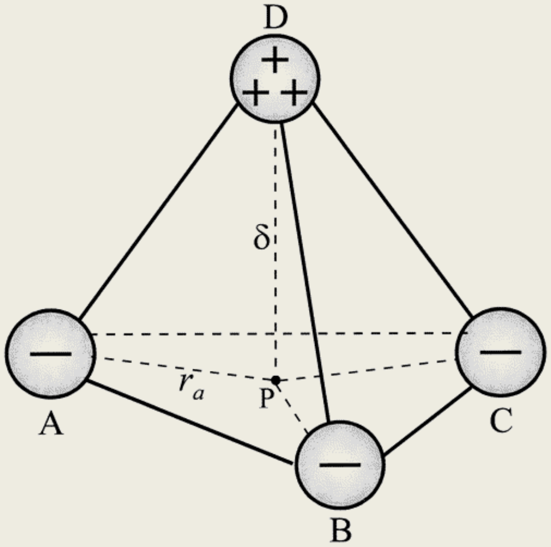
Macromolecules, 39, 3224 (2006)

# 2.5. Synthesis of Organic nanomaterials from O/W Microemulsions polymerization

※ Transition enhancement by the addition of electrolyte

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

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



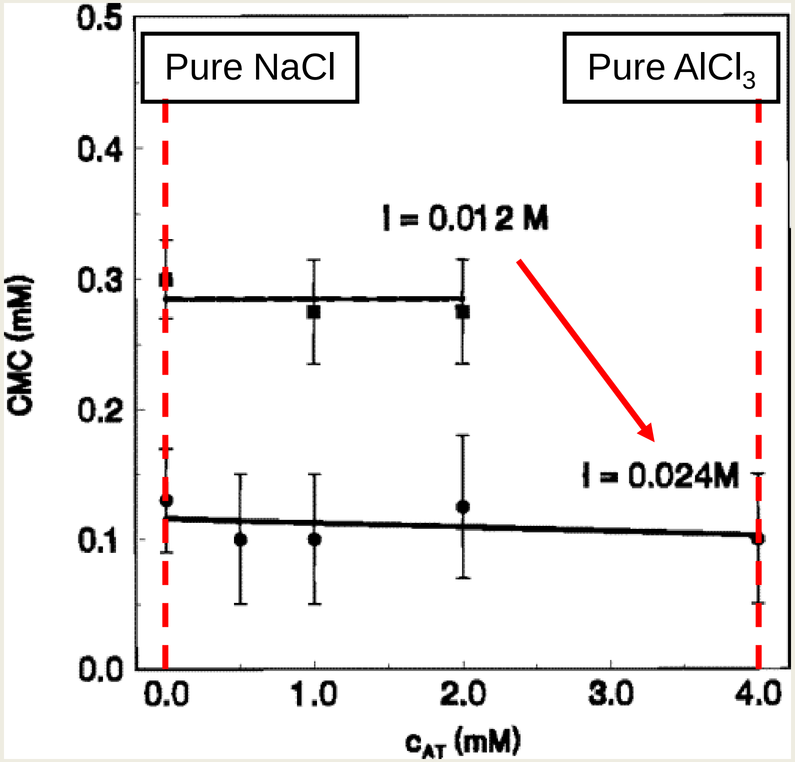
⇒ $Al^{3+}$ can bind together three surfactant head-groups at the micelle surface, thus causing a decrease of the area per headgroup.

⇒ this will induce a transition from spherical to cylindrical micelle

*Langmuir*, **14** (1998)

# 2.5. Synthesis of Organic nanomaterials from O/W Microemulsions polymerization

## ※ Transition enhancement by the addition of electrolyte



**Critical micellization concentration (CMC) of SDP-2S, measured with static light scattering, vs the total $Al^{3+}$ counterions concentration($c_{AT}$),**

The ionic strength is due to a mixture of NaCl and $AlCl_3$

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

In this studies on the growth of rod-like micelles of SDP-2S, they fixed the ionic strength of the added electrolyte, $I = 0.024$ M, but varied the molar fractions of NaCl and $AlCl_3$

*Langmuir*, **13**, 5544 (1997)