The Molecular Basis of Surface Activity

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Molecular Basis – **Basic Structure for Sur. Act.**

Stories about surfactants (surface active agents)

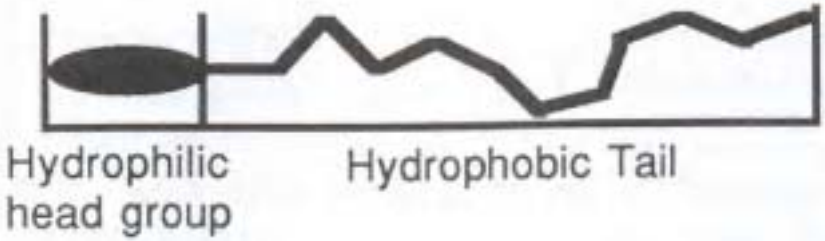

Figure 3.1. The basic molecular structure of surface-active materials.

Molecular Basis – Basic Structure for Sur. Act.

- **BASIC STRUCTURAL REQUIREMENTS FOR SURFACE ACTIVITY**

- **Lyophobic Group - Little attraction to the solvent**
  (Hydrophobic - water repellent)
- **Lyophilic Group - Strong attraction to the solvent**
  (Hydrophilic- fond of water)
- **Amphiphilic ("liking both") - some affinity for two essentially immiscible phases**

- **Lyophobic group and solvent interaction**
  → **unfavorable distortion of solvent structure**
  → **Increase in energy (due to entropy)**
  → **preferential adsorption at interface**
  or undergo low energy system (eg. Micelle formation)

Molecular Basis – Preferrential Orientation

Preferrential Orientation

Orientation of Surfactant Molecules

- **Orientation away from the bulk solvent phase**
  - **change in physical properties**

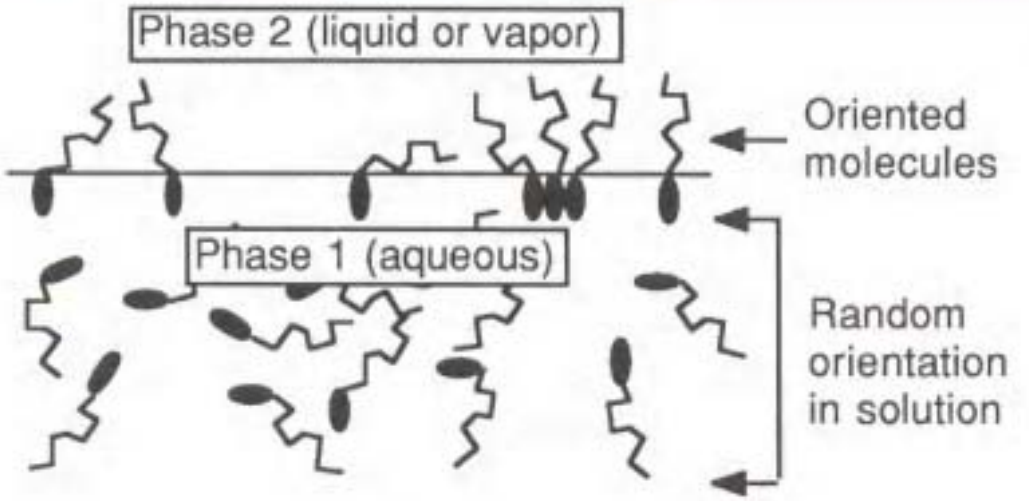

Figure 3.2. Schematic illustration of the preferrential orientation of surfactant molecules at interfaces.

Molecular Basis – Solubility

Solubility

Hydrophobic group - Hydrophilic group balance

물을 예를 들면

Hydrophobic: Hydrocarbon, fluorocarbon, siloxane chain을 사용할 수 있고

Hydrophilic: ionic and polar group 이 용해를 시키는데 유용하다.

Hydrocarbon 용매의 경우에는 반대로 생각하면 된다.

온도, 압력, **surfactant** 주변의 조건이 바뀌면 용해도 및 **interfacial properties**가 변하게 된다.

Molecular Basis – Surfactant Struc. & Sources

SURFACTANT STRUCTURES AND SOURCES

Building Surfactant Molecules

Functional group Modification

Alcohol

dodecane $[CH_3(CH_2)_{10}CH_3]$, insoluble in water

dodecanol $[CH_3(CH_2)_{10}CH_2OH]$, very low solubility in water (increased substantially)

3-dodecanol $[CH_3(CH_2)_8 CH(OH) CH_2CH_3]$, slightly more soluble than primary alc.

: The effects of the position of substitution.

Molecular Basis – Surfactant Struc. & Sources

Acid

Dodecanoic acid [$CH_3(CH_2)_{10}COOH$]: practically insoluble in water

soldium dodecanoate [$CH_3(CH_2)_{10}COONa$] : very soluble in water,
Reasonable surfactant

soldium hexanoate [$CH_3(CH_2)_{14}COONa$] or octanoate
: lower solubility, very good surfactants

:balance between hydrophobic and hydrophilic portions

Molecular Basis – Surfactant Struc. & Sources

Acid - Solvent and Metal Ion Interaction

Effects of di- and Tri-valent salts

In water

carboxylic acid soap은 **surfactant** 능력은 거의 변화 없으나,

단지 **low solubility** 때문에 기능 감소

→ **bathtub ring (scummy deposits)**

In nonaqueous solvents

enhanced solubility → **good surfactant function**

Limited function of carboxylate soap 을 극복하기 위해서

development of effective and versatile soaps 을 합성

Molecular Basis – Surfactant Struc. & Sources

Sulfonated Ester Soap - Sulfate

Alcohol + sulfuric acid

Dodecane sulfuric acid ester : $CH_3(CH_2)_{10}CH_2OSO_3H$

: high water miscibility

Neutralized with alkali or amines : excellent surfactant

[eg. sodium dodecylsulfate (SDS))

Molecular Basis – Surfactant Struc. & Sources

Polyether

Alcohol + ethylene oxide (OE) and base

polyoxyethylene(POE) polyether

$C_{11}H_{23}CH_2$----O--- $CH_2\ CH_2(O\ CH_2\ CH_2)_n\ O\ CH_2\ CH_2\ O\ H$

Solubility *vs*. n (# of OE group added)

- n=10 : completely soluble in water, good surfactant
- $5 \leq n < 10$: water solubility decreased significantly
- $20 \leq n$: high water solubility, limited surfactant quality
- n<5 : little significant water solubility

Molecular Basis – Surfactant Struc. & Sources

Sulfonated acid

Hydrocarbon + sulfuric acid

dodecane sulfonic acid : $CH_3(CH_2)_{10}CH_2SO_3H$

closely resembles the sulfuric acid ester , similar water misciblity

But, solution and surfactant properties are not identical

→ different applications

Neutralization yields good surfactant.

Molecular Basis – Surfactant Struc. & Sources

Ammonium salts

Chlorination + triethylamine

dodecyltrimethylammonium chloride : $CH_3(CH_2)_{10}CH_2N^+(CH_3)_3Cl^-$

Good solubility, some surfactant properties

-not generally useful as the anionic analogs.

Charge-charge interaction을 이용 - 표면 특성 바꿈

THE CLASSIFICATION OF SURFACTANTS

Molecular Basis – Surfactant Struc. & Sources

Amphoteric = Zwitterionic (양쪽성, 양이온성)

Combination of anionic and cationic

N,N-dimethyl-3-amminopropane-1-sulfonic acid :

$(CH_3)_2N\,CH_2CH_2CH_2SO_3H$

$CH_3(CH_2)_{10}CH_2N^+(CH_3)_2CH_2CH_2CH_2\,SO_3^-$

Dodecane으로의 변화처럼 **hydrocarbon** 쪽의 변화 그 동안 나온 **hydrophilic group**들의 조합으로 용해도와 계면활성제로서의 역할을 변화시킬 수 있는 많은 합성 방법들이 가능하다.

Molecular Basis – THE CLASSIFICATION OF SURFACTANTS

BY THE APPLICATION

Emulsifiers, Foaming agents, Wetting agents, Dispersants.

1. **Anionic (음이온성)**
   hydrophilic group w/ negative charge
   eg) carboxyl ($RCOO^-$) , Sulfonate (RSO_3^-), or Sulfate ($ROSO_3^-$)
2. **Cationic (양이온성)**
   Hydrophile w/ positive charge
   eg)ammonium halide ($R_4N^+Cl^-$)
3. **Nonionic (비이온성)**
   Hydrophile w/ nocharge, water soluble
   eg) polyethylene (---OCH_2CH_2O---), polyol groups
4. **Amphoteric (Zwitterionic) (양쪽성, 양이온성)**
   contains or can potentially contain a negative and positive charge
   eg) sulfobetaines ($RN^+(CH_3)_2CH_2CH_2CH_2\ SO_3^-$)

Molecular Basis – Surfactant Solubilizing Groups

Water - Hydrophilic group determines solubility

Organic solvents - hydrophobic group determines solubility

Hybrid type can be advantageous -Flexibility (appl. Personal care system)

Table3.1

Table 3.1. The most commonly encountered hydrophilic groups in commercially available surfactants.

Sulfonate	$R\text{-}SO_3^-\ M^+$
Sulfate	$R\text{-}OSO_3^-\ M^+$
Carboxylate	$R\text{-}COO^-\ M^+$
Phosphate	$R\text{-}OPO_3^-\ M^+$
Ammonium	$R_xH_yN^+X^-$ (x = 1-3, y = 4-x)
Quaternary ammonium	$R_4N^+X^-$
Betaines	$RN^+(CH_3)_2CH_2COO^-$
Sulfobetaines	$RN^+(CH_3)_2CH_2CH_2SO_3^-$
Polyoxyethylene (POE)	$R\text{-}OCH_2CH_2(OCH_2CH_2)_nOH$
Polyols	Sucrose, sorbitan, glycerol, ethylene glycol, etc
Polypeptide	R-NH-CHR-CO-NH-CHR'-CO-...-CO_2H
Polyglycidyl	$R\text{-}(OCH_2CH[CH_2OH]CH_2)_n$- ... - $OCH_2CH[CH_2OH]CH_2OH$

Molecular Basis – Common Surfactant Hydrophobic Groups

8 ≤# of Carbon atoms ≤20 : inexpensive

Natural fatty acids : obtnd from triglyceride esters (12C-18C)

Paraffins: obtnd from petroleum distillates. Sat. (10-20C) mix with many branched isomers.

Olefins: Oligomerization of ethylene or propene or cracking of high mt. Petroleum fraction.

Alkyl benzenes: Friedel-Craft b/w olefins and benzene. Akyl group (C8-12) highly branched.

Alcohols: catalytic reduction of ester. (C8-C18) even or odd number of carbon atoms, w/ significant secondary alc.

Alkylphenols: prod. By rexn of phenol w. olefins. Branched and random substitution along the ring w/ respect to the hydroxyl.

Polyoxypropylene: Base catalyzed oligo. Of propylene oxide. Important in the preparation of block copolymer surf. W. ehtylene oxide.

Fluorocarbon: Electrolytic subs. Of fluorine for hydrogen. Or prepared by oligo. Of tetrafluoroethylene.

Silicones: Oligomers of dimethylsiloxane.

Molecular Basis –ECONOIC IMPORTANCE OF SURFACTANTS

Formulator must know followings:

1. characteristic chemical and physical properties
2. surface and interface phenomena
3. relationship b/w structural properties and pertinent interfacial phenomena
4. application restrictions (food , cosmetic,...)

Table 3.2 , table 3.

Molecular Basis –ECONOIC IMPORTANCE OF SURFACTANTS

- **Table 3.2**

Table 3.2. Some of the major modern applications of surfactants.

Industrial	Consumer Goods
Agricultural crop applications	Adhesives
Building materials	Dry cleaning fluids
Cement additives	Foods and beverages
Coal fluidization	Household cleaning and laundering
Coating and leveling additives	Pharmaceuticals
Electroplating	Photographic products
Emulsion polymerization	Soaps, shampoos, creams
Industrial cleaning	
Leather processing	
Lubrication	
Mold release agents	
Ore flotation	
Paper manufacture	
Petroleum recovery	
Surface preparations	
Textiles	
Waterproofing	

Molecular Basis –ECONOIC IMPORTANCE OF SURFACTANTS

- **Table 3.3.**

Table 3.3. Typical (but not all) characteristics for surfactants which must be evaluated for various applications.

Application	Characteristics
Detergency	Low cmc, good salt and pH stability, biodegradability, good foaming properties
Emulsification	Proper HLB, environmental and biological (safety) aspects for application
Lubrication	Chemical stability, adsorption at surfaces
Mineral flotation	Proper adsorption characteristics on the ore(s) of interest, low cost
Petroleum recovery	Proper wetting of oil bearing formations, microemulsion formation and solubilization properties, ease of emulsion breaking after oil recovery
Pharmaceuticals	Biocompatibility, toxicity

Molecular Basis –SURFACTANTS IN THE ENVIRONMENT

Effects of surfactants on ground water and waste treatment operation

- 화학적으로 완전 제거 가능 - 문제는 비용
- 자연적에서 분해하게 하는 것이 중요

Molecular Basis –Biodegration

Biodegradation of Surfactants

1. **Primary degradation**
   Modification of chemical structure of material sufficient to eliminate any surface active properties
2. **Ultimate degradation**
   complete removal from the environment.
   Carbon dioxide, inorganic salts, or other materials (일반 자연폐기물과 같은)

Molecular Basis –Biodegration

Generalization of the Biodegradation

1. **Primary Factor :** chemical structure of the hydrophobic group
   degree of branching -especially , branching at the alkyl terminus
   → inhibits the biodegradation
2. **Nature of hydrophilic group**
   Minor effect on biodgradability
3. **Distance b/w hydrophilic group and alkyl terminus.**
   Longer distance → faster rate of degradation