Surfactant Aggregation

Background

What Is a Surfactant?

A chemical that, when dissolved in water, moves toward "surfaces"

What Does a Surfactant Do?

Cleans by helping dissolve things that aren't water soluble
Lathers by "solubilizing air" in water
Many biological processes (membranes, digestion, etc.)

How Do They Do It?

TEAMWORK

Individual surfactant molecules do nothing, they spontaneously group together to work ⇒ "Self-Aggregation"
Surfactant Aggregation
Background

What Is Self-Aggregation?

Aggregate = gathered together into a mass so as to constitute a whole
Self-aggregation ⇒ forces exist that direct this process
⇒ What are these forces?

Why Do Surfactants Self-Aggregate?

There are only two "rules of the game":

- **Hydrophobic Interactions**
  - H₂O
  - Oil

- **Electrostatic Effects**
  - +
  - -
  - Repulsion
  - Attraction
  - Repulsion
  - Attraction
Surfactant Aggregation
Background

Why Do Surfactants Self-Aggregate (continued)?

... Surfactant Structure:

CH$_3$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$-CH$_2$

"Tail" Group
- Hydrophobic
- Water Hating
- Lipophilic
- Oil Loving

"Head" Group
- Hydrophilic
- Water Loving
- Lipophobic
- Oil Hating

"Amphiphilic"

... Molecular inhomogeneity leads to molecular recognition and organization.
Behavior of Surfactants in Water

The Origin of the Surface Tension of Water

Water Molecules Hydrogen-Bond to Each Other:

Hydrogen-Bonding Forces are Un-Balanced at the Surface:

Unbalanced Intermolecular Forces Result in Surface Tension

Surfactant Molecules Adsorbing at the Surface Reduce Surface Tension
**Surfactant Aggregation**

Monolayer Formation

- **Addition of Surfactant to Water**
- **Hydrophobic Forces Repel Water**
- **Surfactant Moves to Air-Water Interface ("surface active")**
- **Monolayer at Air-Water Interface**
Monolayer at Air-Water Interface Saturated

SURFACTANT AGGREGATION
Micelle Formation

Additional Surfactant Dispersed in Bulk Water

Enough surfactant to pass “CMC”

Surfactant Aggregates in Spherical Micelles

CMC = Critical Micelle Concentration
= Concentration at which micelles begin to form
- Balance of hydrophobic and electrostatic forces
- Environment-dependent

A Surfactant Micelle
Head groups on “outside”
Hydrophobic “pocket”
If hair (80μ) was as wide as a football field …

… A micelle (0.005μ) would be 6mm in diameter!!
MICELLE

\[ M + M_{(n-1)} \rightarrow M_n \]

Many equilibrium steps, so we approximate

\[ nM \rightarrow M_n \]
Behavior of Surfactants in Water

Surface Tension Reduction: Measurement of CMC's

Surface Tension (mN/m or dyn/cm²)

Surfactant at Surface

Surface Saturated

Micelles Formed

Critical Micelle Concentration (CMC)
## Factors Affecting the Critical Micelle Concentration (CMC)

### Factors Affecting Head-to-Head Repulsion

- **Head Group Charge**
  - Ionic > Nonionic
  - Anionic \( \approx 10^{-3} M \)
  - Nonionic \( \approx 10^{-4} M \)
  - pH can influence

- **Head Group Position**
  - Non-terminal position increases CMC relative to terminal position

- **Ethoxylation** \([R-(OCH_2CH_2)_n-O-R']\)
  - Nonionics: increases CMC
  - Anionics: decreases CMC

- **Counterion of Ionic Surfactants**
  - Anionics
    - CMC decreases in order: \( \text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Cs}^+ > \text{N(CH}_3)_4^+ > \text{Ca}^{2+} \)
  - Cationics
    - CMC decreases in order: \( \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^- \)

- **Hydrocarbon Chain Length** \((nC)\)
  - CMC decreases logarithmically as \( nC \) increases
  - Empirical relationship: \( \log_{10}\text{CMC} = A - BnC \)
  - For anionics, \( A \approx 1.7, B \approx 0.3 \)
  - For nonionics, \( A \approx 3.5, B \approx 0.05 \)

- **Hydrocarbon Structure**
  - Branching
    - Carbon atoms off of a main chain contribute \( \approx \frac{1}{2} \) that of main chain carbons.
  - Unsaturation
    - Increases CMC
    - Cis isomer increases CMC more than trans

- **Other Main Chain Moieties**
  - Benzene Ring
    - Accounts for \( \approx 3.5 \) carbon atoms
  - Propoxylation
    - Each propylene oxide \( \approx 0.4 \) methylene carbons

- **Secondary Polar Functions**
  - C's between 2° polar group and 1° polar group \( \approx \frac{1}{2} \) as effective as those w/o substitution

### Factors Affecting Chain/Chain Attraction

- **Electrolyte**
  - Decreases CMC (more for ionics than nonionics)
  - Effectiveness:
    - \( \text{SO}_4^{2-} > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > I^- \)
    - \( \text{NH}_4^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+ > \frac{1}{2} \text{Ca}^{2+} \)

### Environment (extrinsic)

- **Organic Additives**
  - Low Water Solubility: Slight decrease in CMC
  - High Water Solubility: Minimal effects (below "co-solvent" levels)
  - Partially Soluble Materials: Decreases CMC
### Surfactant Aggregation
Overview of Aggregate Types (The "Surfactant Menagerie")

<table>
<thead>
<tr>
<th>Dilute Solution</th>
<th>Concentrated Solution</th>
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<tbody>
<tr>
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<td>Liquid Crystal Phases</td>
</tr>
<tr>
<td></td>
<td>Crystal Phases</td>
</tr>
</tbody>
</table>

- **Unorganized Monomers**
- **Monomers at Air-Water Interface**
- **Spherical Micelles**
- **Cylindrical Micelles**
- **Vesicles**
- **Planar Bi-Layers**
- **Hexagonal Phase**
- **Lamellar Phase (Neat)**
- **Anhydrous Crystal**
- **Crystal Hydrate**
- **Crystal Phases**

Increasing Surfactant Concentration in Water
**Surfactant Aggregation**
**Overview of Aggregate Types (The "Surfactant Menagerie")**

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- **Monolayer at Air-Water Interface**
- **Unorganized Monomers**

*Increasing Surfactant Concentration in Water*
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<td>Anhydrous Crystal</td>
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Increasing Surfactant Concentration in Water
Surfactant Aggregation
Overview of Aggregate Types (The "Surfactant Menagerie")

- Monolayer at Air-Water Interface
- Spherical Micelles
- Cylindrical Micelles (random)
- Vesicles
- Planar Bi-Layers

Increasing Surfactant Concentration in Water
### Surfactant Aggregation

**Overview of Aggregate Types (The "Surfactant Menagerie")**

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<td>Spherical Micelles</td>
<td>Hexagonal Phase (Middle)</td>
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<td>Lamellar Phase (Neat)</td>
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Increasing Surfactant Concentration in Water
Surfactant Aggregation
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<td>Anhydrous Crystal</td>
<td></td>
</tr>
<tr>
<td>Crystal Hydrate</td>
<td></td>
</tr>
</tbody>
</table>

Increasing Surfactant Concentration in Water
How Does pH Affect Surfactants in Solution?

Carboxylate (Soap):

Sulfate or Sulfonate:

Amphoteric (amphoacetate):

§ The protonated form of the surfactant does not really behave as a "surfactant" (unless there is more than one polar group)

† Micellar surfactants can have $pK_a$'s ~4 units higher than their monomer counterparts (unless electric effects dictate otherwise)
SURFACTANT FUNCTIONALITY

- **Wetting**
  - Water is not attracted on an oily/greasy surface. However, the presence of surfactants facilitate the wetting process
  - Similar as in emulsification
SURFACTANT FUNCTIONALITY

- SOLUBILIZATION
  - Micelles act as solubilizers
  - Hydrophobic molecules are taken into the lipophilic core of the micelle
    - An important application is to make a solvent such as hydrocarbon dissolve in water and surfactant
SURFACTANT FUNCTIONALITY

• **EMULSIFICATION**
  - Adsorption at the water – oil interface results in dispersion of one phase into the other depending on the properties of the system
  • Emulsions water / oil or oil / water
SURFACTANT FUNCTIONALITY

• DETERGENCY
  - It involves wetting, emulsification, solubilization and micellization
Basic Surfactant Chemistry
   - What is a surfactant
   - Behavior of surfactants in water

Surfactant Type Overview
   - Structural variables
   - Surfactant synthesis and range of materials available

Surfactant-Influenced Performance Properties
   - Lather
   - Mildness
   - Rinse feel
   - Deposition of Actives
   - Cleaning

Surfactant-Influenced Product Physical Properties
   - Product Rheology
   - Stabilization of Dispersed Phases

Surfactant Information Resources
What is Lather?
The Structure of Lather
Air-Water Interface

Gravity Drainage

Liquid Lamella

Air-Water Interface
Air

Impeded Drainage

Air
Impact of Electrolyte Level on Lather Volume

Closer packing of head groups increases hydrodynamic friction => slower lamellar drainage.

Minimization of electrostatic repulsion across the barrier => constriction and eventual rupture.
Impact of Co-Surfactants on Lather

1. Reduced drainage (steric blockage)
2. Tighter interfacial packing* (reduced electrostatic repulsion)

* Also lowers CMC, see mildness impact.
Effects of "Soils" on Lather

Soils Can Be Part of the Product Formula or Part of the Surface Being Cleaned

Examples of Soils:
- Fatty Acids
- Fatty Alcohols
- Triglycerides
- Hydrocarbons

Important Variables:
- Length of hydrocarbon chain
- Particle Size
- Melting Point

Diagram:
- Depleted Level of "Free" Surfactant
- Emulsified Soil Particle
- Solubilized Soil
- Plus Soil
Impact of Particulates on Lather

0.01 - 1.0 µ

+ Small Particles

Drainage impeded by particle "dam" => better lather stability

Important factors
• Optimum Size
• Particle shape
• Concentration
• Surface hydrophilicity

+ Large Particles

Particle spanning lamella ruptures bubbles => decreased lather stability

Important factors
• Optimum size
• Surface hydrophilicity

* Particles can be ingredients or form in situ (e.g., rxn. with Ca^{2+})
Surfactant Influences in Active Deposition

Types of Actives

<table>
<thead>
<tr>
<th>Soluble Materials</th>
<th>Insoluble Particles</th>
<th>Dispersed Liquids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclosan (TCS)</td>
<td>Trichlocarban (TCC)</td>
<td>Petrolatum</td>
</tr>
<tr>
<td>Cationic Polymers</td>
<td>Zinc Pyrithione (ZPT)</td>
<td>Oils</td>
</tr>
<tr>
<td>Glycerin</td>
<td></td>
<td>Silicones</td>
</tr>
</tbody>
</table>

Chemical structures:
- Triclosan (TCS)
- Cationic Polymers
- Glycerin
- Trichlocarban (TCC)
- Zinc Pyrithione (ZPT)
- Petrolatum
- Oils
- Silicones
Most actives (except water-soluble non-polymers) associate with surfactants prior to deposition:

<table>
<thead>
<tr>
<th>Water Soluble Polymers:</th>
<th>Nonionic:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cationic:</td>
<td></td>
</tr>
<tr>
<td><img src="image1.png" alt="Diagram of Cationic Polymer" /></td>
<td><img src="image2.png" alt="Diagram of Nonionic Polymer" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Insoluble Solid Particles:</th>
<th>Hydrophobic:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relatively Hydrophilic:</td>
<td></td>
</tr>
<tr>
<td><img src="image3.png" alt="Diagram of Relatively Hydrophilic Polymer" /></td>
<td><img src="image4.png" alt="Diagram of Hydrophobic Polymer" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dispersed Liquid Droplet:</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image5.png" alt="Diagram of Dispersed Liquid Droplet" /></td>
</tr>
</tbody>
</table>
Why Does Surfactant Adsorption Affect Deposition of Actives?

Exposure (adsorption):

Poor adsorption if ....
- Species charge same as surface charge.
- Species surface hydrophilic

Rinse (retention):

If adsorbed species hydrophilic, will be carried away with rinse water.
- Rinse water ions (Ca^{2+}) may alter.
- Phase separation upon dilution (complex coacerva.)
Typical conditions:
- Huge surfactant excess over active, and
- Surfactant mostly anionic

To maximize deposition:
- Minimize surfactant level,
- Minimize surfactant interaction with actives
  - Particle size
  - Dissimilar surfaces
- Have surfactant charge be opposite that of surface,
- Use Ca$^{2+}$ from rinse water
- Employ complex coacervation
SURFACTANT INFLUENCED PRODUCT PHYSICAL PROPERTIES

VISCOSITY

STABILIZATION OF DISPERSED PHASES
Effects of Additives on Surfactant Rheology

Factors that decrease surface charge density of micelle allow closer packing of surfactants and shift phase sequence to lower concentrations:

Examples of Additives:
- Electrolytes (salt)
- Co-surfactants
  = Alkanolamides
Role of Surfactants in Stabilization of Dispersed Phases

For small particles (< 1µ), “molecular” stabilization can occur:

Electrostatic stabilization by ionic surfactants:

Steric stabilization by nonionic surfactants:
For large particles, rheological stabilization relevant:
## Surfactants in Personal Care Products

<table>
<thead>
<tr>
<th>PRODUCT TYPE</th>
<th>LEVEL IN PRODUCT</th>
<th>FUNCTIONS IN PRODUCT</th>
<th>LEVEL IN USE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Personal Cleansing</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bars</td>
<td>~ 60%</td>
<td>• product structure</td>
<td>5-10%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• lather</td>
<td></td>
</tr>
<tr>
<td>Body Wash</td>
<td>~ 15%</td>
<td>• viscosity control</td>
<td>5-10%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• stabilize dispersed phases</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• cleaning</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• rinse feel</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• active deposition</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• mildness</td>
<td></td>
</tr>
<tr>
<td><strong>Hair Care</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shampoos</td>
<td>~ 20%</td>
<td>• viscosity control</td>
<td>2-3%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• stabilize disperse phases</td>
<td></td>
</tr>
<tr>
<td>Dentrifrice</td>
<td>2-5%</td>
<td>• solubilize flavor /oils</td>
<td>1-2%</td>
</tr>
<tr>
<td>Moisturizers</td>
<td>2-5%</td>
<td>• emulsifiers</td>
<td>1-7%</td>
</tr>
</tbody>
</table>
## SURFACTANTS IN FABRIC and HOME CARE PRODUCTS

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<tbody>
<tr>
<td>Fabric Care</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Granules</td>
<td>12-25%</td>
<td>• cleaning</td>
<td>0.02%</td>
</tr>
<tr>
<td>Liquids</td>
<td>16-30%</td>
<td>• viscosity control</td>
<td>0.04%</td>
</tr>
<tr>
<td>Dish Care</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquids</td>
<td>~30%</td>
<td>• viscosity control</td>
<td>0.06%</td>
</tr>
<tr>
<td>Automatic</td>
<td>nil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hard Surface</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Floor Cleaners</td>
<td>2-22%</td>
<td>• cleaning</td>
<td>0.04%</td>
</tr>
<tr>
<td>Gel Cleansers</td>
<td>2-10%</td>
<td>• gel agent</td>
<td>2-10%</td>
</tr>
<tr>
<td>Abrasive cleansers</td>
<td>1-3%</td>
<td>• cleaning</td>
<td>~0.5%</td>
</tr>
</tbody>
</table>
SURFACTANT CLASSIFICATION

• **ANIONIC**
  – Are negatively ionised

\[ R\text{SO}_3^- \]

• **NONIONIC**
  – Do not contain ionisable groups

\[ R\text{O}_\text{O}_\text{O}_\text{OH} \]
SURFACTANT CLASSIFICATION

- **Cationic**
  - Are positively ionised

- **Amphoteric**
  - Have a pH dependent ionisation profile. e.g. Anionic at high pH, cationic at low pH and neutral somewhere in between.
  - Zwitterionic surfactants are charged but have a net neutral charge over most pH’s.
SOLUBILIZING GROUPS

- **Anionic**
  - Sulfonate
  - Sulfate
  - Carboxylate

- **Nonionic**
  - Poly(ethylene oxide)
  - Sugar derived (e.g. glucose)

- **Cationic**
  - Quaternary ammonium

- **Amphoteric**
  - Betaine
  - Sulfo betaine
HYDROPHOBHIC GROUPS

• The hydrophobic group has very little interaction with the solvent.
  – Most common solvent is water, therefore the lyophobic part receive the name of hydrophobic

• *For example for detergents usually the hydrophobic part contains between 8-20 atoms of carbon*
HYDROPHOBIC GROUPS

1. ALIPHATIC HYDROCARBON
   - Straight Chain
     - Trivial names are given to chain length mixtures derived from natural sources. ‘Coco’, ‘Tallow’, ‘Palm’.
   - Branched Chain
     - Introducing branching can deliver unique properties
     - Watch out is rate of biodegradation
HYDROPHOBIC GROUPS

• 2. ALKYLBENZENES
  - Generally present as a mixture of isomers
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