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Editorial

Surfactants and Emulsifying Agents: The Main Classification and Characteristics

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Water-soluble polymers

These types of polymers are divided to three classes: natural polymers, water-soluble and derivatives of synthetic hydrophilic and cellulose polymers.

- The polysaccharides which of natural origin called natural polymers such as, pectin, acacia, sodium alginate, agar, tragacanth, xanthan gum, and, and polypeptides e.g. gelatin and casein.
- The cellulose derivatives are chemically modified therefore, they are considered as semisynthetic products such as methylcellulose, sodium carboxymethylcellulose, and hydroxyethyl and hydroxypropyl cellulose.
- The synthetic water-soluble polymers include vinyl polymers such as polyvinyl alcohol and polyvinylpyrrolidone, Carbomer (Carbopol®), which is a copolymer of acrylic acid, and polyethylene glycols.
- Water-soluble polymers characterize of forming favor o/w emulsions, enhance viscosity, some used as emulsifying agents.
- Some of the mentioned water-soluble polymers rely on the particular chemical structure of the polymer.

Anionic soaps and detergents

Soft soaps

These are salts of fatty acids in which the positive ion is univalent, such as Na+, K+, NH4+. The common fatty acids used are stearic (C-l8), oleic (C- l8 9cis), palmitic (C-16), and lauric (C-12). Often the emulsifier is formed at the time of emulsification by adding an alkali base (e.g., NaOH, KOH, NH4OH, sodium borate) or an organic amine base (e.g., triethanolamine). Soft soaps have the following properties:

- They are water soluble and/or water dispersible.
- They usually form o/w emulsions.
- On the contrary, the w/o emulsions rose water ointment and the cold cream are formed when a solution of sodium borate (borax) is added..
- Soaps with an organic amine as the cation are more balanced, less hydrophilic, and form more stable emulsions than the alkali soap emulsifiers; emulsions made with alkali soap emulsifying agents sometimes require the addition of auxiliary emulsifiers for stable emulsions.
- Soft soaps give emulsions with a pH in the basic pH range.

The alkali soap emulsions have a pH in the range or 8-10 (6) and are most stable above pH 10 (5).

Hard soaps

These are salts of fatty acids salts are formed by the reaction of calcium hydroxide in Lime Water with oleic acid found in olive oil and certain other fixed oils.

Hard soaps have the following properties:

- They are oil soluble and water insoluble.
- Hard soaps form w/o emulsions.

- Like soft soaps, these are salts of a carboxylic acid ($R\text{-}COO^-$), a weak acid, which gives the weakly dissociated R-COOH form upon addition of drugs or other ingredients.
- The $R\text{-}COO^-$ groups of hard soaps may interact with and bind high molecular weight cations like benzalkonium chloride.

Detergents

These are salts of phosphates, alkyl sulfates, sulfosuccinates and sulfonates. The widely used detergents are docusate sodium and sodium lauryl sulfate.

Detergents have the following properties

- They are very hydrophilic and are soluble in water.
- Detergents always form o/w emulsions.
- As strong electrolytes, they are more stable to acids, such as phenolic compounds and salicylic acid, and are not sensitive to high concentrations of electrolytes.
- Because their ionic centers strongly repel each other, detergents do not form firm, intact barriers.
- These surfactants are most often used in conjunction with secondary non-ionic emulsifiers such as cetyl or stearyl alcohol.
- Like soaps, detergents are unsuitable for internal use emulsions because of their "soapy" taste and laxative action.

Cationic surfactants

- They are quaternary ammonium type compounds e.g. cetylpyridinium chloride, benzalkonium chloride..
- They are very hydrophilic and are very soluble in water.
- They are not used as emulsifiers, but are useful as antimicrobial agents.

Finely divided solids

These are usually finely divided hydrophilic inorganic solids. When these solids are in a very fine state of subdivision, they tend not to be easily wetted by liquids, and they orient at interfaces, forming a barrier to coalescence. The most common examples of this type include the colloidal clays, bentonite and Veegum, and metallic hydroxides, such as magnesium oxide and zinc oxide.

- The finely divided solids are not usually used by themselves, but are useful as auxiliary emulsifiers. An exception is the Magnesia Magma-Mineral Oil emulsion described below.
- Large quantities of finely divided solids, which are in a product formulation for therapeutic purposes, may function as emulsifiers if an appropriate order of mixing is used. An example is the emulsification of 25% mineral oil with 75% magnesia magma (Haley's M-O®). Here, the finely divided magnesium oxide of magnesia magma serves as the sole emulsifier agent for the mineral oil.
- Hydrophilic solids favor oil-in-water emulsions and are used most often as auxiliary emulsifier for this emulsion type. There are, however, examples of hydrophilic solids present in water-in-oil formulations. An example is the presence of the hydrophilic solids calamine and zinc oxide in Calamine Liniment, a w/o emulsion that has calcium oleate as the primary emulsifying agent.
- Finely divided hydrophobic solids favor formation of water-in-oil emulsions. If a large quantity of a hydrophobic solid is added to a system with the primary emulsifier favoring an oil-in-water emulsion, the final emulsion type is difficult to predict.

An example is the formulation of an oral o/w emulsion of the water-insoluble hydrophobic drug, sulfadiazine, with a non-ionic emulsifying system that favors an oil-in-water emulsion.

Depending on the exact conditions, the result may be either a w/o or an o/w emulsion. Because oil-in-water emulsions are preferred for oral products, the formation of a water-in-oil emulsion in this case may create a compounding problem.

Natural non-ionic surfactants

These include fatty acid alcohols, such as stearyl alcohol and cetyl alcohol, wool fat or wool wax and its derivatives, wool alcohols and cholesterol, and derivatives of other natural waxes, e.g. spermaceti, synthetic spermaceti and wax.

- These are available as fractions of the natural products or their synthetic versions.
- Some of the natural waxes, such as wool wax, Lanolin USP (wool fat), Hydrous Lanolin (hydrous wool fat) and its synthetic version Hydrophilic Petrolatum USP, are complex mixtures of oils, waxes, and emulsifiers. The purified emulsifying agents in Hydrophilic Petrolatum are the non-ionic emulsifiers stearyl alcohol and cholesterol. Lanolin and Hydrous Lanolin contain mixtures of similar natural emulsifiers.

- Although the purified fractions and their synthetic counterparts may be used to produce w/o emulsions, they are also commonly used as auxiliary emulsifiers to stabilize o/w emulsions when a powerful oil-in-water emulsifying agent, such as a detergent, is present as the primary emulsifier.

Synthetic non-ionic surfactants

This type of surfactants constitute of complex ester-ethers and esters that are derived from fatty acids, polyols, fatty alcohols and alkylene oxides

- The part of the hydrophilic molecules consists mainly of oxyethylene and free hydroxyl groups.
- The lipophilic part has long chain hydrocarbons of fatty acids and fatty alcohol. Although they are given a chemical designation based on the primary component, these are actually complex mixtures of closely related derivatives.

For example, sorbitan monooleate, also known as Span 80, is a mixture, but the primary component is sorbitan monooleate. Polysorbate 80 (Tween 80) is polyoxyethylene 20 sorbitan monooleate; the 20 indicates that there are approximately 20 moles of ethylene oxide for each mole of sorbitol and sorbitol anhydride [1-12].

Non-ionic surfactants have the following characteristics

- They are neutral compounds that are stable over a wide pH range.
- They are relatively insensitive to the presence of high concentrations of electrolytes.
- They are heat stable.
- Because they do not increase the viscosity of the system, emulsions made with these agents may require an auxiliary viscosity inducing agent or a somewhat viscous vehicle.
- They are mixed in various proportions to give either w/o or o/w emulsions. The appropriate amounts of individual emulsifiers needed to form a specific emulsion type can be determined using a mathematic system called the HLB system.

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