Tensides (or Surfactants) and heavy metal soaps

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Metal carboxylates—higher carboxylates of alkali (Soaps) and other metals (metallic soaps)—are used in many areas of daily life and industry. While the basic colloidal and other physicochemical properties of these derivatives have already been extensively studied, there has recently been a revival of interest in the various modes of bonding exhibited by metal carboxylates. Many metal carboxylates have been known from ancient times. The oldest organic derivatives of metals are the alkali metal carboxylates, commonly known as soaps. These soaps are soluble in water, with which they readily produce foam, commonly used for washing or cleansing purposes. Carboxylates of metal other than alkali metals (with the exception of lithium) are generally insoluble in water and are called Metallic soaps. The first use of such soaps in the form of lead linoleates appears to have been made quite early in paints for mummification. Metallic soaps are, therefore, simple carboxylates of alkaline earths or other polyvalent metals with the general formula, M(O₂CR)n, where ‘M’ is a metal in oxidation state ‘n’ and ‘R’ is an organic radical containing at least 6-7-carbon atoms. The term metallic soaps is restricted by some of the salts of fatty acids (i.e. those in which R is an aliphatic radical) although in the broad sense the term also includes salts of certain cyclic acids.

The preparation of soaps and detergents is one of the oldest forms of chemical syntheses. Their use began ever since the man’s desire for cleanliness increased. For washing purposes a mixture proves to be just as effective as a single pure salt. A cut-throat competition among the producers plus an enormous demand necessitated by increasing population have rendered the task highly challenging. Evidently, any consumer would prefer a product that is cheap and best for him. A producer however needs to manufacture an economically viable product of good quality. Both manufacturers and researchers have, in fact, this common goal to achieve. Researchers would be better off in their endeavour to correlate the studied physico-chemical characteristics of the synthesised compounds with their qualitative worth.

Surfactants, also known as tensides are wetting agents that lower the surface tension/interfacial tension of liquid(s) allowing easier spreading. Surfactants are usually organic compounds that are amphiphilic i.e. they contain both hydrophobic and hydrophilic groups. Consequently, they are soluble in both aqueous and non-aqueous solvents. Various technological applications of amphipathic molecules (possessing polar and apolar moieties on the same molecule) have rendered this versatile group of compounds (surface–active agents or surfactants) an interesting subject domain for researchers and academicians alkali. As a matter of fact, biochemists (working on membrane structure and function) have long been aware of the selective solubilizing power of surfactants for membrane components. Chemists already know that surfactants can modify chemical reactions, whereas pharmaceutical scientists are now very much aware of the formulation potential of surfactants.

The effect on environment:

The effect of various surfactants on
environment and health has drawn attention of the researchers world over. In fact, every day, a large number of different kinds of surface-active agents (e.g., detergents, cleaning agents and cosmetics etc.) are used. These are often associated with the substances that adversely affect the environment, irritate the skin and even cause allergy. Manufacturers, researchers and authorities are therefore very much concerned about their harmful effects to consumers and environment. Serious efforts are thus necessary to explore those substances which are easily degraded under anaerobic conditions and not accumulated in living organisms.

**Pulmonary surfactants:**

The term surfactant was coined by Antara Products in 1950. In Index Medicus and United States National Library of Medicine, surfactant is reserved for the meaning “Pulmonary Surfactants”. The most common biological example of surfactant is the coating of surfaces of the Alveoli, the small air sacs of the lungs that serve as the site of gas exchange. Surfactant is a complex substance containing phospholipids and a number of apoproteins. This essential fluid is produced by the type II alveolar cells, and lines the alveoli, and smallest bronchioles. Surfactant reduces surface tension throughout the lung, thereby contributing to its general compliance. It is also important because it stabilizes the alveoli. Laplace Law tells us that the pressure within a spherical structure (such as the alveolus) with surface tension is inversely proportional to the radius of the sphere (\(p = 4T/r\) for a sphere with two liquid-gas interfaces, like a soap bubble, and \(p = 2T/r\) for a sphere with one liquid-gas interface, like an alveolus: \(P = \text{Pressure}, T = \text{surface tension and } r = \text{radius}\)). That is, at a constant surface tension, small alveoli will generate bigger pressures within them than will large alveoli. Smaller alveoli would therefore be expected to empty into large alveoli as lung volume decreases. This does not occur, however, because surfactant differentially reduces surface tension, more at lower volumes and less at higher volumes, leading to alveolar stability and reducing the likelihood of alveolar collapse. Surfactant is formed relatively late in fetal life; thus premature infants born without adequate amounts experience respiratory distress and may die.

**Characterization and classification of surfactants:**

However, different physico-chemical attributes of surface active agents, or surfactants, enable us to extend a well knit characterization of these significant compounds as follows: A surfactant is a compound which will adsorb at an air-water or oil-water interface and at the surface of solids. A study of the adsorption process is of fundamental importance in an understanding of the properties of surface-active compounds since, it is the change in interfacial free-energy and surface charge resulting from adsorption which leads to the ability of these compounds to act as emulsifying and suspending agents. Surface-active agents are characterized by the possession of both polar and non polar regions on the same molecule. The polar or hydrophilic region of the molecule may carry a positive or negative charge, giving rise to cationic or anionic surfactants, respectively, or may be composed of a polyoxyethylene chain, as in most of the non-ionic surfactants. The non-polar or hydrophobic portion of the molecule is most commonly a flexible chain hydrocarbon although there is a large number of compounds including many molecules of biological interest, with aromatic hydrophobic groups. The dual nature of surfactant is typified by sodium dodecyl sulphate (NaDS):

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\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{SO}_3^-\text{Na}^+
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The existence in the same molecule of two moieties, one of which has affinity for solvent and the other of which is antipathetic to it, is termed amphipathy. This dual nature is responsible for the phenomenon of surface activity, and of micellization and solubilization. As a class these substances, which include soaps and detergents, can be called association colloids, a name indicating their tendency to associate in solution, forming particles of colloidal dimension. Owing to their tendency to become adsorbed at interfaces, they are often called surface-active agents or colloidal surfactants.

As regards their classification, a surfactant can be classified by the presence of formally charged groups in its head. A nonionic surfactant has no charge groups in its head. The head of an ionic surfactant carries a net charge. If the charge is negative, the surfactant is more specifically called anionic; if the charge is positive, it is called cationic. If a surfactant contains a head with two oppositely charged groups, it is termed zwitterionic. Some commonly encountered surfactants of each type include:

**Ionic:**

- Anionic (based on sulphate, sulphonate or carboxylate anions)
- Sodium dodecyl sulphate (SDS), ammonium lauryl sulphate and other alkyl sulphate salts
- Sodium laureth sulphate, also known as sodium lauryl ether sulphate (SLES)
- Alkyl benzene sulphonate
- Soaps, or fatty acid salts
- Cationic (based on quaternary ammonium cations)
- Hexadecyl (Cetyl) trimethylammonium bromide (CTAB) and other alkyltrimethylammonium salts

Cetylpyridinium chloride (CPC):
- Poly ethoxylated tallow amine (POEA)
- Benzalkonium chloride (BAC)
- Benzethonium chloride (BZT)

Zwitterionic (amphoteric):
- Dodecyl betaine
- Dodecyl dimethylamine oxide
- Cocamidopropyl betaine
- Coco ampho glycinate

Nonionic:
Alkyl poly (Ethylene oxide):
- Copolymers of poly (Ethylene oxide) and poly (propylene oxide) [commercially called poloxamers or poloxamines] Alkyl polyglucosides, including:
  - Octyl glucoside
  - Decyl maltoside

Fatty alcohols
- Cetyl alcohols
- Oleyl alcohols

Cocamide MEA, cocamide DEA, cocamide TEA:
Apart from the above mentioned surfactants, another significant group of surfactants used in biochemistry (names and structures as under) are as follows:
With regard to their applications and sources, surfactants play an important role in many practical applications and products as:
- Detergents
- Fabric softener
- Emulsifier
- Paints
- Adhesives
- Inks
- Anti-fogging
- Soil remediation
- Wetting
- Ski Wax
- Snow board wax
- Foaming
- Defoaming
- Laxatives
- Agrochemical formulations as herbicides and insecticides

Micellization, micelles and structure:
As regards the structure of a micelle (rarely micella, plural micellae) it is an aggregate of surfactant molecules dispersed in a liquid colloid. A typical micelle in aqueous solution forms an aggregate with the hydrophilic ‘head’ regions in contact with surrounding solvent, sequestering the hydrophobic ‘tail’ regions in the micelle center. This type of micelle is known as a normal phase micelle (oil-in-water micelle). Inverse micelles have the head groups at the centre with the tails extending out (water-in-oil micelle). Micelles are approximately spherical in shape. Other phases, including shapes such as ellipsoids, cylinders, and bilayers are also possible. The shape and
size of a micelle is a function of the molecular geometry of its surfactant molecules and solution conditions such as surfactant concentration, temperature, pH, and ionic strength. The process of forming micellae is known as micellisation and forms part of the phase behaviour of many lipids according to their polymorphism. In a non-polar solvent, it is the exposure of the hydrophilic head groups to the surrounding solvent that is energetically unfavourable, giving rise to a water-in-oil system. In this case, the hydrophilic groups are sequestered in the micelle core and the hydrophobic groups extend away from the centre. These inverse micelles are proportionally less likely to form on increasing head group charge, since hydrophilic sequestration would create highly unfavourable electro-static interactions.

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