STRUCTURED BIOSURFACTANT SYSTEM

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Abstract: Bio-surfactants are a class of surface-active molecules derived from bio based origins such as plants and microorganisms as well. This diverse group of surface active molecules possesses both hydrophilic and hydrophobic moieties in their structure which allows their partitioning the liquid/liquid, gas/liquid or solid/liquid interfaces resulting into lower interfacial tension. This facilitates their emulsification, foaming, solubilization, detergent and dispersing functioning. This nontoxic, biodegradable and eco- friendly bio-molecules are competent to replace/blend with their chemically synthesized counterparts and divulge themselves as a green alternative to be applied in the application field of food, cosmetic, pharmaceutical, petrochemical and others. The chemical composition of bio-surfactants depends on the substrate and the microorganism present. They are also divided into two large sections based on their molecular weight namely low molecular weight and high molecular weight bio-surfactants. The high molecular weight bio-surfactants are also known as bio-emulsifiers. From the scientific investigations of recent times, it is observed that the bio-surfactants and bio-emulsifiers are widely used in the field of applied science.

INTRODUCTION

The story of surfactant probably began in 1929 when Kurt von Neergaard, a German-born Physiologist working in Switzerland filled a porcine lung with an isotonic gum solution to eliminate surface tension of the air tissue interfaces. After expanding the lung with air and liquid, he concluded that a lower surface tension would be useful for the respiratory mechanism. Richard Pattle in England, Charles Macklin in Canada and John Clements at the US Army Chemical Center in Maryland, USA were studying the effects of nerve gases on the lungs. Each in their own way contributed greatly to understanding the importance of surfactant. It is remarkable that three men working on chemical warfare projects in three countries in the 1950s came to similar conclusions independently.

The word "Surfactant" is a contraction of the three words 'Surface Active Agents'. Surfactants are chemical entities which facilitates in reducing surface tension or interfacial surface tension of a solution in contact with other phases, thereby increasing its wetting & spreading properties. Surfactants are organic compounds that are amphiphilic in nature, meaning that they contain both hydrophobic groups (their tails) & hydrophilic groups (their heads). Hence, surfactants contain both a water insoluble (Oil soluble) & water soluble components.

Bio-degradability of surfactants released to environment is an important factor in defining the levels of surfactants in the environment & hence assessing its potential for causing environmental damage. Based on precautionary principle, very major quantities are released to environment, regardless of whether the anticipated levels in the environment appear likely to cause harm, the substance should be biodegradable to safeguard against the possibility of future harm due to build up in the environment. The term "**HLB ratio**" comes across more often when dealing with surfactants which measure the degree/affinity of it towards water or oil. These values help in knowing the properties and functioning of surfactants.

A structured surfactant system is a system with a very high degree of clarity which comes as a rescue for these cases; the system comprises water and a mixture of at least one surfactant having a HLB (Hydrophilic Lipophilic Balance) value of less than 10, and at least one surfactant having an HLB value of 10 or greater. In structured system, geometry of lamellar phases have been encouraged(these are bilayer sheets of surfactants, with the polar heads on the outside and non-polar tails in the middle.Depending on the conditions, geometry can also be encouraged in the form of spherulites.These spherulites have concentric bilayers which is different from micelle of conventional cleansers.

CHEMICAL SURFACTANTS

- Chemical Surfactants are mainly petroleum based and are used in cleaning products, detergents and various cosmetics like shampoos, shower gels and bath products.
- The main disadvantages of using chemical based surfactants are that they contribute to the depletion of non-renewable resource and are highly polluting. They are slightly biodegradable and they can release toxic chemicals when they decompose.
- The extent of damage of surfactants to aquatic plants relates is related to its concentration. When the content of surfactants is high in the water, it will affect the growth of algae and other microorganisms in water, resulting in decreased primary productivity of water bodies, thereby undermining the food chain of aquatic organisms in water bodies. The main ingredients of modern life detergents are surfactants, long-term use cause skin irritation effect and lead to some degree of damage. If the surfactants enter into the human body, they damage the enzyme activity and thus disrupt the body's normal physiological function.
- From the chemical structure, the relationship between the chemical structure of surfactants and the toxicity of water to aquatic organisms can be summarized as the following three points:

  (1) The greater hydrophobicity (HLB value is smaller) of surfactants, the greater the aquatic toxicity;

  (2) The more ethoxylate group, the lower toxicity of aquatic organisms;

  (3) Compared with non-ionic surfactants, the toxicity of anionic surfactants decreases.

Drawbacks of Using Chemical Surfactants & Need of an Alternative

Most of the surfactants which are widely being used are totally dependent upon the sulphur which has various disadvantages and harmful effects on humans as well as environment. Most widely used surfactants such as SLS, SLES are anionic surfactants which contain major part of the sulphur compound. This leads to major drawback of using them.

Some of the disadvantages and harmful effects of convention/chemical surfactants are

- **The effects of surfactants on aquatic plants: The** damage degree of surfactants to aquatic plants relates to its concentration. When the content of surfactants is high in the water, it will affect the growth of algae and other microorganisms in water, resulting in decreased primary productivity of water bodies, thereby undermining the food chain of aquatic organisms in water bodies.
- **The effects of surfactants on aquatic animals**: A certain toxicity of surfactants will pass into the animal through animal feeding and skin penetration way. When the surfactant concentration in water is too high, surfactants can enter the gills, blood, kidney, pancreas, gallbladder and liver, and produce aquatic toxicity effect
- **The effects of surfactants on the human body**: The effects of surfactants on the human body are divided into effects on the skin and into the body. The main ingredients of modern life detergents are surfactants, long-term use cause skin irritation effect and lead to some degree of damage. After the surfactants enter into the human body, they damage the enzyme activity and thus disrupt the body's normal physiological function.

In the past 10 years, bio-surfactants have received pronounced attention owing to their excellent interfacial activities, low toxicity, high biodegradability, and stability under extreme conditions of temperature, pH and salinity. As a result of these properties, bio-surfactants could replace chemical surfactants in many industrial applications.

BIO-SURFACTANTS & STRUCTURED BIO-SURFACTANTS

- Bio-surfactants refer to culturing the microorganism under certain conditions as well as plant based, dissolving out surface active metabolites in its metabolism. Depending on the chemical structure, biological surfactants can be divided into single sugar esters, polysaccharides esters, proteins and phospholipids esters. Bio-surfactants are widely applied in the petrochemical industry, and are extensively used for emulsification, emulsion breaking, wetting, foaming and anti-static. They also have important applications in the textile, cosmetics, pharmaceutical, food and other fields.
- Surfactants are important auxiliary in the production process; they are usually used as wetting, emulsification, dispersion, penetration, levelness. They facilitate or improve the physical and chemical action of the tanning process, shorten the production cycle, save chemical materials, increase productivity and improve the quality of leather into purpose.
- A **structured surfactant system** is a system with a very high degree of clarity. The system comprises water and a mixture of at least one surfactant having a HLB (Hydrophilic Lipophilic Balance) value of less than 10, and at least one surfactant having an HLB value of 10 or greater. The structured surfactant system forms multilamellar vesicles and has suspending properties without added electrolytes, carbohydrates, or polymeric thickeners. This makes the structured surfactant system particularly useful in personal care compositions.
- The term 'structured system' as used herein means a pourable composition comprising water, surfactant, and optionally other dissolved matter, which together form a mesophase, or a dispersion of a mesophase in a continuous aqueous medium, and which has the ability to immobilize non-colloidal, water-insoluble particles, while the system is at rest, thereby forming a stable, pourable suspension. Surfactants and water interact to form phases that are neither liquids nor crystals; these are usually termed 'liquid crystal phases' or alternatively 'mesomorphic phases' or 'mesophases'.Gums and polymeric thickeners, which increase the viscosity of the liquid medium, retard, but do not prevent sedimentation, and at the same time make the composition harder to pour. They do not provide stable suspensions. Colloidal dispersions are prevented from sedimenting by Brownian motion. Such systems are usually incapable of dispersing relatively coarse particles. It has been found that transparent structured surfactant suspending systems can be formed by mixing a particular selection of surfactants in particular amounts in the substantial absence of electrolytes or carbohydrates.
- The transparent structured surfactant systems are particularly useful in personal care compositions to achieve a variety of aesthetically pleasing visual effects. The surfactant systems are mobile, have good suspending power and are phase stable.
- In another aspect, This technology provides an aqueous structured surfactant system comprising water and a mixture of surfactants, wherein the mixture of surfactants, comprises at least one surfactant having an HLB value of less than 10, alternatively less than 8 ; and at least one surfactant having an HLB value of 10 or greater, the mixture of surfactants having an overall HLB value in the range of about 11 to about 13 ; wherein the structured surfactant system is free of electrolytes and polymeric thickeners; and wherein the structured surfactant system is substantially transparent in the absence of any suspended matter and has suspending properties.
- Surfactants are amphiphilic molecules with hydrophilic and hydrophobic parts composing its chemical structure. When dispersed in water, these molecules can spontaneously form molecular organized aggregates, such as micelles, vesicles and liquid crystalline phases. The structured surfactant system forms multilamellar vesicles. Most commonly observed aggregates in this system is a lamellar phase. The basic idea of structure of bilayers is important for understanding of functioning of structured surfactant system.

LAMELLAR PHASE

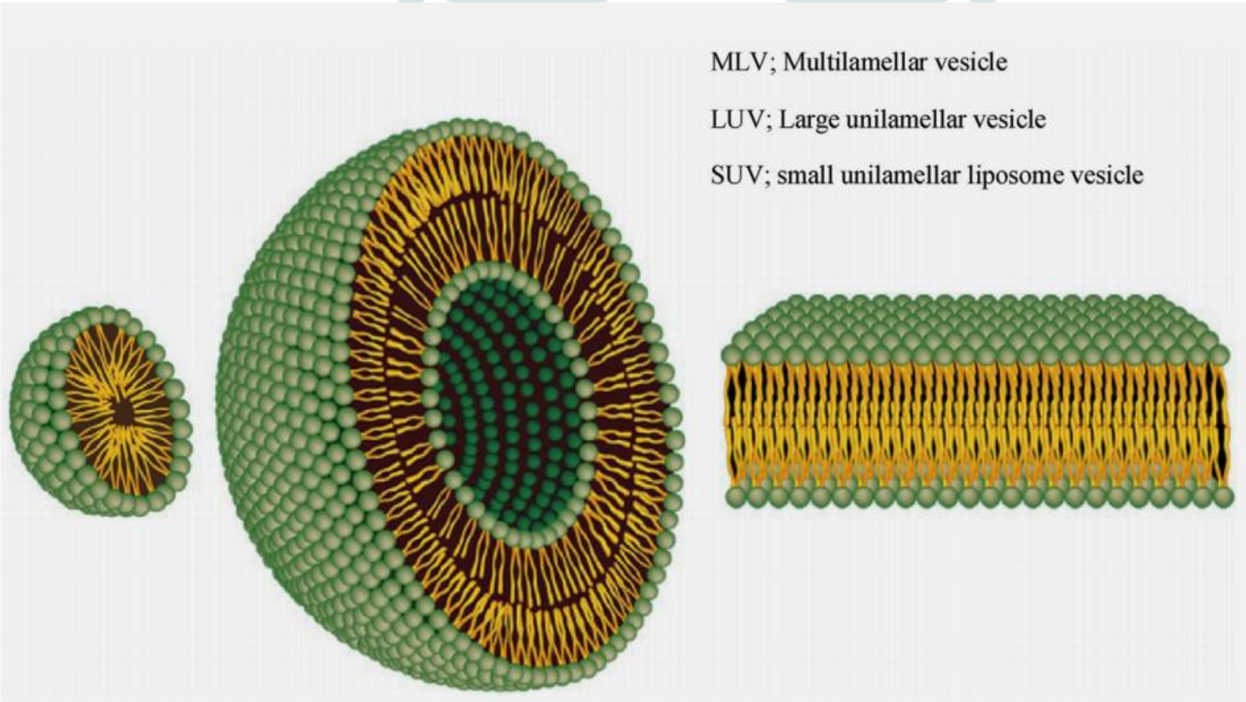
1. In detergency two commonly encountered aggregates are the lamellar and micellar arrays. The microstructure that is of importance of this work is the lamellar phase.

2. In general, lamellar phases are known to consist of a stack of ordered bilayers aggregate separated by aqueous layers. In an excess of aqueous phase, the lamellar phases may exist in a dispersed form.

3. During the formation of lamellar phases, structural changes can occur in the bilayers under certain conditions, so that the surfactant molecules forming bilayers eventually reorganize themselves to form other types of molecular aggregates with particular structures.

4. This dispersed form is normally spherical or oval structures, where one or several bilayers entrap water in its interior. These vesicles can be further classified in unilamellar vesicles (ULV) and multi lamellar vesicles (MLV). The term 'liposomes' is often used and referred to vesicle-like structures.

5. The most common surfactant mesophase is the lamellar phase (Lα), also known as the 'neat phase'. Within this phase, the surfactant molecules are arranged into stacks of ordered bilayers extending over large distances, which are separated by water layers.



Representation of the steric organization of a micelle (left), a liposome (center), and a lipid bilayer (right)

(Image Source: ResearchGate; Liposomes as nanomedical devices by Guiseppina Bozzuto)

ADVANTAGES OF BIO-SURFACTANTS

When compared to synthetic surfactants, bio-surfactants have several advantages including high biodegradability, low toxicity, low irritancy and compatibility with human skin. Therefore they are superior to the synthetic ones. The most significant advantage of a microbial surfactant over chemical surfactant is its ecological acceptance. Some more advantages of bio-surfactants over synthetic ones include selectivity, specific activity at extreme temperatures, pH, salinity etc. Some of the advantages of bio-surfactants are discussed below:

1. Biodegradability: Bio-surfactants are biodegradable in nature. Biodegradability is a very important issue concerning environmental pollution. Being able to be broken down by natural processes by bacteria, fungi or other simple organisms into more basic components, they do not create much problem to the environment and particularly suited for environmental applications such as bioremediation and dispersion of oil spills.

- **Cultivation of culture:** Approximately 20ml of sewage water and some amount of cow dung was added into 5L distilled water and it was saturated with oxygen using an aerator so that only aerotropic bacteria would flourish. Initially glucose was used as a feeding material and after some days the polymer was also introduced along with glucose.
- **COD analysis as per Indian standards**: In the reflux flask, 0.4 g of HgSO4, 20 ml of diluted sample were added and mixed well. Subsequently 10 ml of 0.25 N $K_2Cr_2O_7$ and 30 ml H_2SO_4-Ag_2SO_4 solution were added with constant stirring and the contents were refluxed for 2 hours. After refluxing the contents were cooled, the reflux condenser was washed with about 60ml of distilled water and the content was titrated against standard ferrous ammonium sulphate solution using ferroin indicator. The color change at the end point was green blue to wine red.
- **Dissolved oxygen analysis as per Indian standards**: The sample was collected in 125 ml bottle; 2 ml of manganese sulphate solution followed by 2 ml of alkaline iodide and sodium azide solution were added. The contents were mixed thoroughly by shaking the bottle several times by placed thumb over it. The precipitate was allowed to settle at the bottom. After settling 2 ml of concentrated sulphuric acid was added to dissolve the precipitate. Again it is mixed and shacked to dissolve liberated iodine. This solution was taken and titrated immediately against standard sodium thiosulphate solution by adding 3-4 drops of starch indicator solution. The end point was pale blue to colourless. The dissolved oxygen in mg/L is equal to the volume in ml of the standard thiosulphate solution used for titration.
- **BOD analysis as per Indian standards**: The required volume of distilled water was aerated in a container by bubbling compressed air for 8 to 12 hours to attained dissolved oxygen saturation level. It was allowed to stabilize for 4 hours at room temperature. At the time of use, 1 ml each of phosphate buffer, magnesium sulphate, calcium chloride and ferric chloride were added for each litre of dilution water. 5 ml of treated sewage per liter of dilution water was added for seeding purpose and the sample was incubated at 20 degrees. The value of COD of a polymer for a particular dilution remains same and taking the same amount of dilution for BOD we can conduct the BOD/COD biodegradability test. Taking the COD as a base value, the calculation for BOD/COD can be done.

2. Low toxicity: Bio-surfactants do not cause serious damage/harm of the biotic ecosystem since their toxicity level is low. Many chemical surfactants are toxic to the living beings making them less useful for being used in different industries. Very little data are available in the literature regarding the toxicity of microbial surfactants. They are generally considered as low or non-toxic products and therefore, appropriate for pharmaceutical, cosmetic and food uses.

3. Biocompatibility and digestibility: Bio-surfactants are biocompatible in nature means they are well tolerated by living organisms. These when interact with living organisms do not change bioactivity of the organisms. This property allows their application in cosmetics, pharmaceuticals and as functional food additives.

4. Availability of raw materials: Bio-surfactants can be produced from cheap raw materials like rapeseed oil, potato process effluents, oil refinery waste, cassava flour wastewater, curd whey and distillery waste, sunflower oil etc. which are available in large quantities. The carbon source may come from hydrocarbons, carbohydrates and/or lipids, which may be used separately or in combination with each other.

5. Use in environmental control: Bio-surfactants can be efficiently used in handling industrial emulsions, control of oil spills, biodegradation and detoxification of industrial effluents and in bioremediation of contaminated soil.

6. Specificity: Bio-surfactants, being complex organic molecules with specific functional groups, are often specific in their action. This would be of particular interest in detoxification of specific pollutants, de-emulsification of industrial emulsions, specific cosmetic, pharmaceutical and food applications.

CONCLUSION & SCOPES

Synthetic surfactants leading to contamination of the environment represents a serious threat to the health of humans and ecosystems. Given the human health effects of synthetic surfactants, effective and cost-competitive remediation technologies are required. Bioremediation has shown promise as a potentially effective and low-cost treatment option, but concerns about the slow process rate and bioavailability limitations have hampered more widespread use of this technology.

The success of the commercialization of a biotechnological product mainly depends on the economics of process. The prices of microbial surfactants are not currently competitive with those of synthetic surfactants because of costlier production and low yield. It is therefore important to optimize the biological production and engineering of the process to obtain economically viable products. The use of low-cost substrates, the establishment of microbial growth under ideal production conditions, the development of novel purification methods and the use of hyper producing microbial strains can make biosurfactant production economically feasible. While a large number of biosurfactant-producing microorganisms are reported in the literature, studies on the increase in production have generally been concentrated on few of them. Biosurfactant are viable candidates for the replacement of synthetic surfactants, especially in the oil industry. Investments in strategies for improving the processing of these natural compounds will pave the path to large-scale biosurfactant production.

Concerning future scopes, one of the objective is related to large scale and cheap production of bio-surfactants. Large quantities are particularly needed in petroleum and environmental applications, which, due to the bulk use, may be expensive. For this, processes should be coupled to utilization of waste substrates combating at the same time their polluting effect which will balance the overall costs.Another objective may be encountered in obtaining pure substances which is of particular importance in pharmaceutical, food and cosmetic applications. Downstream processing is involved with multiple consecutive steps. Therefore, high yields and bio-surfactant concentrations in bioreactors are essential for their facilitated recovery and purification.

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