Interfacial Science & Engineering

Introduction and Applications

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Institute of Chemical Technology

Institute of Chemical Technology

- Established in 1933 - Industry's wish
- Chem Engg + Pharma + seven Chem Tech
- 250 graduate with Bachelors/yr (~1000)
- 100 to 150 complete Doctorates/yr (~700)
- Close to 200 complete post graduation/yr (~400)
- Highest Chemical Tech/ Engg publications in India
- 4th rank by publications per faculty across the globe
- 42% of Chem + Pharma Industry in India votes for ICT
- ~30% are enterpreneurs - who's who in CI, Padma Awardees
- CII-AICTE award for best industry related institute

Outline

Fluids

Intermolecular interaction forces in fluids:

- van der Waal's attractive forces
- Hydrogen Bonding - most important force in the most abundant solvent.
- Metallic bonds

in increasing order of magnitude.

- Molecules such as *n*-octane, *n*-dodecane are incapable of hydrogen bonding
- Consequently their presence in water results in unsatisfied hydrogen bonding needs of water molecules
- This increases the free energy of the solution and restricts the solubility of these molecules in water.

The Hydrophobic Effect

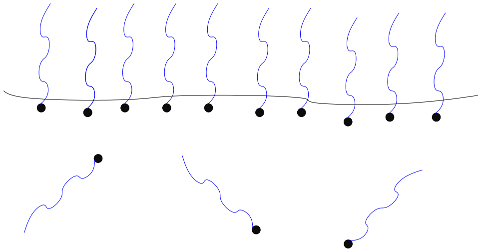
- The origin of the hydrophobicity of a molecule as a solute is more in the interactions between water molecules than solute molecules themselves.
- It is the strong desire of the water molecules to stay together that leads to pushing out of the hydrophobic molecules.
- In turn it is the strong hydrogen bonding between water molecules that brings them close together and causes them to resent the presence of other molecules in their midst.

Surfactant

A typical surfactant molecule

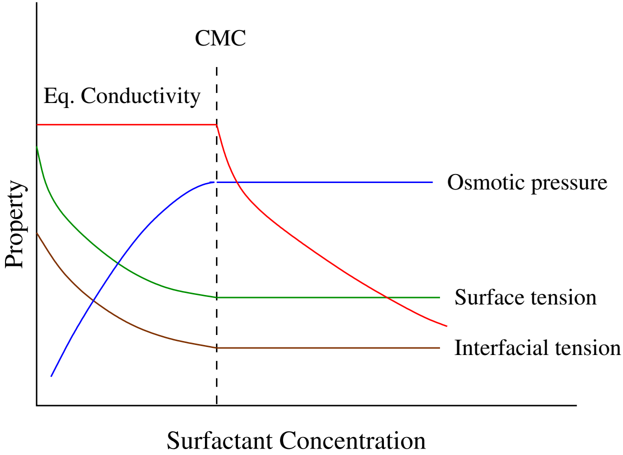
The dichotomy of the affinity in a surfactant molecule is matched perhaps only by a slippery politician's fence sitting attitude!

Adsorption

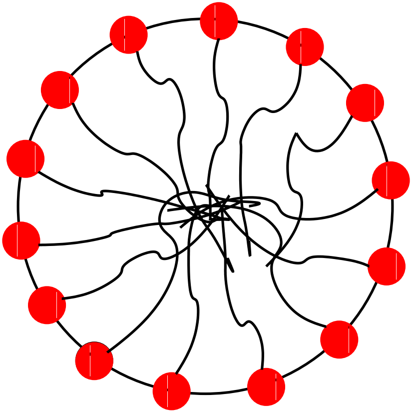


The first choice that the unwanted molecules have is to go to the 'wall' or the interface.

Unusual property changes



Micelle



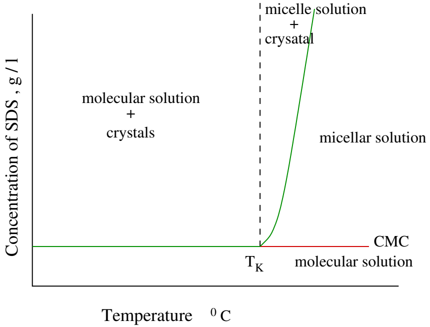
SCHEMATIC OF A NORMAL MICELLE

Aggregates

EXPECTED AGGREGATE CHARACTERISTICS

$\frac{v}{l a_g}$	Expected structure	Molecule Type	
<0.33	Spherical/ Ellipsoidal		Large head group
0.33 − 0.5	Large cylindrical/ Rod shaped		Small head group
0.5−1	Vesicles, Flexible bilayers		Flexible double chain, large head group
1.0	Extended bilayers		Rigid double chain, small head group
> 1.0	Reverse micelle (water core)		Double chain bulky hydrophobe small head group

Krafft Point

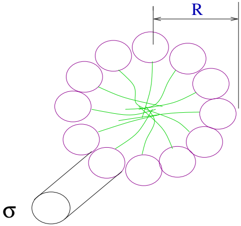


ABOVE THE KRAFT POINT, SOLUBILITY INCREASES RAPIDELY.

THE SOLUTION THUS FORMED IS NOT A NORMAL MOLECULAR SOLUTION

Micellar shapes

SPHERICAL MICELLE



Interior --- $R \le l_c$

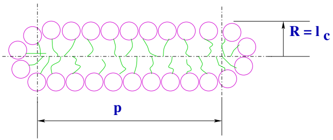
$$\text{Volume} = N \times V_c = 4/3\,\Pi\, R^3$$

$$\text{Area} = N \times \sigma = 4\,\Pi\, R^2$$

$$\frac{\text{Volume}}{\text{Area}} = \frac{R}{3} = \frac{V_c}{\sigma}$$

Max. Spherical Micelle $\rightarrow \dfrac{V_c}{l_c \sigma} = 1/3 = f$

CYLINDRICAL MICELLE



$$\text{Volume} = N \times V_c = 4/3\,\Pi\, R^3 + \Pi\, R^2 P$$

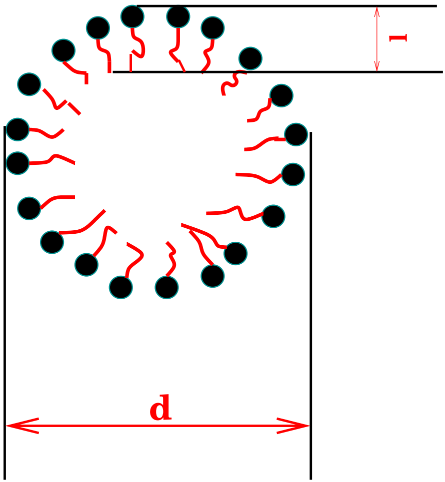
$$\text{Area} = N\,\sigma = 4\,\Pi\, R^2 + 2\Pi\, RP$$

And $R = l_c$

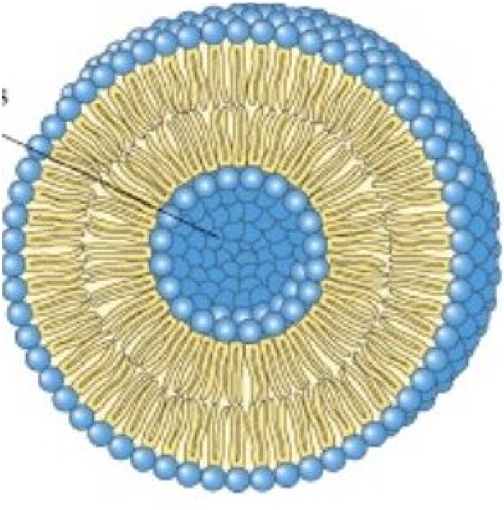
$f = 1/3$ to $1/2$

For infinite cylinder $f = 1/2$

Core vs skin



Vesicles



Surfactants

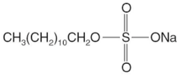
Tail- hydrocarbon, flurohydrocarbon

- Branching
  - Straight chain
  - Branched
- Aromaticity
  - with aromatic ring
  - without aromatic ring
- Origin
  - Natural based
  - Petroleum based

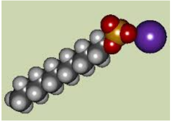
Surfactants

- Head group
- Ionic
  - Cationic
  - Anionic
  - Zwitterionic
- Non-ionic
  - Origin:
    - Natural : Sugar based
    - Petroleum :Ethylene oxide based
  - Solubility
    - Oil soluble (low HLB)
    - Water soluble (high HLB)

Surfactants

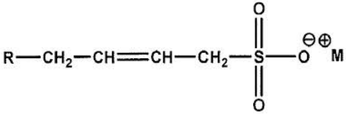


sodium lauryl sulphate

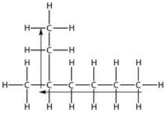


Straight, natural chain, anionic

Straight, Petroleum based, anionic

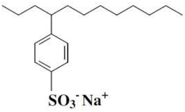


Petroleum based, Branched

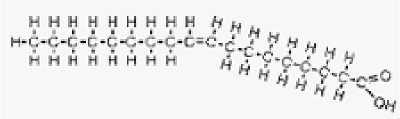


Surfactants

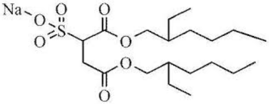
With aromatic ring



Natural, with double bond

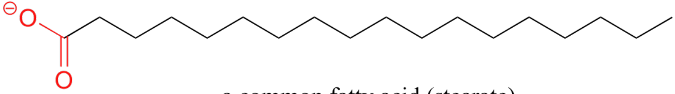


Multiple

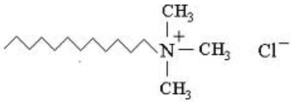


Surfactants

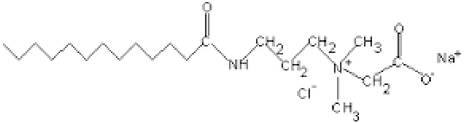
Head group: anionic



a common fatty acid (stearate)



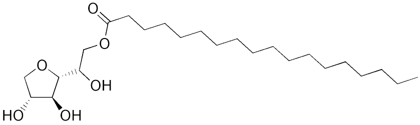
Cationic:



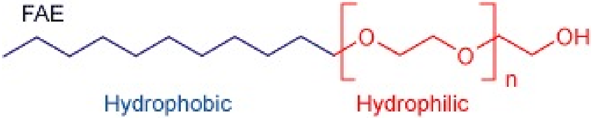
Zwitterionic

Surfactants

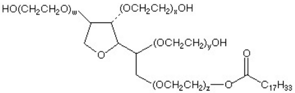
Non-ionic: sugar based



Non-ionic: Ethoxylate

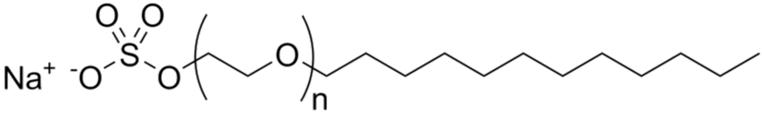


Nonionic mixed



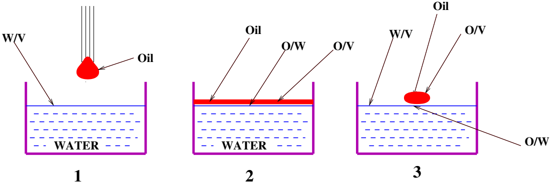
Polysorbate 80
(Sum of w, x, y, and z is 20)

Mixed ethoxylate ionic :



Spreading

SPREADING OF LIQUIDS



2) $E = A\,\gamma^{o/w} + A\,\gamma^{o/v}$

3) $E = (A - a_2)\gamma^{w/v} + a_1\,\gamma^{o/v} + a_2\gamma^{o/w}$

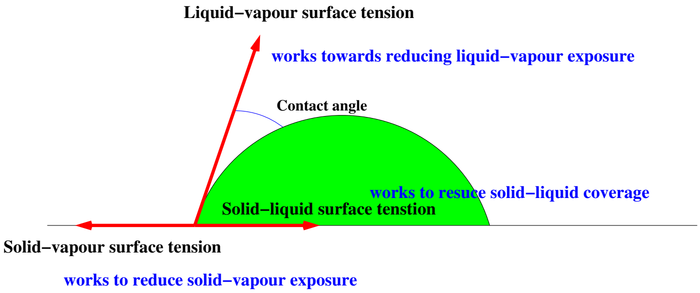
$a_1\,,\ a_2 << A$

$\approx A\,\gamma^{w/v}$

State of lower E is preffered

$S_{o/w} > 0 \longrightarrow$ Spreading occures

Contact angle



Force balance (Young-Dupre equation):

$$\gamma^{LV} \cos\theta = \gamma^{SV} - \gamma^{SL}$$

Powder wetting

- Powder wetting can be measured indirectly instead of contact angle.
- Washburn equation relates the rate of uptake of a liquid in packed powder to the contact angle.
- Two measurements - one with a low surface tension liquid (typically hexane) - and one with the solution are required.

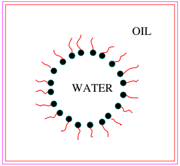
Emulsions

- Dispersion of two incompatible phases
- Higher proportion - continuous (exceptions)
- Stability limited (kinetic and not thermodynamic stability)
- Destabilization
  - Creaming (density, viscosity)
  - Ostwald ripening (Kelvin equation)
  - Wall breaking (Gibbs elasticity, surface viscosity)

Foams

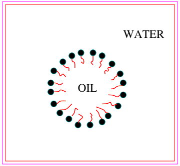
- Dispersion of gas in liquid
- Foam formation ability - foamability
- Foam stability
- Dynamics of surface tension (interfacial tension for emulsions)
- Bubble formation and coalescence before stabilization
- Rupture of wall (surface elasticity, surface viscosity)
- Foamability measurement

Microemulsion types



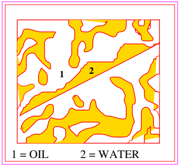
WATER IN – OIL MICROEMULSION DROPLET

V / al > 1



OIL – IN – WATER MICROEMULSION DROPLET

V / al < 1

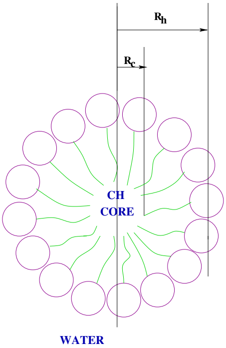


BICONTINUOUS STRUCTURE

$$\frac{V}{al} \cong 1$$

Microemulsion vs swollen droplet

SWOLLEN MICELLE



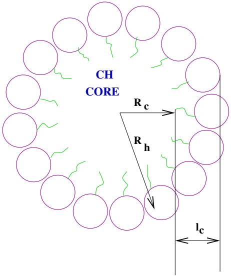
$$N V_c = 4/3 \ \Pi \ (R^3 - R_c^3)$$

$$N \sigma = 4\Pi \ R^2$$

$$R - R_c = l_c$$

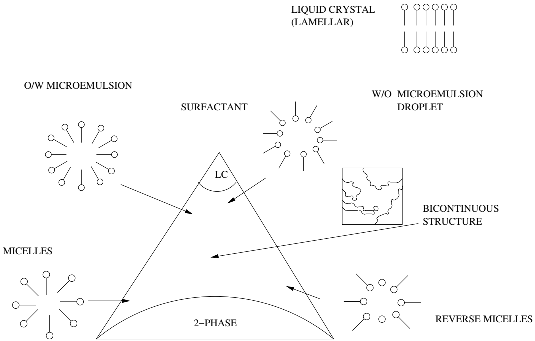
$$V_c \ / lc \ \sigma \ <= \ 1/2$$

MICROEMULSION DROPLET



$$V_c \ / lc \ \sigma \ = \ 1/2$$

Structures in O-W-S systems



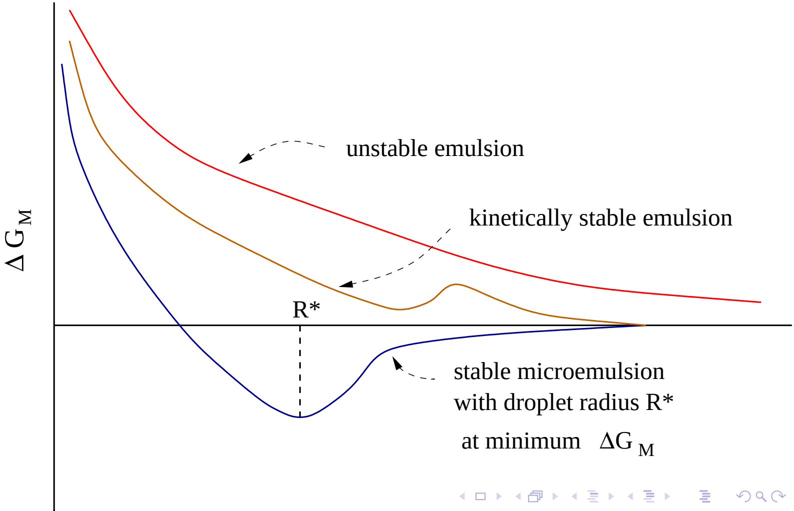
Nano-structuring in surfactant solutions

Relative Thickness of Interphase and interfacial area

	Diameter (nm)	Interphase (nm)	Volume (%)
Macroemulsions	~ > 1000	2.5	1.5
Microemulsions	10-100	2.5	15-85
Micelles	~ 2.5	2.5	~ 100

	Interfacial area (cm^2/cm^3)
L/L dispersions (5 mm size)	~ 1
Emulsion (50 μm size)	~ 10
Microemulsions (10 nm size)	~ 10^6

Free energy minimum



Other free energy source

MICROEMULSIONS HAVE VERY LARGE O/W INTERFACIAL AREA.

TO ACHIEVE THIS, $\gamma^{o/w}$ SHOULD BE VANISHINGLY LOW.

EQUILIBRIUM SIZE IS ATTAINED WHEN THE CHANGE IN FREE ENERGY DUE TO CHANGE IN SIZE IS ZERO.

TOTAL FREE ENERGY HAS TWO TERMS:

(1) SURFACE FREE ENERGY $\gamma \cdot A$.

(2) ENTROPY OF MIXING. $-R \sum x_i \ln x_i$

$$\Delta G^s - T\Delta S = \Delta G$$

VOL. FRACTION $= \phi$

NO. OF DROPLETS / UNIT VOLUME $= \phi / \frac{\pi}{6} d^3$

NO. OF SOLVENT MOLECULES / UNIT VOL: $\frac{(1-\phi)N_S}{V_M}$

$$X_{droplets} = \frac{\phi/(\frac{\pi}{6}d^3)}{(1-\phi)N/M + \phi/(\frac{\pi}{6}d^3)} \approx \frac{v_M}{N^3}\frac{\phi}{\frac{\pi}{6}d^3}$$

$$X_{solvent\ molecules} = 1 - X_{droplets} \approx 1$$

$$\text{Entropy} = -R\left[\frac{v_M}{N}\frac{\phi}{\frac{\pi}{6}d^3}\ \ln\left(\frac{v_M}{N}\frac{\phi}{\frac{\pi}{6}d^3}\right) + 1\ln 1\right]$$

$$\text{Surface free energy} = \gamma^{o/w}\cdot\frac{\phi}{\frac{\pi}{6}d^3}\cdot\pi d^2 = \frac{6\phi}{d}\gamma^{o/w}$$

Total free energy

$$= -\left(-kT\cdot\frac{\phi v_M}{\frac{\pi}{6}d^3}\ln\left(\frac{v_M}{N}\cdot\frac{\phi}{\frac{\pi}{6}d^3}\right)\right) + \frac{6\phi}{d}\cdot\gamma^{o/w}$$

SOLVING THIS FOR A $d \sim 50$ nm, $\phi = 0.05$,
$\gamma^{o/w}$ HAS TO BE ~ 0.001 dyne/cm.

Microemulsions

- A microemulsion is a single phase composed of water, a water immiscible oil, surfactant and cosurfactant; which is optically isotropic and thermodynamically stable.
- It appears transluscent or transparent to visible light. In the case of oil -in -water microemulsions, the oil forms extremely small droplets of size in the range of 10-100nm that are surrounded by surfactant molecules.
- The criterion generally accepted for the size of these droplets is that the diameter should be less than 1/4th of the wavelength of visible light.
- These 'microdroplets' consist of a cluster of a few hundred molecules or less and can, therefore, behave very differently from macroemulsion droplets.

Applications of surfactants and microemulsions

Formulations where there is a need for mixing hydrophobic and hydrophillic substrates

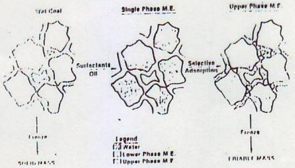
- Paints
- Pharmaceuticals
- Dyeing
- Fuel additives
- Food additives
- Pesticides
- Petroleum

Applications of Surfactants

- Pulp and paper: wetting, waste de-inking, resin removal
- Mineral and metallurgical engineering: hydrometallurgy, coal antidusting agents, coal crushing
- Leather: degreasing, pigment formulations
- Cosmetics: formulations
- Printing: stable ink for jet printing
- Safety and pollution abatement: fire fighting foams, absorbent for pollutants
- Civil engineering: additives for water reduction, plasticizers, and superplasticizers
- Electronics: special surface treatment of semiconductors
- Explosives: formulations

Coal antidusting

MICROEMULSIONS AS
COAL FREEZE CONDITIONING AGENTS



Microemulsions Reduce Coal Crush Strength

- Phase behavior criteria defined

Systems/ Conditions	Water:Oil (95:5) T = 25°C	Water:Oil (95:5) 0°C	On Coal T = 25°C	Coal Crush Strength (psi)
Glycol (Corexit 181)	--	--	--	200
Diesel Oil	-	--	-	140
C_{12}BS-Et5/7	Homogeneous	2 Phase(L)	Homogeneous	105
C_{12}BS/DM530	2 Phase(L)	2 Phase(L)	2 Phase(U)	75
CHB/DM430	Homogeneous	2 Phase(U)	2 Phase(U)	35
C_{12}XS/DM530	Homogeneous	2 Phase(U)	2 Phase(U)	18

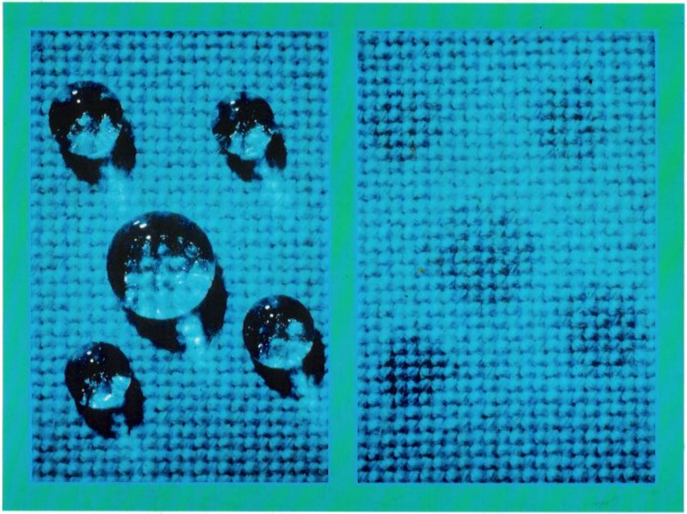
Textile applications:

- Scouring of wool: wool grease, soil and salts
- Scouring of cotton: Hemicellulose and lignin
- Scouring of synthetics: Oligomer removal

And

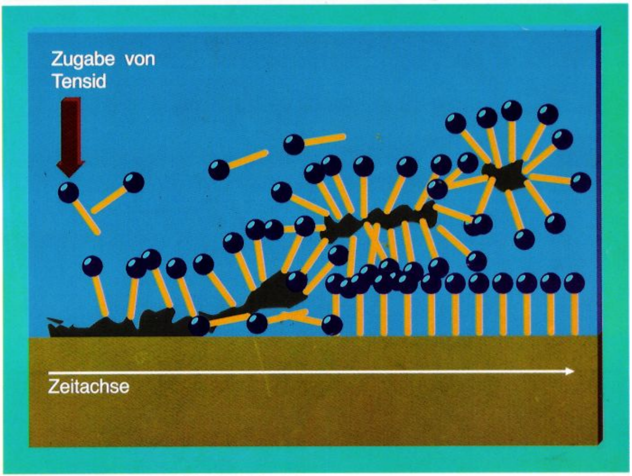
- Spin finishes: at all stages
- Dyeing: Wetting and dispersing agents
- Softening: nonionic and cationic surfactants
- Laundering: simultaneous removal of hydrophobic and hydrophilic soil

Fabric wetting



Textile wetting

Detergency



Pharmaceutical Technology

- Prolonged action and protection of biodegradable molecules
- Better handling and ease of preparation
- Water insoluble drugs in aqueous media
- Incorporation of high oxygen carrying capacity substances
- Faster diffusion rates
- Better penetration ability
- Decreased toxicity and improved potency

Pesticides and drug delivery

- Controlled release formulations, gels
- Many bioactives are insoluble/ rendered inactive in water
- Rapid diffusion
- Targetted delivery (bacteriophage)
- Wetting of foliage
- Artificial blood- (fluorocarbon)
- Models of cell wall

Lubricants and additives

- Combustion products are acidic and hence corrosive
- Alkaline particles can neutralise these
- Particles should aid in lubrication
- neutralised products tobe non-corrosive and inobtrusive
- Prepared in reverse microemulsions acting as 'Microreactors'

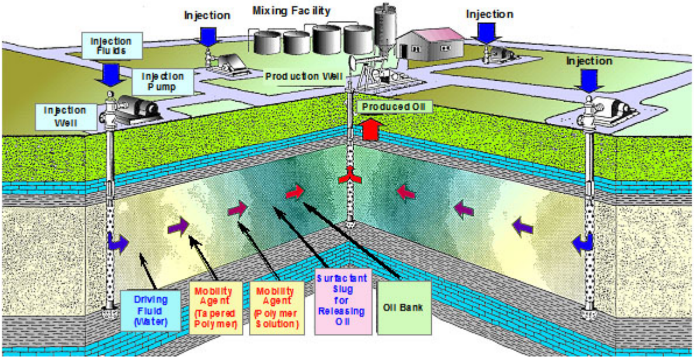
Upper half leaf : wetting

Upper half of the leaf - wetting.

Petroleum Recovery

- Microemulsion flooding
  low interfacial tension aids oil displacement
  optimal salinity- maximum recovery efficiency
  o/w, w/o, middle phase - all useful
  e.g. Na petroleum sulfonates, dialkyl quaternery ammonium compounds
- Drilling fluids: high viscosity, good heat capacity
- Plugging agents

Petroleum recovery



Fuels

Gasoline, diesel, fuel oils microemulsions

- Reduced peak temperature leading to lower NO_x emission
- Higher flash point
- controlled pool burning
- Safety in storage and transport without affecting atomised burning in engine
- Can water help fuel burn? Yes! Better fuel atomization

Advantages of Surfactant media for reactions

- Enhancement in overall reaction rate
- Favorable orientation of molecules
- Manipulation of Regio- and Stereo selectivity
- Localised concentration of reagent
- Change in locale of reaction

Solubilization and Orientation

- Micellar solubilization of phenols is greatly affected by position of the substituent group in aromatic ring
- Difference in solubilities can be explained in terms of the orientation of molecule adsorbed on the micelle
- The solubilization with specific orientation is useful in micellar regioselective synthesis

Alkaline Hydrolysis

- 2,4-dinitrochlorobenzene – by cationic micelles – sp. rate increase 10-100 fold
- p-nitrophenyl diphenyl phosphate – hexadecane in water microemulsion stabilized by CTAB & 1-butanol.
- p-nitrophenylbenzoate – CTAB & sodium dodecyl sulphate microemulsions.
- 2,4 dichlorophenyl benzoate – sp. rate increases by 45 fold

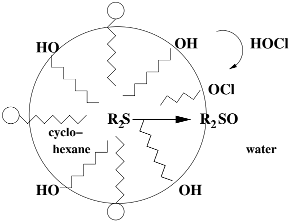
Half mustard oxidation by tert-butyl hydroperoxide & hypochlorite

$ClCH_2CH_2{-}S{-}CH_2\ CH_2\ Cl$

MUSTARD

$CH_3CH_2{-}S{-}CH_2\ CH_2\ Cl$

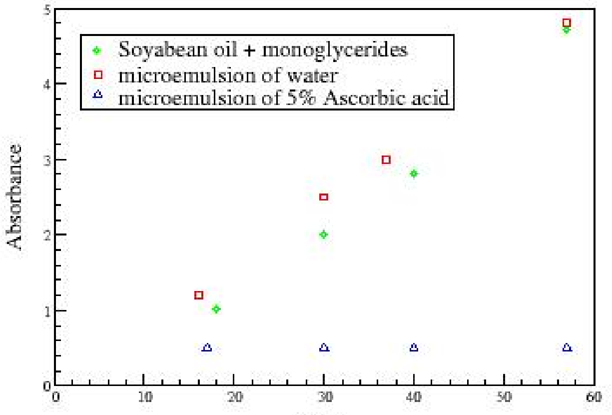
Half MUSTARD



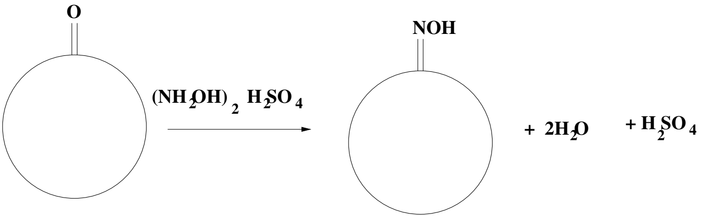
Destruction is very rapid in microemulsion

Oxidation - prevention

Oxidation of fats results in rancidity. Most antioxidants are oil insoluble

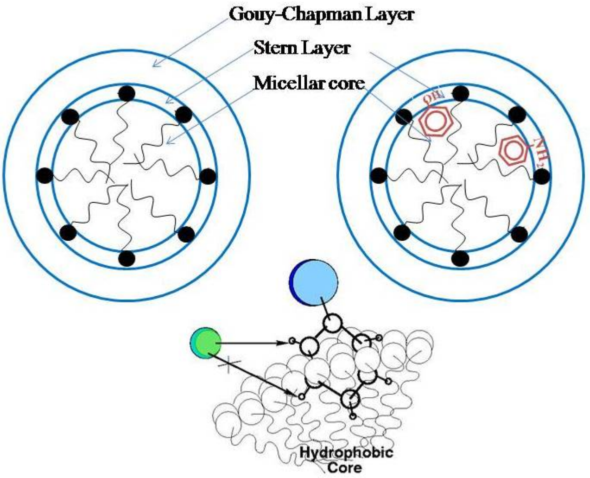


Oximation of cyclododecanone



600 fold enhancement in the specific rate of the reaction in microemulsions of SLS/n-butanol

Reactions

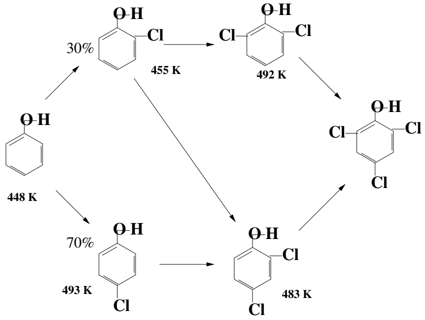

Gouy-Chapman Layer
Stern Layer
Micellar core
OH
NH2
Hydrophobic
Core

The chlorination of aromatic compounds

- Substituted benzenes show strong orientation effects for this electrophilic substitution reactions
  Deactivating -NO_2 *meta*- directing
  Activating -CH_3 *ortho*- *para*- directing
  Activating -Cl *ortho*- *para*- directing
  Activating - OH *ortho*- *para*- directing
- Different agents for chlorination include chlorine gas, sodium or calcium hypochlorite, phosgene, sulfuryl chloride, HCl-O_2, HCl-H_2O_2

Phenol Chlorination

Excess chlorination –> Trichlorophenol



Close boiling points –> Isolation difficult

Orientation

Orientation of phenol in micelles indicated by NMR shift

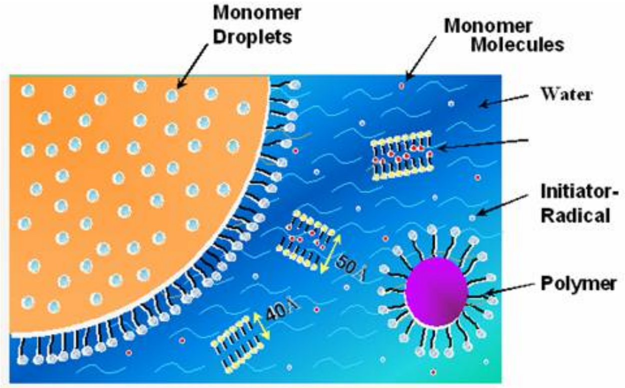
Medium	*para*-shift	*meta*-shift	*ortho*-shift
0.25M SDS	40	30	10
0.1M CTAB	60	40	05
0.1M CPC	100	70	20

Phenolic -OH is a polar group affeted by pH.
micellised phenol : *ortho*-position exposed while the *para*-position burried deep in the micelle
NMR shift for the *ortho*- position is more than 3 times larger than that for the *para*-position
Our results: *ortho*- / *para*- ratio of upto 8 in dichloromethane solvent, upto 12 in aqueous medium with $HCl - H_2O_2$ reagent.

Emulsion polymerisation

Dual role of surfactant in emulsion polymerisation

1. Formation of initial monomer emulsion
2. Stabilization of growing and final polymer particles



Types of Emulsion polymerisation

Types	Particle size
Macroemulsion	1-100 μm
Seeded dispersion	200-330 nm
Miniemulsion	50-500 nm
Microemulsion	10-50 nm

Latex is an industrially important product form
e.g. Paints, Tyres, paper coatings, textile binders adhesives etc.

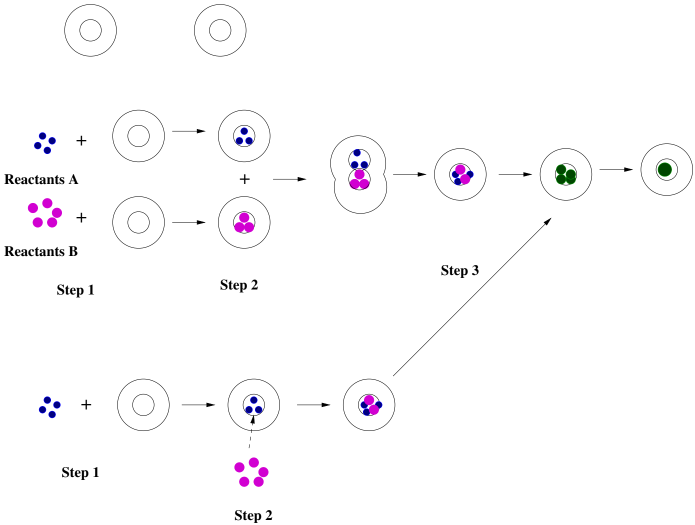
Paints and Surface coatings

Both water and solvent based systems have shortcomings while microemulsions combine advantages of both[1]

- Higher molecular weight material than water borne
- Non polluting compared to solvents
- High gloss film with strain resistance since system remains isotropic throughout evaporation
- Excellent penetration

[1] e.g. Pol 25, 1357

Growth of ultrafine particles in microemulsions



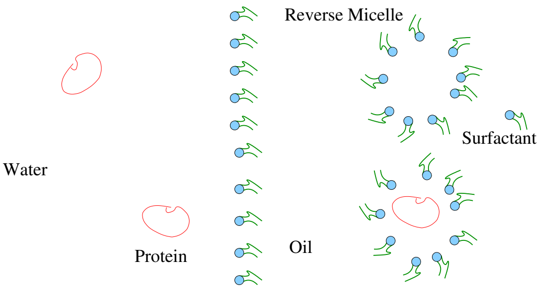
Enzymatic Reactions

Enzymes are inactive in hydrocarbon environment

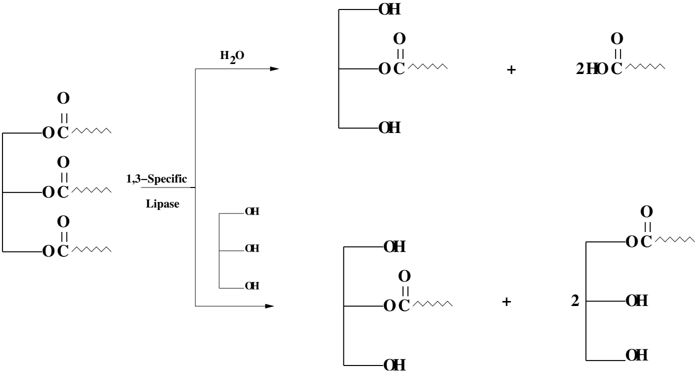
- Enzyme activity is retained in W/O microemulsion, sometimes enhanced
- Substrate (e.g. steroids) is solubilized in the continuous phase of the microemulsion
- Enzyme is trapped in the water pools
- Large interfacial area between the two helps in reaction

Protein solubilization in reverse micelles

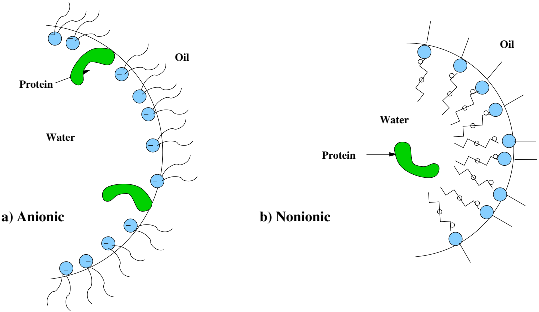
V



Enzymatic glycerolysis: synthetic coco-butter



Protein location in microemulsion



Enzymatic activity is higher in (a) owing to better enzyme-substrate contact.

Nano-structured media for chemical reactions

- Micelles are known to catalyze various chemical reactions
- Micelles can alter selectivity of reactions
- Micelles can offer physical protection of a group
- Solubilization leads to enhanced rates of reaction
- Orientation of molecules is responsible for the selectivity
- Orientation can be established by NMR shift

Summary

- Interfacial science has applications in many fields
- Fundamentals behind these applications have many things in common
- Studying the common governing principles gives a better understanding of the underlying phenomena
- Applications are in physical systems as well as reactive systems
- Proper characterization of the materials involved as well as the surfactants reduces development time and improves efficacy

THANK YOU

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