Southwest Society of Cosmetic Chemists

SCC

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Surfactants: Meeting Today's Market Needs

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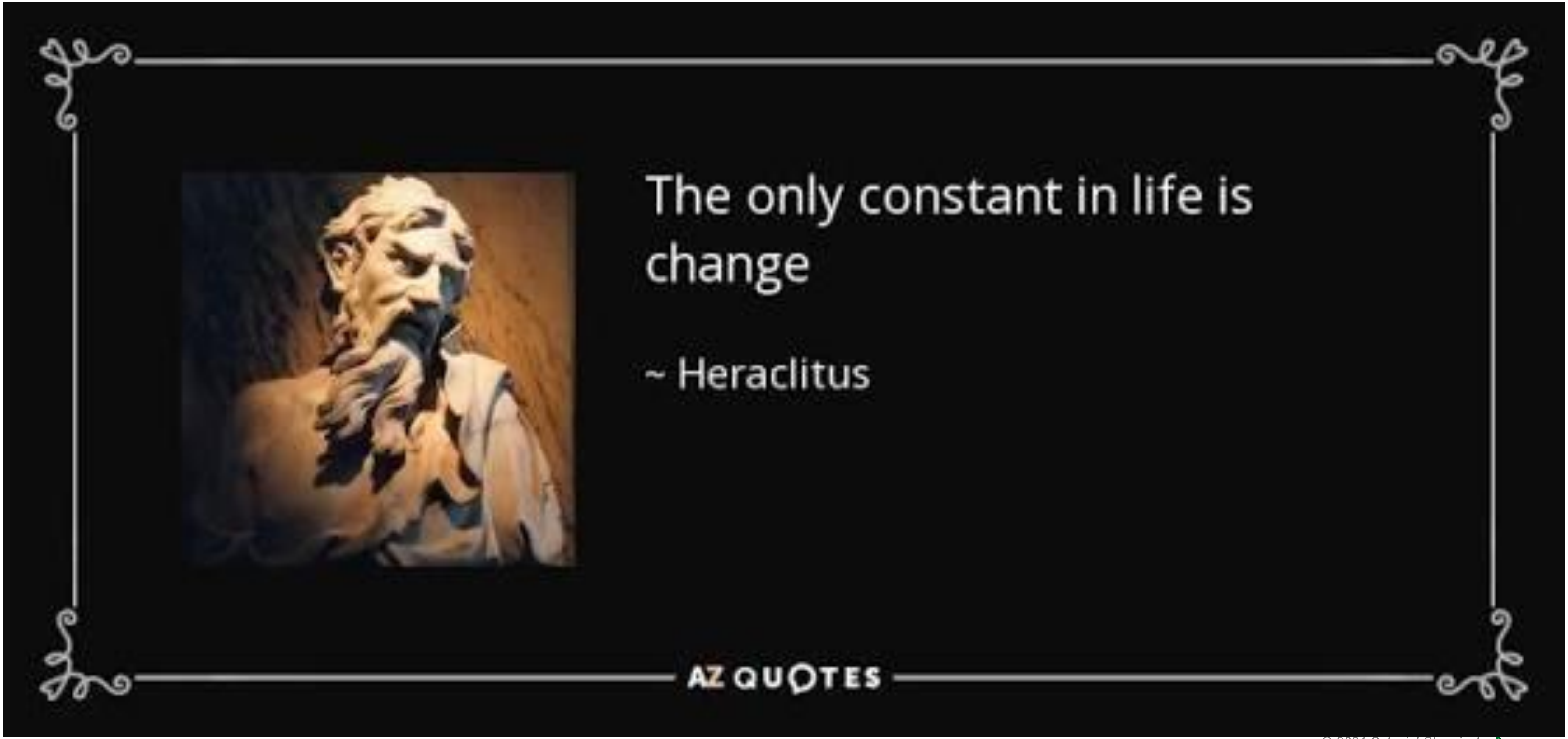

The only constant in life is change
~ Heraclitus
AZ QUOTES

Agenda

- Surfactants Overview
  - What is a surfactant?
  - Surfactant classes and functions
  - Key functional groups

- Key Market Trends
  - PEG/Dioxane Free
  - Sulfate Free
  - Low Irritation
  - All Natural
  - Low/No Preservative

- Question & Answer

Surfactants Overview

What is a Surfactant?

- Surfactant = Surface Active Agent
  - *"A chemical compound which when dissolved or dispersed in a liquid is preferentially adsorbed at an interface, lowering surface tension or interfacial tension."*

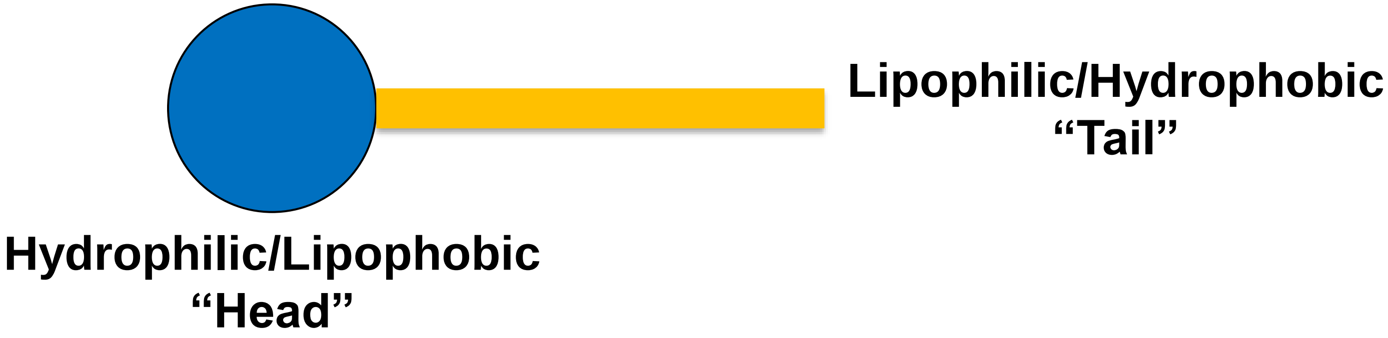
- Surfactants:
  - Make oil and water mix
  - Make water wetter

What are Surfactants Good For?

- Wetting
- Foaming
- Dispersion
- Lubrication
- Detergency
- Paper sizing
- Solubilization
- Emulsification

How Surfactants Work

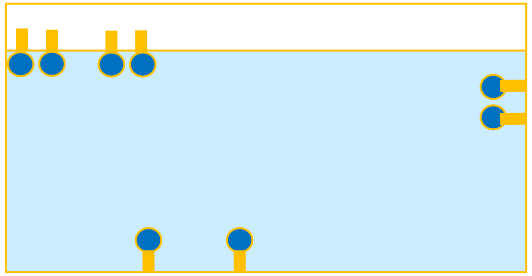
- “Tadpole” structure is key to functionality



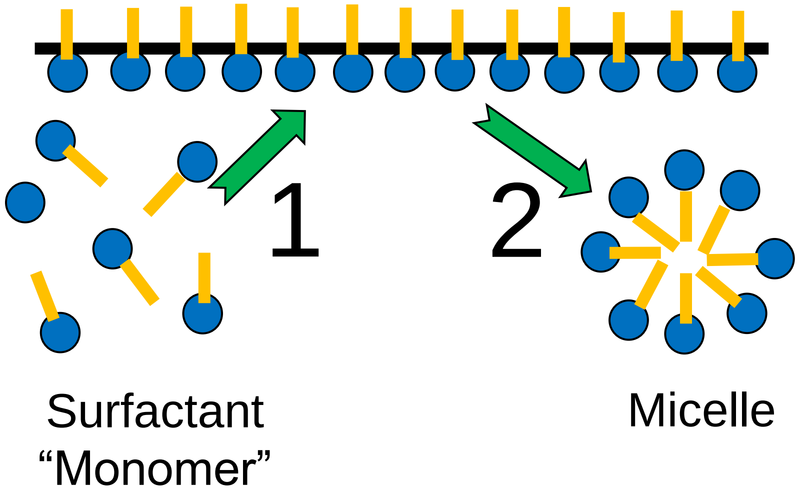
- Relative and absolute sizes of groups dictates function

Micelle Formation

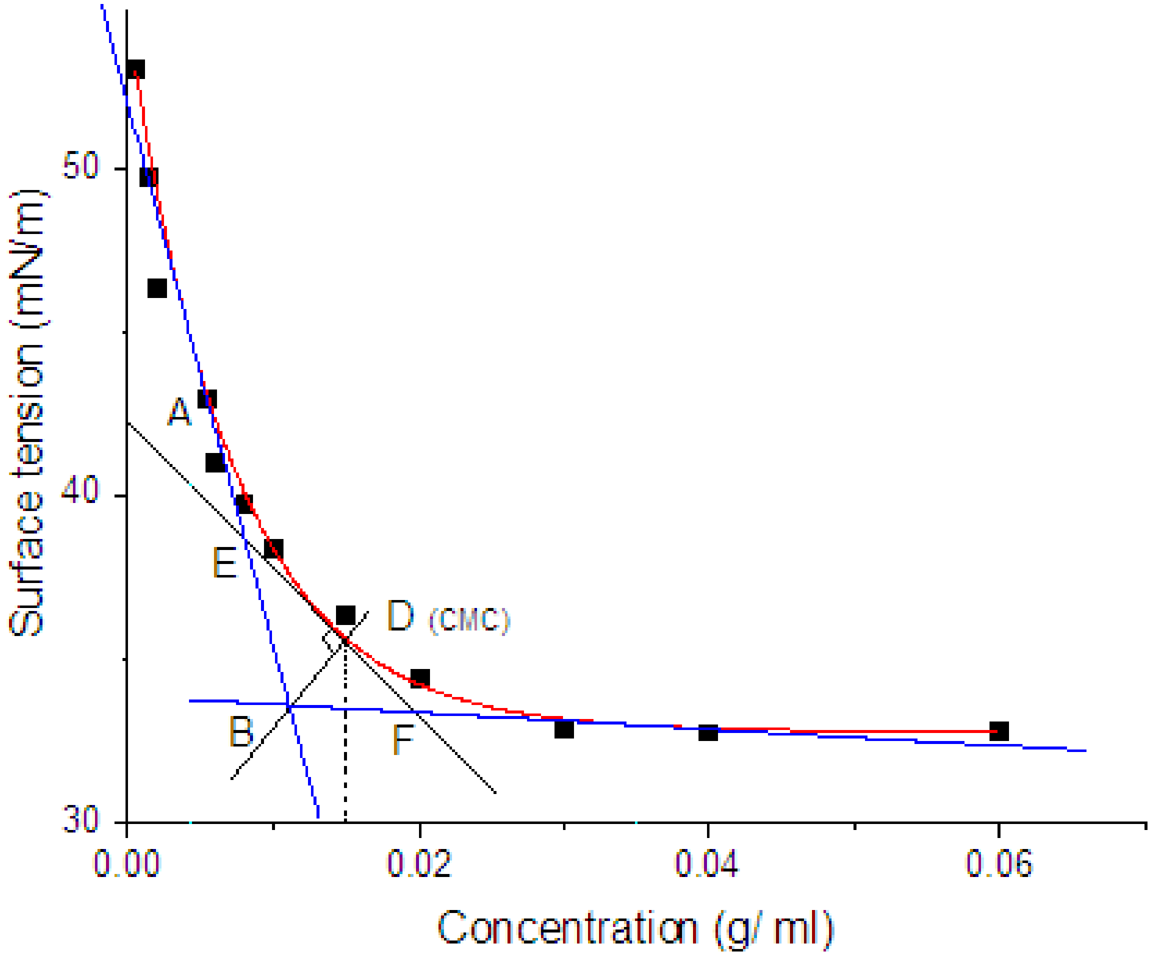
- At low concentrations, surfactants migrate to the edges of the water



- Once the surfaces are filled, surfactants assemble into spheres

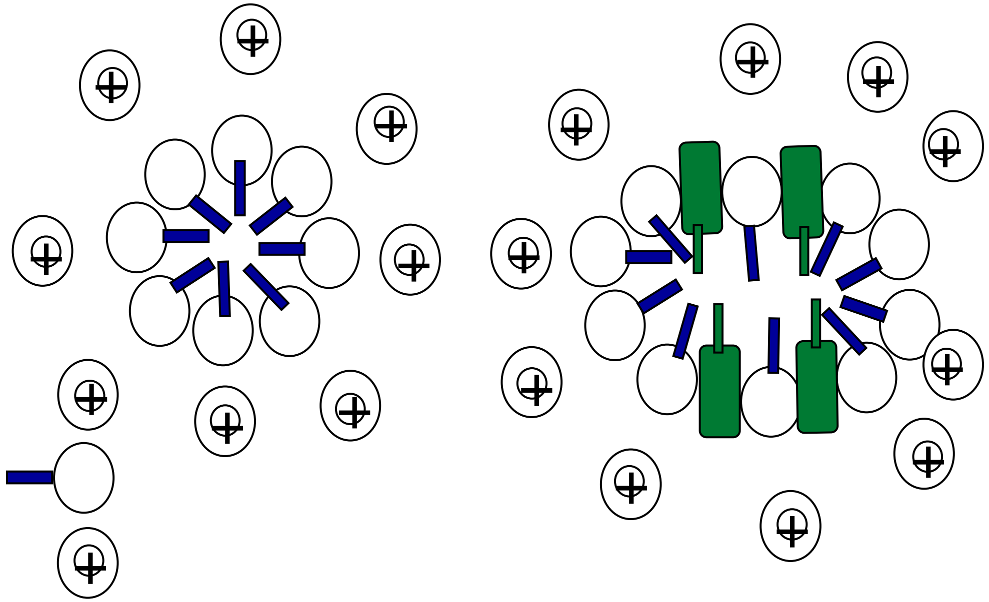


Critical Micelle Concentration



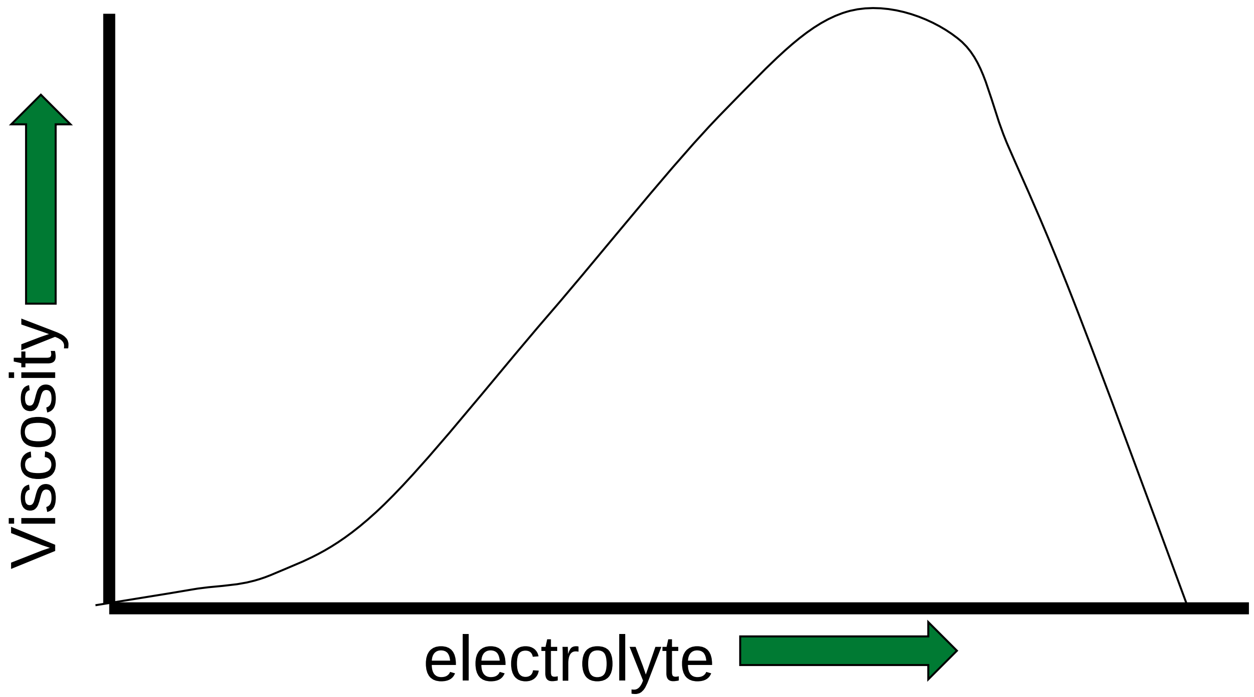
Surfactant Thickening

- Micelles can contain dozens or thousands of surfactant “monomers”
- As surfactant concentration increases, new micelle shapes can form
- Charged hydrophilic “heads” are kept apart by electrostatic repulsion
  - Salt reduces electrostatic repulsion
  - Nonionic surfactants (amides) increase packing



Surfactant Thickening

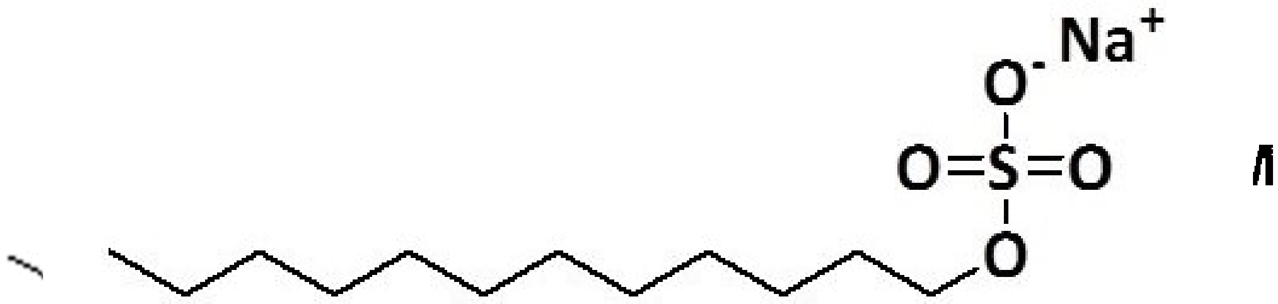
- Surfactant packing dictates micelle shape and size
- Micelles are always in flux
- Over-salting **reduces** viscosity



Types of Surfactants

- Anionic
  - Most detergent surfactants
  - High foaming for personal care
  - Combine with amphoteric surfactants for optimum aesthetics

- Sulfate
- Sulfonate
- Isethionate
- Glutamate
- Sarcosinate



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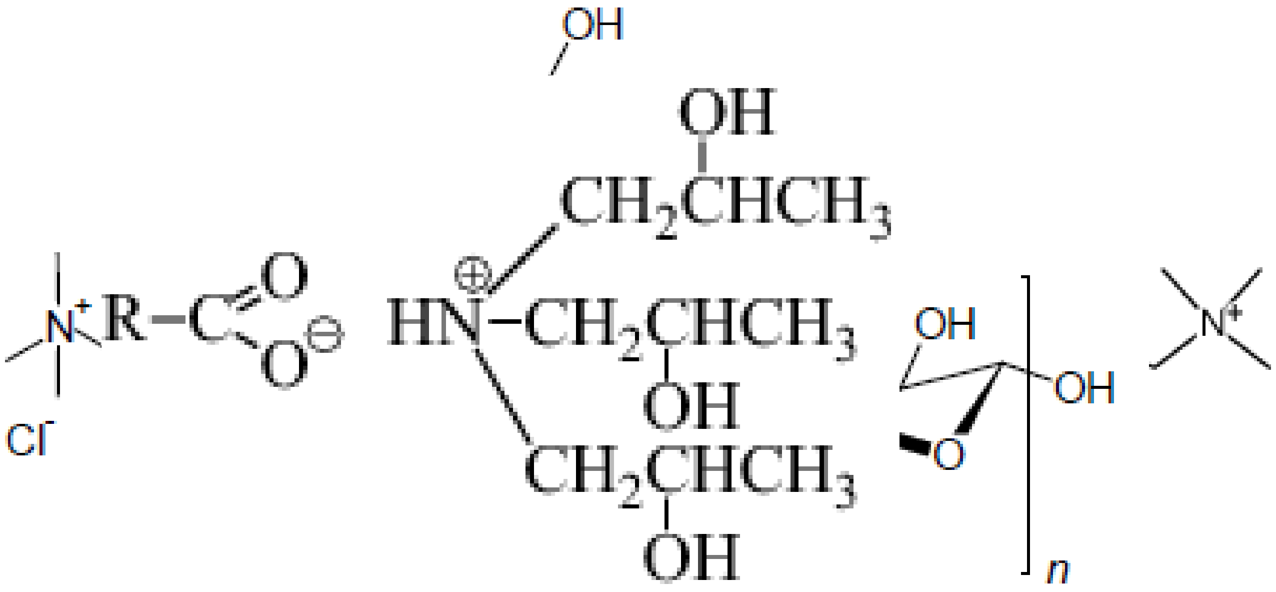
Types of Surfactants

- Cationic
  - Most conditioning agents
  - Typically moderate or low foaming
  - Variable compatibility with anionic surfactants

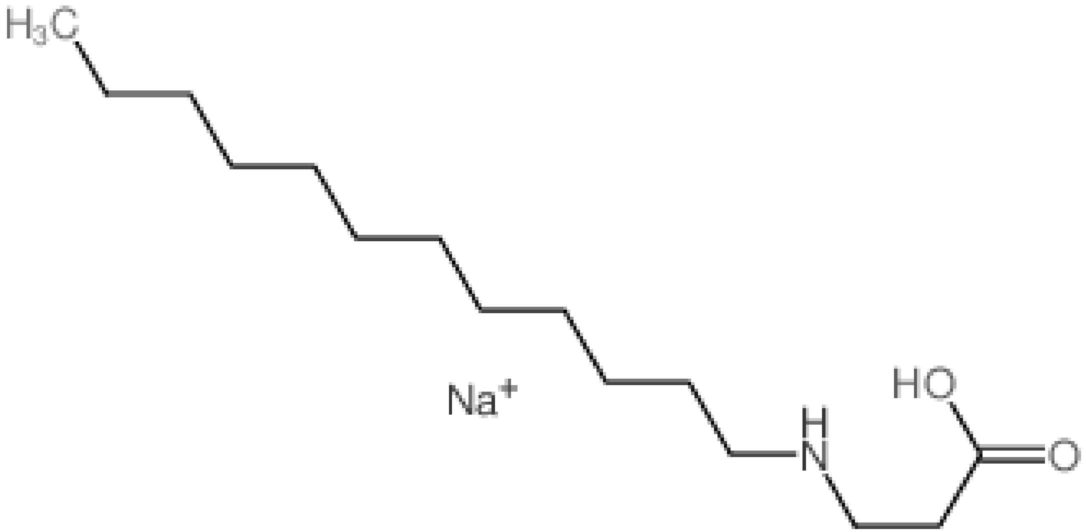
- Methyl Chloride
- Methyl Sulfate
- Hydroxypropyl
- Amine salts



Types of Surfactants

- Amphoteric/Zwitterionic ±
  - Viscosity, foam enhancement
  - Reduce irritation of anionic surfactants
  - Amphoteric vs zwitterionic

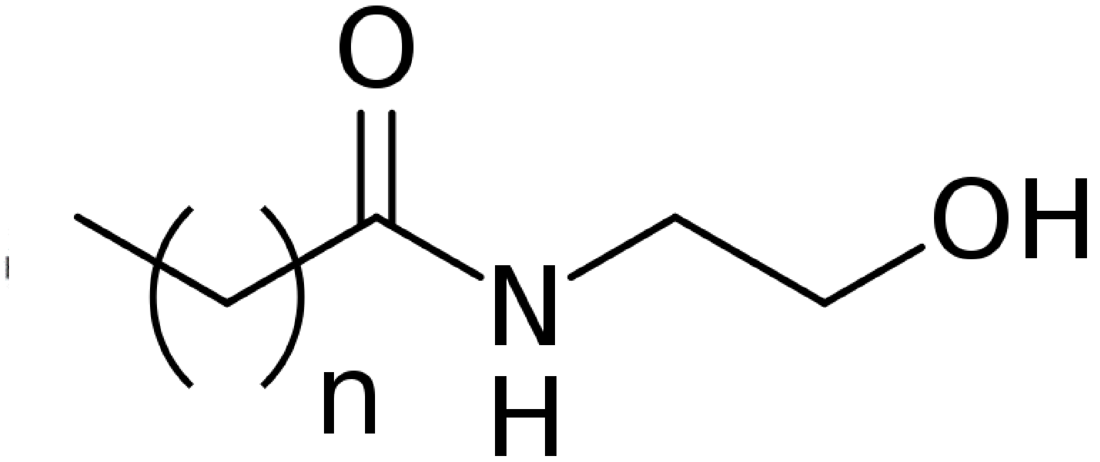
- Betaine
- Phosphobetaine
- Sultaine
- Amphoacetate
- Propionate

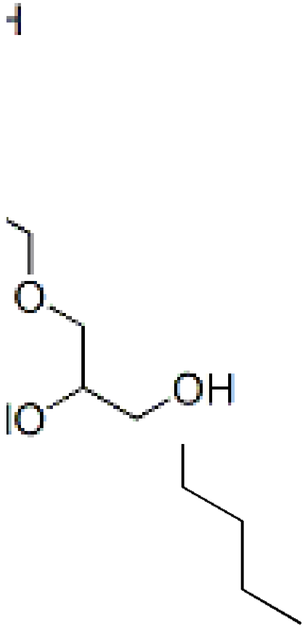


Types of Surfactants

- Nonionic
  - Huge variety of chemistry
  - Include ethoxylates
  - Low irritation potential

- Alcohol ethoxylates
- PEG esters
- Polyglyceryl esters
- Alkanolamides
- Glucosides



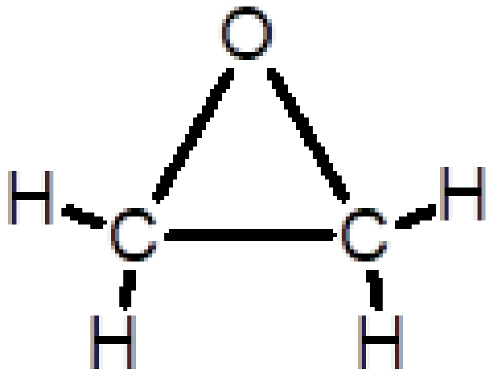


Key Market Trends

Trend: PEG-Free, Dioxane-Free

What is ethoxylation?

- Addition of ethylene oxide (EO) to base molecule
- Most commonly performed on alcohols
  - Natural or synthetic
  - Fatty or short chain
- Production of glycols (ethylene glycol, polyethylene glycol)
- Production of ethanolamines
  - MEA, TEA, DEA
- Production of isethionic acid
- Typically produces new alcohol which can be further reacted
  - More EO
  - Sulfation
  - Carboxylation
  - Esterification.



Ethylene Oxide

Common Ethoxylates and Their Uses

Ingredient	Function
Steareth-2, Steareth-20	Workhorse o/w Emulsifier Combo
Polysorbates	Workhorse o/w Emulsifiers
PEG-40 Hydrogenated Castor Oil	Fragrance Solubilization (End Use)
Alkylphenol Ethoxylates	Fragrance Solubilization (In Fragrance)
Sodium Laureth Sulfate	Lower Irritation Sulfate
Poloxamer	Zero Irritation Surfactant (Oral Care)
PEG-150 Distearate	Surfactant Thickening
PEG-120 Methyl Glucose Dioleate	Surfactant Thickening
PEG-7 Glyceryl Cocoate	Emollient/refatting (Rinse-Off)
PEG-75 Lanolin	Emollient/refatting (Rinse-Off)
Dimethicone PEG-7 Isostearate	Emollient/refatting (Leave-on)
PEG-5 Castor Oil	Emollient/refatting (Leave-on)

Dioxane Issues

For many ethoxylates,
a by-product is 1,4-Dioxane:

Ethylene Oxide : C_2H_4O

1,4-Dioxane : $C_4H_8O_2$

Dioxane Issues

- 1,4-Dioxane is a CMR (Carcinogenic, mutagenic and reprotoxic) substance
  - NTP “reasonably anticipated to be a human carcinogen”
  - IARC 2A “possibly carcinogenic to humans”
  - Known to be a carcinogen in animals
- Multiple organ toxicant (liver, kidneys, central nervous system)
- Toxic to aquatic plants and invertebrates
- Moderately persistent in the environment
- Regulated exposure limits in household and cosmetic products vary worldwide
- Many states have reporting requirements for children’s products (MN, ME, OR, VT, WA).

Dioxane Found in Cosmetics

Levels Reported	Number of Products	Percent of Total
0.0 – 1.0 ppm	111	65%
1.1 – 5.0 ppm	32	19%
5.1 – 10.0 ppm	14	8%
10.1 – 25.0 ppm	11	6%
>25.1 ppm	2 (35.2, 35.0 ppm)	1%

SCCS (Scientific Committee on Consumer Safety), Opinion on the Report of the ICCR Working Group: Considerations on Acceptable Trace Level of 1,4-Dioxane in Cosmetic Products, 15 December 2015, SCCS/1570/15

Dioxane Limits in Cosmetics

- Based on this information, the following limits have been proposed or enacted for cosmetics

- EU: SCCS opinion from 2015 sets safe limit at 10ppm
- ASEAN: 25ppm limit by June 19, 2020, 10ppm limit by June 19, 2023
- FDA: No guidance but use ICCR info
- California: Safe Cosmetics Act requires notification of products with Prop 65 contaminant
  Recent efforts point toward 10ppm limit
- NY State: Cosmetics: 10ppm limit by Dec 31, 2022
  Personal Care: 2ppm limit by Dec 31, 2022, 1ppm limit by Dec 31, 2023.

- Others??

Considerations for Replacement Selection

- Bio-renewable content
- Toxicity
  - Human
  - Environmental
- Brand positioning
- Ease of use
- Efficiency
- Cost.

Workhorse Emulsification – Small Molecules

- **Glyceryl Stearate with Stearic Acid**
  - Key benefit: 100% naturally derived
  - Key drawback: pH sensitive Stearic Acid
- **Polyglyceryl Esters**
  - Key benefit: Wide variety
  - Key drawback: Generally darker in color
- **Amino Acid Esters**
  - Key benefit: Can be all naturally derived
  - Key drawback: Pricey
- **Phosphate Esters**
  - Key benefit: High purity
  - Key drawback: Phosphate name.

Workhorse Emulsification – Hydrophobically Modified Polymers

- **Synthetic (acrylates)**
  - Key benefit: low cost
  - Key drawback: poor sustainability (currently)

- **Natural (cellulosics, crosspolymers)**
  - Key benefit: biobased content
  - Key drawback: cost

- **Inorganic (silicones)**
  - Key benefit: luxurious feel
  - Key drawback: negative perception.

Fragrance Solubilization

- Some emulsifiers can function as fragrance “solubilizers”
- Fragrance solubilization is really micro-emulsification
- Typically looking for high HLB emulsifiers

- **Polyglyceryl esters**
  - Key benefit: High biobased content
  - Key drawback: No “workhorse” product yet
- **Small molecules**
  - Key benefit: Ease of handling
  - Key drawback: Few choices
- **Surfactant combinations**
  - Key benefit: Optimized performance
  - Key drawback: Adds several ingredients.

Low Irritation Cleansers

- **Alkyl Glucosides**
  - Key benefit: 100% biobased
  - Key drawback: Difficult to formulate with
- **Alkyl Glucoside Derivatives**
  - Key benefit: Expanded application range
  - Key drawback: Few suppliers
- **Sulfosuccinates**
  - Key benefit: Good foam possible
  - Key drawback: Poor stability in acid/base
- **Amino Acid Surfactants**
  - Key benefit: Excellent stability
  - Key drawback: Costly.

Surfactant Thickening

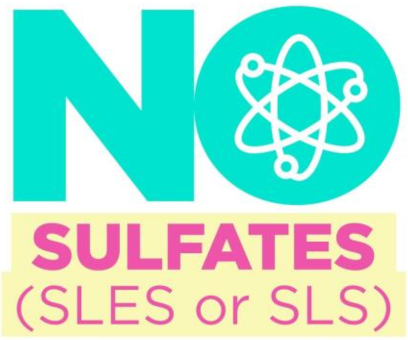
- **Synthetic Polymers (HASE/HEUR)**
  - Key benefit: Highly customized performance
  - Key drawback: Mostly or purely petrochemical feedstocks
- **Alkanolamides**
  - Key benefit: Economical
  - Key drawback: Potential secondary amine issues
- **Amine Oxides**
  - Key benefit: Excellent performance
  - Key drawback: Not well characterized for personal care
- **Long-Chain Amphoterics**
  - Key benefit: Very effective viscosity boosters
  - Key drawback: Low active products or contain solvents.

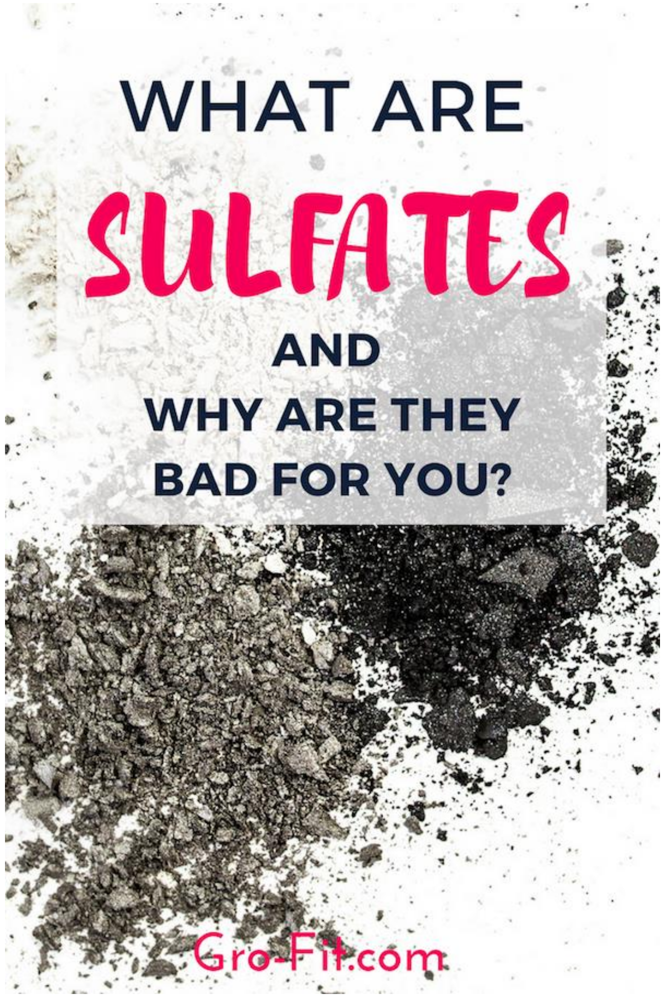
Emolliency/Refatting

- **Glyceryl Oleate/Polyglyceryl Oleate**
  - Key benefit: 100% biobased
  - Key drawback: Easy to overwhelm system
- **Phosphate amphoterics**
  - Key benefit: Very high substantivity
  - Key drawback: Negative association with phosphate
- **Lecithin/Phospholipids**
  - Key benefit: All natural
  - Key drawback: Can be pricey
- **Long-Chain Amphoterics**
  - Key benefit: Economical
  - Key drawback: Lack of efficacy data.

Trend: Sulfate-Free

Why Sulfate-Free?





Going Sulfate-Free

- There are many challenges associated with moving from traditional sulfate surfactants to next generation products

  - Different impurities
  - Different foam properties
  - Different functional groups
  - Different packing capabilities
  - Different salt responsiveness
  - Different solubility parameters.

Considerations for Replacement Selection

- Bio-renewable content
- Toxicity
  - Human
  - Environmental
- Brand positioning
- Ease of use
- Efficiency
- Cost.

Common Sulfate Replacements

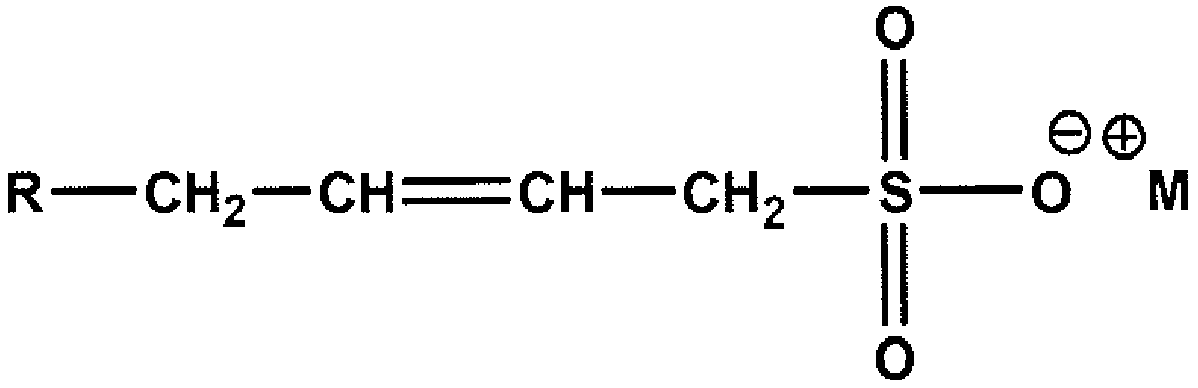
- Anionic
  - High foaming for personal care
  - Combine with amphoteric surfactants for optimum aesthetics

- Watch for:
  - Acid pKa values
  - Instable groups
  - Impurities
  - Hard water tolerance
  - Size of head group.

Sulfate Free Examples - Sulfonate

- **Key Benefits**
  - Can be very low cost
  - Extremely stable

- **Key Drawbacks**
  - Petrochemical olefins dominate
  - Slower viscosity response



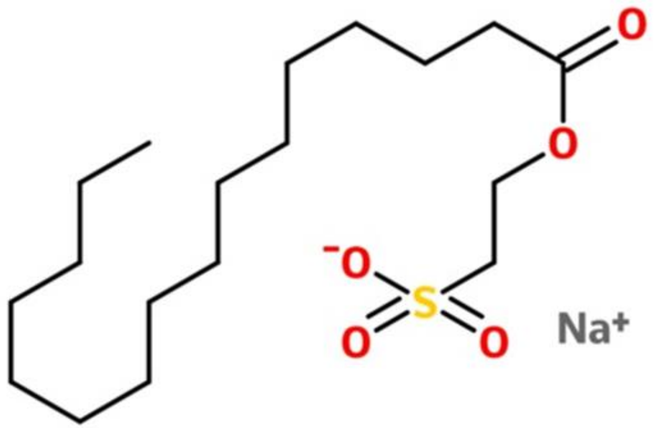
- **Watchouts**
  - Sultones should be kept as low as possible
  - Start with increased amount of secondary surfactants
  - Krafft point issues.

Sulfate Free Examples - Isethionate

- **Key Benefits**
  - Widely used
  - Residual fatty acid offers added benefits

- **Key Drawbacks**
  - Ester functionality can be instable
  - Residual fatty acid offers added challenges

- **Watchouts**
  - Try to keep pH near neutral
  - Formulate with chelant
  - Watch fatty acid content.

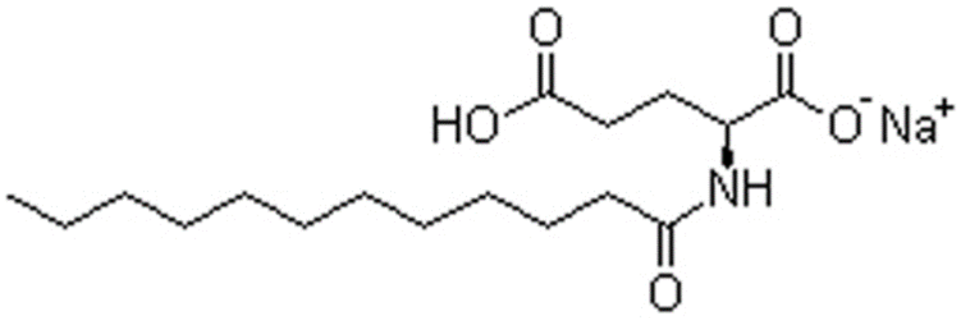


Sulfate Free Examples - Glutamate

- **Key Benefits**
  - High biobased content
  - Low irritation

- **Key Drawbacks**
  - Relatively costly
  - Poor viscosity response

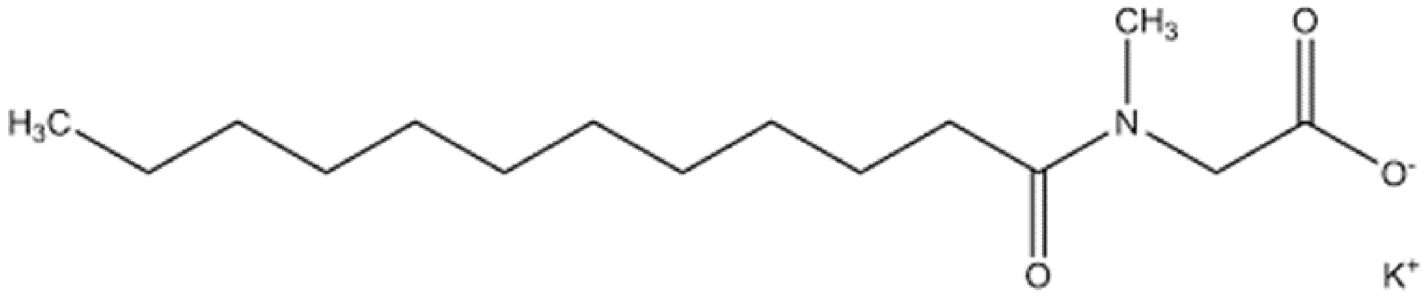
- **Watchouts**
  - Multiple pKa values
  - Combine with additional sulfate-free surfactants
  - Check biobased content if important.



Sulfate Free Examples - Sarcosinate

- **Key Benefits**
  - Unique advantages in syndet bars
  - Low in-use toxicity

- **Key Drawbacks**
  - Partially petrochemical
  - Poor viscosity response



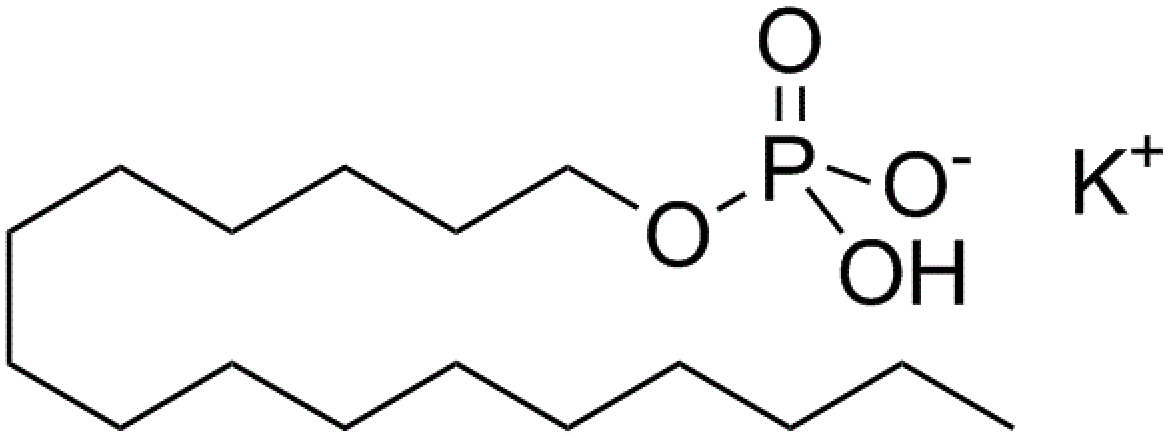
- **Watchouts**
  - Avoid using too much in gel cleansers
  - Foaming can be enhanced by salt addition
  - Synergistic surface tension reduction has been observed.

Sulfate Free Examples - Phosphate

- **Key Benefits**
  - Can be high biobased
  - Low irritation

- **Key Drawbacks**
  - Association with inorganic phosphates
  - Typically need to be ethoxylated

- **Watchouts**
  - Water hardness may impact solubility
  - Can be supplied in acid or neutral forms
  - Poor viscosity response.



Surfactant Thickening

- **Natural Polymers (Gums)**
  - Key benefit: Natural
  - Key drawback: Non-Newtonian flow characteristics
- **Synthetic Polymers (HASE/HEUR)**
  - Key benefit: Highly customized performance
  - Key drawback: Petrochemical feedstocks
- **Alkanolamides**
  - Key benefit: Economical
  - Key drawback: Potential secondary amine issues
- **Amine Oxides**
  - Key benefit: Excellent performance
  - Key drawback: Not well characterized for personal care
- **Long-Chain Amphoterics**
  - Key benefit: Very effective viscosity boosters
  - Key drawback: Low active products or contain solvents.

Trend: Low Irritation Cleansers

Demonstrating Reduced Irritation

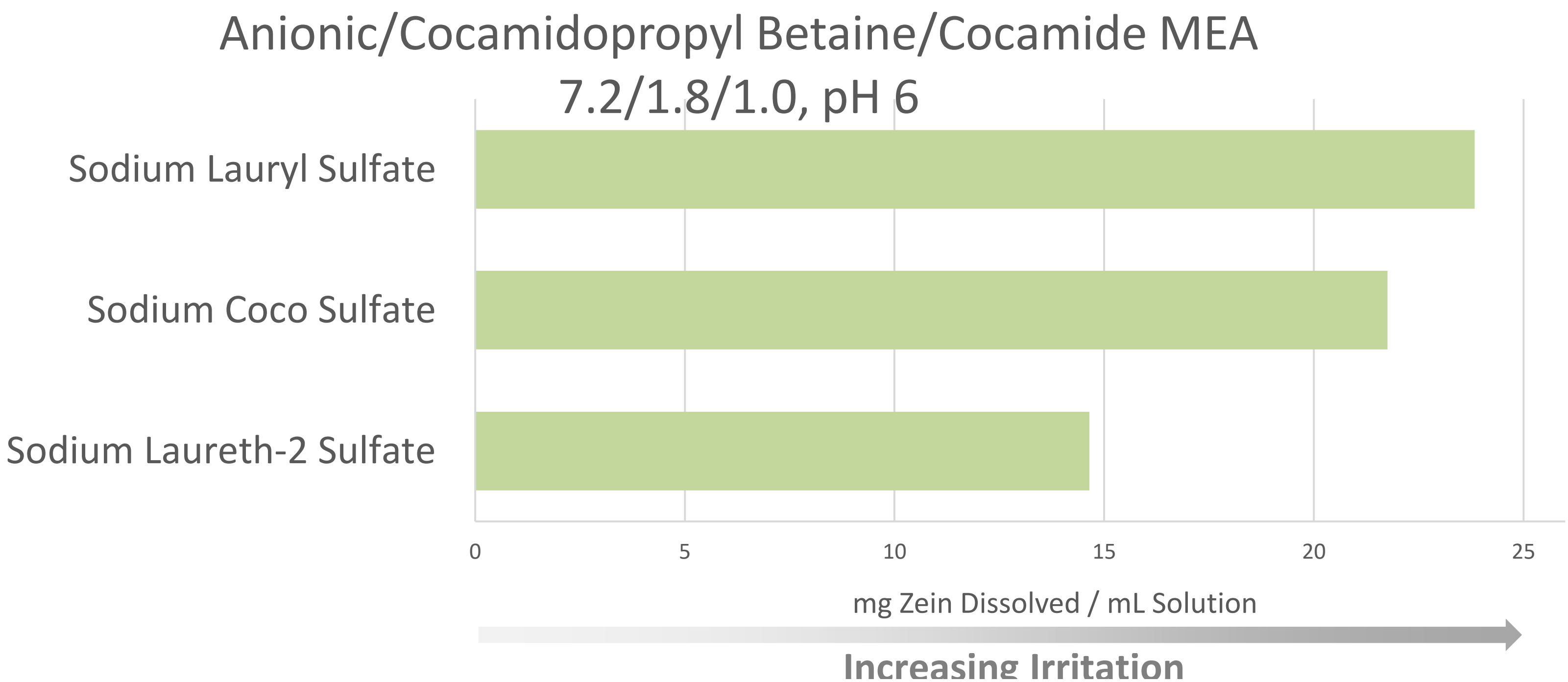
- Zein Test for In-vitro Irritation
  - Uses zein (corn) protein
  - Uses protein denaturization to assess irritation
  - Zein protein is insoluble in water
  - As surfactant denatures the protein, water solubility increases
  - Remaining insoluble protein is filtered, dried, and weighed
  - Results are presented here in mg Zein dissolved / mL product

- Model Formulation

Component	Concentration
Anionic surfactant or blend	7.2% solids
Amphoteric (Cocamidopropyl Betaine)	1.8% solids
Alkanolamide (Cocamide MEA)	1.0% solids
Water, citric acid	Qs to 100%, pH 6

Reducing Irritation of Sulfates

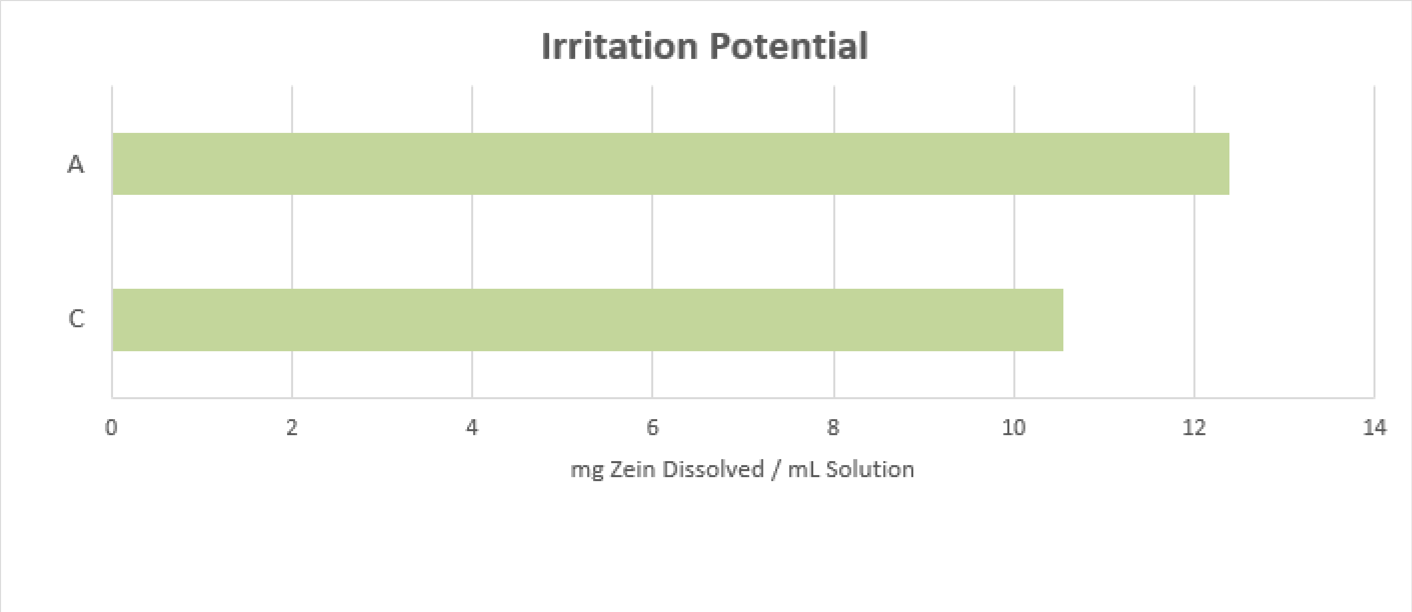
- Even if “sulfate-free” is not a priority, NY State dioxane limits are coming:
  - 2ppm limit by Dec 31, 2022
  - 1ppm limit by Dec 31, 2023
  - These limits will be very hard to achieve, even with “low dioxane” ether sulfates
- SLES is preferred to SLS because of reduced irritation potential



Ingredient Selection Matters

- Coco-Sulfate based system
  - Sodium Coco-Sulfate, Coco-Glucoside, Cocamidopropyl Hydroxysultaine
  - At 11.6% solids measures 12.4 mg zein / mL solution (System A)
  - Betaine/amide system at 10% solids measures ~22 mg zein / mL solution

- Replaced 25% of surfactant solids with low irritation anionic (System C)
  - Reduced test result to 10.5 mg zein / mL solution



Trend: All Natural Cleansers

Considerations for Replacement Selection

- Bio-renewable content
- Toxicity
  - Human
  - Environmental
- Brand positioning
- Ease of use
- Efficiency
- Cost.

What's Natural

- No FDA definition for personal care

- Factors to consider
  - % Biobased
  - ISO 16128
  - Feedstocks
  - By-products
  - Consumer experience
  - Avoiding the "all-or-nothing" approach

Future of Natural Surfactants?

- Biosurfactants
- Microorganisms convert carbon sources to a variety of surfactant molecules
  - Glycolipids
  - Rhamnolipids
  - Sophorolipids
  - Sphingolipids
- Carbon can come from wide variety of sources
  - Traditional triglyceride oils, including waste oils
  - Sugars, starches, carbohydrates
  - Hydrocarbons
- Currently limited by low yield

Trend: Low/No Preservative Formulations

Dwindling Preservative Choices

- Common preservatives have come under fire for a variety of real or perceived risks
  - Formaldehyde donors: carcinogenicity
  - Parabens: carcinogenicity
  - Isothiazolinones: contact sensitization
  - Phenoxyethanol: irritation
  - Organic acids: irritation or sensitization

- Formulators are faced with a dwindling basket of “friendly” preservatives

Surfactants as Preservatives

- A variety of surfactants can function as preservatives
- They function best in “hurdle” systems with multiple chemistries

- **Nonionic surfactants**
  - Caprylyl Glycol
  - Glyceryl Laurate
- **Amphoteric surfactants**
  - Capryloyl Glycine
  - Cocamidopropyl PG-Dimonium Chloride Phosphate
- **Cationic Surfactants**
  - Benzalkonium Chloride
  - Polyquaternium-80
- **Anionic surfactants**
  - Citrate monoesters.

Thank You!

Question & Answer

More questions?: dennis@colonialchem.com
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