Role of Surfactants in Drug Delivery, Pesticides, Antimicrobial Activity and Bioremediation

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Editor

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Preface

This book offers a comprehensive exploration of the application of surfactants and advances research work in industrials and society. It begins with a detailed overview of application of surfactants disucc in Chapters 1-11.

Chapter 1 we discuss the general introduction of Surface-Active Agent, CMC, and it can lower interfacial and surface tension at these intersections to allow solids, gases, and liquids to mix or disperse easily, like dispersions in water or other solutions.

Chapter 2 discuss the classification of surfactants in four main groups: cationic, nonionic, zwitterionic, and anionic surfactants. Every variety has unique physicochemical characteristics and uses. This study provides a thorough grasp of the importance of these surfactants in a range of sectors by examining their structural traits, functioning, and varied uses.

In chapter 3 we discuss the different properties, interfacial parameters, and thermodynamic parameters of different surfactant systems.

This chapter 4 we highlight the vital function that surfactants play in the delivery of drugs, emphasizing their special physicochemical characteristics that help with important pharmaceutical issues such as low drug solubility, stability, and bioavailability. As amphiphilic molecules, surfactants make it possible to create a variety of delivery systems that encapsulate hydrophobic medications and improve their therapeutic potential.

In this chapter 5 explain the Application of Surfactant in Personal Care Products Formulation, As a responsive ecosystem that interacts with the environment to promote general health, the human skin is essential to the immune system. Because of its capacity to lower surface tension, emulsify oils, wash, and produce foam, surfactants are frequently employed in cosmetic compositions. They are essential components of many different kinds of products, including face cleansers, body washes, shampoos, and lotions. Cosmetics and customised care items that contain surfactants can help protect and nourish the skin.

Chapter 6 study the Host-guest chemistry involving macrocyclic hosts is one of the most promising research areas in chemistry, materials science, and biochemistry. This chapter briefly describes the physicochemical properties, preparation method, and mechanism of host-guest complexes. In addition, we also highlight the characterization methods of synthesized host-guest complexes and their various applications, especially in amphiphilic molecules like surfactants, ionic liquids, and surface active ionic liquids.

Chapter 7 discuss the Amphiphilic compounds known as surfactants reduce surface tension and create micelles in solutions. Micellar systems are essential in many industries, such as food, detergents, cosmetics, medicines, and environmental applications. The categorisation, creation, and uses of micellar systems are examined in this work, with an emphasis on how they contribute to improved chemical reactions, emulsification, and solubilisation. Future directions in surfactant research are also covered, as well as difficulties including toxicity and environmental issues. The surfactant is a crucial component of emulsifying agent, foaming agent, cleaning agent, wetting agent, dispersing agent, and anti-foaming agents and is used in a wide range of goods. Surfactant molecules have a drive to assemble above the critical micelle concentration (CMC) to create micelle-like structures.

Chapter 8 discuss the surfactants are crucial to modern farming practices because they increase the efficacy and sustainability of pesticide treatments. Additionally, biosurfactants have antibacterial properties that make them promising as biopesticides against pests, fungi, and diseases while enhancing plant resistance. Research highlights their contribution to sustainable agriculture, including enhancing trace element bioavailability and maintaining soil moisture levels for optimal crop growth. To improve soil texture, improve nutrient uptake, and reduce environmental toxicity, these substances are increasingly being used in soil amendments, pesticide formulations, and herbicides

This chapter 9 we study the solubilization of hydrophobic active ingredients allows for the creation of more effective formulations, especially for pesticides with low water solubility. Surfactants improve the absorption of active ingredients into plant tissues by disrupting cuticular barriers, thereby enhancing systemic action. Recent advancements in surfactant technology include the development of biodegradable biosurfactants and polymeric surfactants, which aim to mitigate environmental persistence and toxicity issues, thereby providing sustainable alternatives to traditional surfactants. Responsive surfactants, engineered to activate under defined environmental conditions, offer targeted control in agricultural applications. The incorporation of surfactants in pesticide formulations leads to less amount requirement which contributes to decreased environmental contamination and expanded pest control effectiveness

This chapter 10 we explores the mechanisms by which various classes of surfactants, including cationic, anionic, nonionic, and zwitterionic types, exhibit antimicrobial effects against bacteria, fungi, and viruses. Cationic surfactants, such as quaternary ammonium compounds, have demonstrated potent bactericidal activity, primarily by targeting the negatively charged microbial membranes. Nonionic and zwitterionic surfactants, on the other hand, show promising synergistic effects when combined with antibiotics, enhancing their efficacy.

This chapter 11 we explore the solubility and mobility of hydrophobic pollutants, surfactants aid in their removal from the soil. The success of surfactant-based remediation methods, however, depends on several factors, such as the nature of the contaminant, soil characteristics, and the concentration and type of surfactant used. While surfactant-enhanced soil remediation offers a promising and sustainable solution for addressing soil contamination, the ideal conditions for their use vary depending on specific site conditions and the pollutants involved. Additional research is needed to refine and optimize surfactant use in soil remediation. This chapter focuses on various types of soil pollutants worldwide and explores how surfactants can be used to remove them.

In chapter 12 we discuss the application of Surfactant in Bioremediation Various pollutants such as heavy metals, total petroleum hydrocarbons (TPHs), polynuclear aromatic hydrocarbons (PAHs), nonaqueous phase liquids (NAPL) and hydrophobic organic compounds (HOCs) toxicity has emerged as a major ecological issue that poses a major risk to public health and impacts ecosystems through bioaccumulation. Thus, areas contaminated by these pollutants have been decontaminated and restored using a variety of traditional techniques. However, because to their high energy requirements, post-waste disposal issues, secondary pollutant formation and high operating costs, these traditional methods are not environmentally safe for pollutants treatment.

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Chapter 1 : Introduction of Surfactants

Rashmita Khuntia, Manoj Kumar Banjare, and Prashant Mundeja

Abstracts: Surface-active material can lower interfacial and surface tension at these intersections to allow solids, gases, and liquids to mix or disperse easily, like dispersions in water or other solutions. Many emulsifiers derived from petroleum presently dispense a high demand for surfactants. The structural components of surfactant molecules are two halves. While the second component is hydrophilic and disperses in oil but is insoluble in hydrous media, the first part dissolves in an aqueous medium and is hydrophilic. Despite having different structural paths, these two groups are linked to the same molecule at their ends. They create a polar and asymmetrical framework. "Parent structure" (amphiphilic structure) is often used to increase the structure.

Keywords: Surface-Active Agent, Amphiphilic, CMC, Surface Tension.

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1.1 Introduction

Surfactants are a family of commonly used chemical molecules that usually have hydrophilic and hydrophobic molecular parts. They are often referred to as tensioactive substances or tensides. Surfactant substances are amphiphilic. This makes surfaces like the metal/metal oxide water contact more appealing for adsorption. The level of adsorption is determined by surfactant characteristics, as well as their interaction with metal oxide or metal and the environment of the surrounding solution [Zhu et al. 2015]. Understanding surfactant behavior is critical for optimal surfactant use in surfactant applications in fields such as particle removal, pharmaceuticals, and cosmetics; adsorption on a metal or metal oxide surface; and aggregation and partitioning in aqueous and/or organic phases. Surfactants are generally divided into 4 classes based on the nature of their head groups: cationic (C), anionic (A), zwitterionic (Z), and nonionic (N) shown in Table 1.1.

As their names imply, cationic and anionic surfactants are charged, and in order to preserve charge neutrality, a counterion of the opposite charge is attached to the head group. For cationic surfactants, this is usually a halogen ion, and for anionic surfactants, it is usually a metal cation.[Shah et al. 1997][Free et al.2004] Zwitterionic surfactants have two distinct and opposing charges (positive and negative) on the molecule at nearby or nonadjacent places, while nonionic surfactants have no charge connected to their head group. The term "amphoteric," which describes a subclass of Zwitterionic surfactants with a pH-dependent charge, is also often used.

1.2 Hydrophobicity and Hydrophilicity of Surfactant

Surfactant compounds' lipophilic functional group tends to interact with polar substances, including metals, water, and ions. Surfactants usually adhere to metal surfaces, blocking dynamic locations, including those near corrosive liquids, and therefore reducing assault by corrosion. It is thought that the heterocyclic surfactant molecules' structure has a significant impact on surfactant sorption. The adsorption process is significantly impacted by the presence and configuration of certain atoms, such as O and N, in these molecules. The nonpolar hydrophobic component enjoys interacting with hydrophobic materials, such as the hydrocarbon phase [Zhu et al. 2015] [Ryu et al. 2004] [Zhu et al. 2015].

As a result, liquid-air surfaces and solid-liquid interfaces are among the surfaces and interfaces that surfactant molecules are likely to adsorb and cover in order to avoid polar solvents like water by the packing and association of hydrocarbon chains [Free et al. 2004][Hegazy et al. 2012][Free et al. 2004]. The surfactant concentration at which a monolayer of surfactant molecules adsorbs on and covers a metal surface is referred to as the concentration of surface aggregation.

Surfaces are more likely to generate bilayers/multilayers when the surfactant concentration rises. During solubility saturation, surfactant molecules may also group together in the aqueous phase, orienting their hydrophilic head groups toward water or hydrophilic surfaces and their hydrophobic tails toward adjacent surfactant molecules [Victorov et al. 2014].The critical micelle concentration (CMC) is the concentration of surfactant at which molecules start to collect in solution, micelles, for example [Valkovska et al. 2004]. It has been demonstrated that the sac is typically significantly less than the CMC and the fact that great surface coverage sufficiency can be reached at the sac if the surfactant works well as an adsorbent.

Suitable for oil and water	**Application**	**HLB**
HLB soluble in water >10	Detergents	13-15
	Solubilizing agents	15-18
	Emulsifying agents for oil and water	8-16
Oil- soluble HLB<10	Wetting and spreading agents	7-9
	Agents that wet and spread	1-3
	Agents that prevent foaming	3-6

Table 1.1: The scale known as Hydrophilic Lipophilic Balance (HLB), which classifies the applications of surfactants.

The size and strength of a substance are measured by its hydrophilic lipophilic balance (HLB) of a surfactant molecule's hydrophilic and hydrophobic moieties. [Van Hove et al. 2010][Wanless et al. 2003] The HLB concept, developed through Griffin [1949], is the most well-known semi-empirical technique for selecting an appropriate surfactant for a certain application. A surfactant's HLB number is assigned using a semi-empirical process based on its chemical structure. Surfactants are classified for diverse uses based on the HLB value, which varies from 0 to 20 (Table 1.2). The surfaces of metals and metal oxides are hydrophilic. [Goodwin et al. 2009][Victorov et al. 2014]

As a result, surfactant compounds' functional groups bind to metal and metal oxide surfaces. The hydrophobic component is drawn to other hydrophobic molecules and regions of nearby molecules of surfactants on surfaces, which strengthens its adhesion to surfaces. As a result, surfactant adsorption on metal and metal oxide surfaces is driven, orienting A hydrophobic surface is produced by the surfactant's hydrophilic group close to the solid surface and its hydrophobic hydrocarbon chain pointing out into the solution. Surfactant molecules gather on surfaces as a result of this pushing force. [Heydar et al. 2012] [Shah et al. 1998].

A second or many layers of surfactant may adsorb if there is sufficient surfactant in the solution, producing a range of adsorbed structures. At modest concentrations over the CMC, aggregation structures like micelles form, and surfactants function similarly in solution [Shah et al. 1998] [Rajagopalan et al. 1997] [Lukanov et al. 2014].

Surface coverage or surfactant adsorption when surfactant concentrations are low (generally less than micelle formation concentration frequently defined by the quantity of substrate active surface sites that are coated by surfactant adsorption). [Graciaa et al. 2000] [Gallotti et al. 2008] [Warszynski et al. 2010].

Surfactants cover a more active surface area with increasing concentration, forming monolayers and multilayers/micelles near the sac and CMC. They create micelles in the aqueous phase at solubility saturation, aqueous CMC in the aqueous phase, and reversed micelles in the oil phase [Bonacucina et al. 2020].

1.3 Adsorption Mechanism

The surfactant adsorption is often calculated using the adsorption free energy ΔGo ad, which is linked to the adsorption constant by the equation.

Kad = 1 Cmwexp (-ΔGo ad/RT) ……………………………..(1.1)

Several adsorption isotherms, which will be discussed in Section 12.2, are frequently used to calculate the equilibrium adsorption constant, Kad: The molar concentration of water, or Cmw, is 55.5 M, the absolute temperature is T, and the gas constant is R.

A negative ΔGo_{ad} value often indicates that steel is one example of a metal surface where surfactant adsorption happens spontaneously and shows a strong interaction between surfactant molecules and hydrophilic surfaces with appropriate bonding sites. [Marangoni et al. 2006][Ettarhouni et al. 2020]. The interaction between a surfactant and a surface is frequently categorized as physical adsorption because of electrostatic interaction if ΔGo ad is more positive than 220 kJ/mol. Adsorption, also known as chemisorption, typically entails Coordination bonds are formed via charge sharing or transfer between the surfactant molecules and the surface. whenΔGo ad is more negative than 240 kJ/mol [Uslu et al. 2023]. However, due to several factors that affect adsorption, chemisorption can occasionally have very weak binding energy, while physical adsorption can occasionally be energetically advantageous and important [Langley et al. 1975][Patel et al. 2016].

Chemical absorption, including a chemical exchange between the adsorbate and the surface to establish a particular bond, is often confined to a monolayer. In contrast, physical absorption has no explicit bonding requirement and, in some cases, might demand many layers. Chemisorption's strong bonding energy frequently necessitates excessive temperatures or the desorption of chemisorbed molecules by exposure to concentrated competitive ions. At moderate temperatures or by reducing their vapor pressures or concentrations, physisorbed molecules can be readily desorbed. Surface tension, wettability, and other phenomena are associated with surfactant adsorption, and their effects have been extensively researched [Shah et al. 1997].

1.4 Surface Tension

When molecules have cohesive energy, surface tension forms. In watery media, water molecules interact with one another through hydrogen bonds and van der Waals forces. However, H-bonding is incomplete above the water-air contact. Similarly, the lack of interacting molecules in the air phase reduces van der Waals interactions at the interface. Molecules near the air-water interface have more available energy and fewer bonding opportunities than those in the bulk phase. The cause of surface tension is this excess energy. The hydrophobic portion of surfactant molecules in aqueous environments has a tendency to go to accessible interfaces in order to stay away from the undesirable polar solvent. When surfactant molecules are adsorbed at the air-water contact, surface tension is decreased.

Surfactant molecules are therefore more active close to the air-water interface. The word "surface active agent," which lowers surface tension, is also the root of the name "surfactant." Surface tension is predicted to rise with compounds that have a larger cohesive energy at the air-water interface than between water molecules. For detailed cleaning, use these eight surfactants. The mathematical connection between surface tension and adsorption density is explained by the Gibbs adsorption equation [Bonacucina et al. 2020].

$\Lambda i = -(\frac{1}{RT}.\frac{dY}{dlnai})_{TP}$………………………………..[1.2]

whereΛi is the surfactant's surface excess or adsorption density. Y is surface tension in force per unit length (mN/m), i is the number of molecules per unit area (mol/m²), and ai is the activity of a surfactant.

The adsorption density increases when the surface tension vs. concentration logarithm slope steepens, according to the Gibbs adsorption equation. Volumetric concentration units are produced by multiplying the adsorption density by the surfactant layer's effective thickness; it shows that the surfactant (solute) concentration is higher at the surface than in the bulk.

Surfactant is more evenly distributed and diluted in bulk solution than it is at the interface, where it packs tighter and aggregates. The concentration of surfactant at the adsorption site is hence the adsorption density.

As the surfactant concentration rises, the solution's surface tension progressively falls until it achieves a low plateau value. More surfactant molecules gather in solution and at solid-liquid interfaces as the contact density rises. To create aggregate structures such as micelles, more surfactant is added than is necessary for the minimal surface tension. The CMC reflects the surfactant concentration necessary to form micelles. The highest concentration of surfactant monomers that may dissolve in the solution is indicated by the CMC. When the surface tension hits its lowest plateau level, the CMC is computed. The Gibbs equation is invalid due to the aggregation phenomenon above the CMC. Every surfactant in solution that is higher than the CMC forms micelles and functions as a distinct phase. At ambient temperature, water's tension at the air/water interface is 72 mN/m [Haider et al. 2019]. Surface tension may often be reduced to roughly 35 mN/m using well-chosen hydrocarbon surfactants. Surfactants with fluorocarbon chain groups can lower surface tension to 25 mN/m [Hafiz et al. 2008]. By decreasing the repulsion between the ionic head groups of surfactant molecules, salt can further lower surface tension and promote molecular packing [Goodwin et al. 2009].

1.5. Improvement in Wettability

Young's equation states that the balance of three interfacial tension values is physically expressed by the contact angle of a liquid droplet on a solid surface [Javidi et al. 2012].

$\cos\Theta = \frac{YSV - YSW}{YWV}$…………………………………………………….[1.3]

According to Young's equation, the physical expression of the equilibrium of three interfacial tension values is the contact angle of a liquid droplet on a solid surface [Javidi et al. 2012] [Perinelli et al. 2020]. According to Young's equation, introducing surfactant lowers interfacial tension at the solid-water contact.

The angle of contact. A decrease in the contact angle indicates enhanced wettability. The spreading coefficient [Khilar et al. 2005] mathematically describes a liquid's capacity to spread or wet a surface.

$\Delta Y = Y_{SV} - (Y_{SW}\text{-}Y_{WV})$………………………………………………………… [1.4]

Wettability is mostly determined by the hydrophilicity of the surface. Highly hydrophilic surfaces have extremely low contact angles. According to Young's equation, the contact angle varies with surface tension. Surface tension is a thermodynamic characteristic. As a result, wettability is a thermodynamic consequence of the interactions between the related phases. Wettability can be regulated by adjusting surface tension values using surfactants, as well as by selecting liquids and solids.

Whereas hydrophobic surfaces oppose water, hydrophilic surfaces reject organic phases like oils. Because of this, even in the presence of oil phases, water will adhere to hydrophilic surfaces like steel, precipitated salts, and corrosion product layers. Nevertheless, the surfactant may alter a surface's wettability when it adsorbs on it. Surfactants can occasionally change a surface's characteristics from hydrophilic to hydrophobic or from hydrophobic to hydrophilic. Wettability can be influenced by surface roughness. Previous studies have shown that roughness affects wettability, as stated by the following relation [Mehreteab et al. 1988]:

$\mathrm{Cos}\Theta = f.\frac{YSY-YSL}{YL} = f.\ \mathrm{Cos}\Theta$……………………………………………[1.5]

Where Θ_0 is the contact angle of a rough solid surface; YS stands for solid surface tension; YL for liquid surface tension; and YSL for solid-liquid interfacial tension. For rough surfaces, f is a roughness factor greater than unity. The contact angle has been shown to be influenced by thin films, deformation, surface heterogeneity (contamination caused by the presence of attached small particles), and other processes [Hafiz et al. 2008]. Surfaces that are ordinarily hydrophobic can become "superhydrophobic" or very hydrophobic by adding microscale roughness [Khalid et al. 2019].

1.6 Langmuir-Blodgett Films

A Langmuir-Blodgett (LB) balance is often used to measure and modify surface pressure, often referred to as molecular surface area and surface tension for monolayer films at the air-liquid interface [Hafiz et al. 2008]. Interesting characteristics of adsorbed surfactant molecules can be uncovered using the LB approach. [Graciaa et al. 2000] is the definition of the surface pressure of LB films, or PLB:

$P_{LB} = Yo - Y$ ……………………………..……………….……... [1.6]

Surface tension without an adsorbed layer is represented by Yo, and surface tension with an adsorbed layer is represented by Y. Because surface compression with a moving barrier alters the adsorbed film's surface area, surface pressure may be measured using the LB balance. As a result, the LB technique can be employed with a variable compression barrier to change the area occupied by each surfactant molecule.

Surfactant molecules are widely dispersed and seldom align vertically at the interface when the surface pressure in an LB film device is low and the surface area per molecule is large. Because it resembles dispersed gas molecules, this well-distributed molecular state is frequently associated with the gas phase. For a two-dimensional surface, the ideal gas equation analog is obtained by multiplying surface pressure by surface area [Gallotti et al. 2008][Hafiz et al. 2008]:

$P_{LB}A_{LB} = n_{LB}.RT$ ……………………. [1.7]

wherenLB is the number of moles of adsorbed surfactants on the LB film and ALB is the surface area of the film. Surface pressure increases when surfactant molecules are packed closer together as the LB surface area decreases. This often produces a molecular state that resembles a liquid. Surface pressure reaches its maximum as the surface area continues to decrease, forcing tight molecular packing. The molecules can form two-dimensional, crystal-like structures that resemble solid phases due to their tight packing. By transferring them to substrates that are gradually pushed over the air-water interface, oriented multilayer films may be produced using the LB film balance.

Therefore, surfactant films with varying packing densities may be transferred as monolayers or multilayers to any solid substrate using the LB film balance. Consequently, these films may be used to evaluate properties such as hydrophobicity and diffusion barrier performance concerning molecular packing and/or the quantity of multilayers on a substrate.

1.7 Krafft Point

Once the Krafft point is reached, surfactant molecules do not dissolve properly in aqueous solutions. [Shehata et al. 2008]. Surfactants can form micelles at temperatures above the Krafft point. 12 Surfactants in Precision Cleaning, which dramatically increases overall surfactant solubility. Figure 1.3: shows a representation of the interaction between the Krafft point, monomer, and micelle surfactants. Thus, the Krafft point serves as a critical boundary condition for surfactant usage.

1.8 Surfactant States

Surfactants can exist in a variety of states or phases. A surfactant's phase or condition is frequently correlated with its concentration. Monomeric surfactants aggregate into micelles when their concentrations are above the CMC. In the parts that follow, the characteristics of micelles, the micellization procedure, and related models will be covered in more detail. The quantitative relationships between micelle concentration, monomer concentration, total surfactant concentration, and the related CMC are displayed in Figure 1.4. Micelles and other surfactants can gel at gel temperatures

[Bonacucina et al. 2020][Erkmen et al 2023]. Liquid crystals can also be produced by surfactants. The change from the liquid crystal phase to the solid state is known as the gel state. Gel-based surfactants have the ability to spin and change orientation.
Surfactants dissolved in solution, on the other hand, can be completely free unless they are part of aggregate structures.

Certain surfactants lose their solubility at high temperatures. This decrease results from conformational changes in the surfactant structure and increased energy, which decrease hydrogen bonding and bonding with water. As a result, some surfactant solvents become hazy at high temperatures because of decreased solubility above the "cloud point" caused by secondary phase development. Nonionic surfactants are commonly used to produce the cloud point effect.

1. 9 Micelles

Surfactant aggregation numbers are influenced by temperature, hydrophobic chain diameters, head group properties, and ionic strength. The aggregation number may change if the solution's ionic strength changes. While the repulsion of the hydrophobic tail from the aqueous medium increases with increasing ionic strength, the repulsion between ionic head groups decreases, hence increasing the likelihood of aggregate. Outside the hydrophobic micelle core, the size of surfactant molecules is determined by their head groups. Small head groupings enhance aggregation. Temperature also affects aggregation [Langley et al. 1975]. Raising the temperature can cause surfactants to remove their hydrophilic groups, resulting in increased hydrophobicity. However, higher temperatures reduce the propensity to adsorb at surfaces.

Micelles and individual surfactant molecules are constantly interacting and exchanging information. Within microseconds, individual monomer surfactant molecules enter and exit micelles [Shah et al. 1998][Graciaa et al 2000]. In contrast, micelles form and dissolve in milliseconds. However, these time frames alter dramatically when the surfactant concentration, size, and properties change.

Micelle aggregates take many morphologies, including vesicles, hemimicelles, rod-like or cylindrical micelles, spherical micelles, and plate-like micelles[Goodwin et al 2009][Patel et al. 2016]. The packing of the surfactant's hydrocarbon chain determines the form of the micelle. Israelachvili demonstrated that a packing parameter influences the probability of creating spherical or non-spherical micelles [Khilar et al. 2005].

The packing parameter Ps can be represented as follows:

$$P_S = \frac{Vs}{aols} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots [1.8]$$

wherels is the critical chain length, ao is the surfactant head group's optimal surface area, and vs is the volume of a hydrocarbon chain.

Micelles are commonly thought to have a distinct liquid phase. From the perspective of thermodynamics, micelles function as a separate phase. In a similar manner, some substances dissolve in liquid micelles [Khilar et al 2005]. In aqueous solutions, hydrophobic materials dissolve in the hydrophobic interior of micelles. Aqueous or polar compounds dissolve in the micelle interior of organic media with inverted micelles and polar interiors.

1.10 Microemulsions

Fluids that include micelles are similar to microemulsions. They are functionally expanded micelles that contain a liquid droplet that ranges in size from 5 to 100 nm. They can exist in a water-continuous phase with oil droplets within, or in an oil-continuous phase with nanosized water droplets inside a surfactant shell. Alcohol, water, oil, and an ionic surfactant combine to form microemulsions, which have several uses. Water, oil, and a single surfactant, such as sodium bis-(2-ethylhexyl)-sulfosuccinate (AOT), can also be used to create microemulsions. Microemulsions are emulsions with high thermodynamic stability [Hegazy et al. 2008].

1. 11 Surfactant Mixtures

Surfactant combinations have received great attention in practical applications due to their dominating physicochemical behavior and ability to adsorb, solubilize, disperse, suspend, and transport efficiently [Migahed et al. 2012][Victorov et al. 2014][McLachlan et al. 2006]. Solutions containing mixed surfactants may frequently be easily modified to attain desired qualities by altering the combination composition. To save money, greater surface-active and costly surfactants are typically blended with low surface-active and low-cost surfactants [Migahed et al. 2012]. Mixed surfactants are thought to have a synergistic impact on metal adsorption and surface coverage [Valkovska et al . 2004][Manohar et al. 2005], resulting in better performance than pure surfactants. Synergistic adsorption is an efficient approach for increasing adsorption efficiency, reducing dose, and broadening surfactant applications [Patel et al. 2016].

Add halide ions to the aqueous medium. Depending on the concentration, Cl, F, Br, and I ions may enhance/prevent surfactant sorption. It has been observed that the restrictive actions of halides occur in the following order: I_2, Br_2, Cl_2. The substantial synergistic action of iodide ions can be discussed by chemical absorption with particular surfaces, likewise steel, which is bigger and more polarizable. [Patel et al. 2016]

It has also been shown that properly mixed surfactant solutions improve a number of desired interfacial properties. Shiao and colleagues looked at how melting points, evaporation retardation, micellar stability, foaming, lubrication, enhanced oil recovery, corrosion, and microemulsion formation were affected by matching the chain lengths of mixed surfactants. According to this study, molecular packing is enhanced when an ionic and a nonionic surfactant are mixed in a one-to-one ratio. Chain length compatibility affected optimal properties such as surface viscosity, evaporation retardation, melting temperature, corrosion resistance, enhanced oil recovery, and foam formation. The rise in features is explained by the fact that surfactant molecules in the adsorbed layers can form more stable bonds when their chain lengths match [Haider et al. 2019].

1.12 Surface/Interface Adsorption

1.12.1 Adsorption Basics

With four adsorption areas (I, II, III, and IV), surfactant adsorption is essential for surface coverage. Because of electrostatic attraction, adsorption trends in Region I are linear, and the adsorption density is determined by the Gouy-Chapman equation.

$$\Lambda_{-} = -\frac{\sigma_{-}}{ZF} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots [1.9]$$

Z is the valence charge of an ion, F is the Faraday constant, and σ_ is the surface charge density of a solid surface or substrate.Higher surfactant concentrations cause adsorption to rise, which results in Region II, where aggregate structure development takes place. Lateral adsorption is made possible in Region III by the neutralized surfactant surface, which renders electrostatic attraction ineffective. Due to the development of solution micelles, Region IV is saturated, and the concentration of residual solution is rising. Local bilayer regions create micelles during adsorption, which mostly happens through hydrophobic contact.

On solid surfaces, nonionic surfactants with polar head groups create weaker hydrogen bonds with hydroxyl groups, which causes the Region III adsorption isotherm to rise sharply. Ionic and nonionic surfactants show comparable characteristics. Surfactant adsorption, which prevents surface-active sites from being exposed to corrosive environments, determines the surface coverage of metals and metal oxides. Electrostatic interactions and van der Waals forces are responsible for this process. Inhibiting the flow of water, carbonate, halide, hydrogen, and oxygen species, surfactants chemically alter surfaces by partly donating electrons and creating a hydrophobic barrier.

1.12.2 Adsorption Isotherms

Adsorption models like Langmuir, Flory-Huggins, Temkin, Frumkin, Dhar-Flory-Huggins, Freundlich, Bockris-Devanathan-Muller, Bockris-Swinkels, van der Waals-Stern, and Stern are commonly used.[Erkmen et al. 2023][Manohar et al. 2005][Hegazy et al. 2008],

The Langmuir adsorption isotherm, based on the assumption that all surface adsorption sites are equivalent, provides a method for expressing the adsorbed adsorbate concentration.[Hegazy et al. 2008]

$$K_{ad}C^{W}_{m} = \frac{\theta}{1-\theta} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots [1.10]$$

The Langmuir model, which considers surface coverage, adsorption equilibrium constant, and monomeric surfactant concentration, can be applied to data by plotting θ versus CWm and evaluating linearity. However, it neglects molecular interactions, multilayer coverage, and heterogeneous surface sites, making it generally the best and widely utilized.

The following is the formula for a multicomponent system represented as a proportion of sites occupied (θi) [Langley et al. 1975].

$$\theta i = K_{adi} C^{w}_{mi} /1+\sum_{i} \text{Kadi Cwmi} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..[1.11]$$

The surface coverage of surfactant I is represented by the equation θi, its equilibrium constant is Kadi, and its monomeric concentration in aqueous solution is Cw mi. An empirical model that takes non-uniform site distribution into account is the Temkin adsorption isotherm and adsorbate concentration. It expresses the concentration as

$$K_{ad}\, C^{w}_{m} = \exp\,(\xi\theta)\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..[1.12]$$

Considering molecular interaction constants and assuming a linear decrease in adsorption heat. A model that determines surface coverage based on fluctuating adsorption site free energy values is the Freundlich adsorption isotherm.

$$K_{ad}\, Cw_{m}\ 1/\varsigma = \theta\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..[1.13]$$

The Langmuir equation measures surface heterogeneity or adsorption intensity, with values below unity indicating chemisorption and above one indicating cooperative adsorption, indicating more heterogeneous surfaces as concentrations approach 0.

The following formula can be used to express the Frumkin isotherm:

$$K_{ad}\, C^{w}_{m}= \frac{\theta}{1-\theta}[\exp\,(-\xi\theta)\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots[1.14]$$

Like the Temkin isotherm, the Frumkin isotherm takes into account lateral interactions between adsorbed surfactant molecules. Its application is assessed by plotting ln(θ/(CWM(1-θ))) vs. θ and assessing the data's linearity. One technique for expressing the practical and spontaneous character of an adsorption process is the Flory-Huggins isotherm.

$$K_{ad}\, C^{w}_{m}= \frac{\theta}{\varsigma(1-\theta)\varsigma}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots[1.15]$$

A plot of ln(θ/Cwm) against ln(1-θ) yields the linear form of the Flory-Huggins model. With one exponential element, the Dhar-Flory-Huggins isotherm is a model that is similar to the Flory-Huggins model.

$$K_{ad}\, C^{w}_{m}= \frac{\theta}{(1-\theta)\varsigma\ \exp(\varsigma-1)}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots[1.16]$$

To confirm the linear shape of the Dhar Flory Huggins model, plot ln θ/Cwm against ln (1-θ). The "FloryHuggins isotherm" is incorrect due to different configurational terms.

The Bockris-Swinkels isotherm evaluates organic compound adsorption on metal electrodes.

$$K_{ad}\, C^{w}_{m}= \frac{\theta\ \ (\theta+\varsigma(1-\theta\,)(\varsigma-1)}{(1-\theta)\varsigma\ \exp(\varsigma-1)\varsigma\varsigma}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots[1.17]$$

Other less often used isotherms are van der Waals-Stern, Stern Adsorption, and Hillde Boer; the Bockris-Swinkels isotherm reduces to the Langmuir isotherm when ς = 1. With the exception of the Langmuir isotherm, adsorption isotherms are based on experimental evidence and have some theoretical support.

1.12.3 Adsorption Thermodynamics

The standard free energy of surfactant adsorption for the equilibrium of the adsorption solution is given by equation [1.18].

$$\Delta Goad = -RTlnaSad / aSaq = -RTlnCSad / C_{Saq} \quad\text{[1.18]}$$

The equation can be rearranged to include the activity coefficient for both adsorbed and non-adsorbed forms, assuming they are equivalent.

$$C_{Saq}exp(-\Delta Go\ ad/ RT) = C_{Sad} \quad\text{[1.19]}$$

The adsorbed surfactant concentration is determined by dividing the surface excess concentration per unit area by the thickness of the surfactant layer, rewriting equilibrium adsorption as Λ :

$$\Lambda = C_{Saq}\ l_m\ exp (-\Delta Go\ ad/ RT) \quad\text{[1.20]}$$

The surface excess may be estimated at various surfactant concentration levels, and the rearranged equation can be used to compute the change in free energy associated with adsorption.

$$\Delta Goad = -RTln (C_{Saq}l_{m)} + RTln\Lambda \quad\text{[1.21]}$$

Analyzing the equilibrium adsorption constant allows you to calculate the free energy of adsorption [Wanless et al. 2003].

$$\Delta Goad = -RTln(CmwKad) \quad\text{[1.22]}$$

The free energy of adsorption may be determined using equilibrium adsorption data, with temperature significantly influencing surfactant adsorption, as per the traditional thermodynamic format.

$$\Delta Goad = \Delta Hoad - T\Delta Soad \quad\text{[1.23]}$$

The equation for surfactant adsorption is negative due to its exothermic nature. To achieve negative free energy, the entropy term should be less than the enthalpy term. As temperature increases, the positive entropy term becomes dominant, leading to desorption. This reduces the adsorption effectiveness of surfactant molecules, and the enthalpy of adsorption changes with temperature.[Free et al. 1998]:

$$[dlnKad/dT]_\theta = \Delta Hoad/ RT2 \quad\text{[1.24]}$$

The process of comparing enthalpy change to a constant coverage differential results in [28]:

$$(dlnCSaq / dT)_\theta = - (d\ lnKad/ dT)_\theta = - \Delta Ho\ ad /RT2 \quad\text{[1.25]}$$

The process of comparing enthalpy change to a constant coverage differential results in [28]:

$$[dlnC_{Saq}/ d(1/T)]_\theta = \Delta Hoad/ R \quad\text{[1.26]}$$

The slope of a graph of bulk surfactant concentration against temperature change is equal to the enthalpy change associated with adsorption divided by R. Adsorption on a surface is the process by which water molecules and disordered ions are removed. Adsorption experiments at various temperatures are plotted to calculate enthalpy and entropy, with a slope equal to entropy and an intercept equal to enthalpy.

1.12.4 Adsorption Kinetics

Adsorption of surfactant is influenced by surfactant molecules' packing sufficiency and comparison with another species. However, studies on kinetic aspects are limited. Understanding surfactant adsorption and desorption kinetics is crucial for optimizing injection frequency and surface coverage, as surfactant concentration decreases over time. [Ullah et al. 2019].

Adsorption of surfactants is influenced by surfactant concentration and competitive ions. For instance, the adsorption of sodium oleate on fluorite surfaces is inhibited by competitively adsorbing ions such as hydroxide, carbonate, and fluoride. Anions like hydrogen have a substantial impact on adsorption kinetics, followed by carbonate and fluoride. Adsorbed surfactant molecules become increasingly orientated when they pack together.

The first-order reaction defined may be proved as [Lukanov et al. 2014]:

$$d\theta /dt = k_f C_{Saq} (1 - \theta) \text{ ……………………………………………..[1.27]}$$

The equation integrates Eq. (1.27), involving surface coverage, forward reaction rate constant, reaction time, and bulk concentration of adsorbing species.[Erkmen et al. 2023]:

$$\ln [1/ (1 - \theta)] = kfC_{Saq}\, t \text{ ……………………………………………… [1.28]}$$

The adsorption of 1.31025 M oleate on fluorite may be depicted using a first-order process involving the adsorption density at a fixed bulk concentration. The graphic depicts a linear connection between ln [1/(1-θ)] and time, with an intercept at zero. The first-order kinetics appear to be appropriate at a concentration of 1 3 1025 M oleate [Langley et al. 1975]:

$$d\theta /dt = (k_f/ Co)C_{Saq\,(1} - \theta) - (k_b /C_{o)}.\, \theta \text{ ………………………………[1.29]}$$

1.13 Surfactant Aggregation and the Aqueous CMC

The addition of aq. CMC to MLA enhances surfactant adsorption models by accounting for lateral interactions, aggregation formation, and environmental considerations. Accurate assessment of pure with blended surfactants is important for MLA use. Aggregation depletes surfactants, lowering monomeric surfactant availability. [Patel et al. 2016].

The impact of particular ions and salts on surfactant characteristics makes studying aqueous micelle aggregation (CMC) difficult. Counterions have varying impacts on distribution, aqueous CMC, micelle form, mixed micelle composition, size, and phase separation. Cationic surfactants have a greater counterion impact on aggregation than anionic surfactants. The process of counterion binding is not well understood or debated. The cation impact on CMC, sphere-to-rod, and aggregation number transition is negligible at low salt concentrations but increases as salt concentration increases. The CMC is significantly proportional to electrolyte content. The MLA aqueous CMC prediction model accurately describes surfactant adsorption on substrates by taking into account factors such as the head group-counterion pair, ion/salt effect, hydrocarbon chain length, electrostatic interactions, steric interactions, and solvent-surfactant interactions, thereby accurately describing surfactant properties.

1.14 Surfactant Partitioning Between Water and Oil

Surfactant particles generate distinct phases in oil and water mixes, resulting in a variety of structures under certain circumstances. They may split into oil and aqueous phases, adsorb on solid surfaces, form dimers and micelles, and react with metals or hydrogen ions to create metal salts and hydrogenated molecules. Solving these equilibrium processes can help calculate the surfactant concentration required for successful adsorption.

When an aqueous surfactant solution comes into contact with an immiscible organic liquid, such as oil, the surfactant monomers can partition into the organic liquid until equilibrium is attained. This surfactant partitioning determination has an impact on the hydrophobic-hydrophilic balance, monomeric surfactant availability, and sorption on metal oxide/metal surfaces. Pure surfactants are described by their partitioning coefficient.[Javidi et al. 2012]:

$Ki = Comi / Cwmi$ ………………………………………………..[1:30]

Nonionic surfactant partitioning research has been concentrated on low-concentration systems, with less attention paid to higher surfactant-concentration systems. The investigation of partitioning above aqueous CMC and apparent CMC is crucial because it is a monomer process influenced by monomer concentrations in the oil and oil phases. Individual mixed species, as well as adsorption at the oil/water interface, complicate surfactant mixture partitioning. As surfactant concentration rises, it approaches a plateau in the oil or aqueous phase. Mixed surfactants distribute more hydrophobic components into the oil phase, making experimental and quantitative modeling difficult. The link between partitioning and aqueous CMC is critical in discussions about partitioning models. The aqueous CMC of pure or mixed surfactants is thought to be the same as the aqueous CMC in the presence of nonpolar oil. However, micelle production in the aq. phase is unaffected by the nonpolar oil phase.

The Water Oil Surfactant Distribution Model (WOSDM) is a more accurate surfactant partitioning prediction model for calculating the distribution of mixed surfactants in water and oil environments. Semi-empirical modeling and quantum chemistry approaches are used to estimate the partitioning coefficient of surfactant Ki, which is far from realistic in oilfield circumstances [Javidi et al. 2012]:

$Ki = Co_{mi} / Cw_{mi}$ ………………………………………………..[1:30]

Nonionic surfactant partitioning research has been concentrated on low-concentration systems, with less attention paid to higher surfactant-concentration systems. The study of partitioning above aqueous CMC and apparent CMC is critical because it is a monomer process controlled by monomer concentrations in the oil and oil phases.

Individual mixed species, as well as adsorption at the oil/water interface, complicate surfactant mixture partitioning. As surfactant concentration increases, it reaches a plateau in the oil or aqueous phase. Mixed surfactants distribute more hydrophobic components into the oil phase, making experimental and quantitative modeling difficult.

The link between partitioning and aqueous CMC is critical in discussions about partitioning models. The aqueous CMC of pure or mixed surfactants is believed to be the same as the aqueous CMC in the presence of a nonpolar oil phase. However, micelle production in the aqueous phase is unaffected by the nonpolar oil phase.

The Water Oil Surfactant Distribution Model (WOSDM) is a better surfactant partitioning prediction model for determining the distribution of combined surfactants in water and oil environments. Semiempiricalmodeling and quantum chemistry approaches are used to estimate the partitioning coefficient of surfactant Ki, which is far from realistic in oilfield circumstances.

$$Ki = [\gamma w_{mi\ Cmo} / \gamma o_{mi\ Cmw]} \exp [- \Delta\mu o\ tri / RT] \ldots\ldots [1.31]$$

The study focuses on the activity coefficients of monomeric surfactants in oil and water phases, with γo mi and γw mi representing ionic and nonionic surfactants, respectively. The activity coefficients are illustrated using Pitzer's technique or Davies equation, with the molar concentrations of oil and water being Cmo and Cmw, respectively [Rajagopalan et al. 1997].Two approaches are used to determine the standard free energy change ($\Delta\mu$o tri) from water to oil: free energy transfer and quantum chemical.

1.15 Surfactant precipitation and colloid formation

Ionic surfactants interact with the other ions in solution to generate precipitates such as carboxylates and hydrophobic particles. This method diminishes water solubility while enhancing the lipophilic or oil phase.[Ettarhouni et al. 2020]pH has a significant impact on phase stability, as seen in Fig. 1. 18. Oleate combines with H-ions to generate oleic acid at low pH, whereas aggregate formations develop at larger pH and oleate concentrations. Iron dissolution ions Fe21 and Fe31 can form complexes with surfactant molecules, reducing the attainability of monomeric surfactants and complicating sorption on metal surfaces. Other components, such as sand, can also function as surfactant adsorption sinks. While experimental approaches and mechanistic models can aid in the characterization of complicated formation processes, quantum chemical methods are difficult to reproduce in actual WOS systems.

1.16 The impact of salt and ions on surfactant behavior

The aq. phase in oil fields consist of inorganic salts, which accelerate metal corrosion and interfere with surfactant activities. These impacts should be considered while doing experimental evaluations and modeling. [Ettarhouni et al. 2020] Ion effects on surfactant adsorption can be used in processes such as aggregation and micellization. Mechanistic modeling approaches have been created for simple salts, but more complicated salts require more effort.

1.17 Summary

The literature on surfactant adsorption performance is broad, with emphasis on concentration, amphiphilic characteristics, surface qualities, and surface defects. Surfactants generate monolayer/hemi micelle, sub monolayer, or bilayer/cylinder micelle structures close to interfaces and surfaces. Aggregation produces spherical micelles that function as buffers, keeping surfactant concentration constant. Adsorption levels may be estimated using material parameters, surfactant properties, and solution conditions. Fundamental modeling of surfactant adsorption, aggregation, and partitioning is difficult because of metals' dynamic surface states, ambiguous ion/counter ion binding processes, and a lack of study on surfactant adsorption kinetics and diffusion. More complicated molecular or multivalent ions require experimental verification and model development. Additional experimental work at increased temperatures and pressures is required to validate thermodynamic models of surfactant-associated processes.

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Chapter 2 : Classification of Surfactant

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Abstract

Surfactant they have lower surface and interfacial tension, surfactants—amphiphilic substances—are essential in a wide range of industrial, pharmacological, and biological uses. They may interact with both water and oil phases because of their hydrophilic head and hydrophobic tail. Surfactants are frequently found in detergents, emulsifiers, dispersants, and foaming agents because of their capacity to alter surface characteristics. The charge of the hydrophilic head group serves as the primary basis for their classification, which results in four main groups: cationic, nonionic, zwitterionic, and anionic surfactants. Every variety has unique physicochemical characteristics and uses. This study provides a thorough grasp of the importance of these surfactants in a range of sectors by examining their structural traits, functioning, and varied uses.

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2.1 Introduction

Surface-active agents, often known as surfactants, are substances that reduce the surface tension between two substances, such as solids, liquids, or gases(Azarmi et al., 2015). They are useful in a variety of industries, including cleaning goods, medicines, agriculture, and even the food sector, thanks to their amphiphilic character(Barman et al., 2024). Surfactants' versatility in different formulations is further enhanced by their capacity to self-assemble into micelles, bilayers, and vesicles.

It is essential to comprehend surfactant classification in order to choose the right kind for a certain application. Their hydrophilic head group, which controls how they behave in aqueous and non-aqueous settings, is the main factor used to classify them. Each of the four main categories—cationic, nonionic, zwitterionic, and anionic—has special traits and uses.In addition to their industrial applications, surfactants are crucial for biological systems. For example, lung surfactants lower alveolar surface tension, facilitating effective gas exchange. They are also used in enhanced oil recovery, drug delivery, and nanotechnology. With the advancement of green chemistry, biodegradable and environmentally friendly surfactants are being developed to minimize ecological impact(Verma et al., 2022).

2.2 Classification of surfactants

Surfactants are available in many forms, and are generally classified based on charge of the surface-active molecules such as anionic, non-ionic, cationic and amphoteric, types of surfactants and their molecular structure show in figure 2.1 and 2.2.

2.2.1 Anionic surfactants

Anionic surfactants are made up of anionic functional groups like sulphate, sulfonate, phosphate, and carboxylate. The majority of detergent formulations contain anionic surfactants, which we use more frequently than any other kind of surfactant. The best detergency is provided by alkyl and alkyl-aryl chains with a length of C12–C18 (Banjare et al., 2024). Soaps are anionic surfactants produced by saponifying natural fats and oils, making them the most prevalent type of surfactant. The metal salt of an alkali carboxylic acid [R-COOH] that was originally generated from plant- or animal-based fats is referred to as "soap" in this context. The bulk of the time, the base of soap bars is a mixture of tallow and coconut fatty acids and its applications such as laundry detergents, dishwashing liquids, shampoos. Example of anionic surfactants are ALS, SLS, SDS, AEP, SDBS, Sodium dodecyl sulfate (SDS), Linear alkylbenzene sulfonates (LAS) etc.

2.2.2 Cationic surfactants

In this category, the hydrophilic element is positively charged. It sticks to surfaces and may have soil-repelling, antistatic, softening, antibacterial, or corrosion-inhibiting properties despite the fact that this group doesn't have any wash activity. In many typical uses, they serve as softeners (fabric softeners) and antistatic. The counter ion of cat$^+$ surfactants is often a halide or methyl sulphate (Barman et al., 2024, Banajre et al., 2024). The pH affects the primary, secondary, or tertiary amines and its applications such as fabric softeners, disinfectants, hair conditioners. Example of cationic surfactants are alkyl ammonium chloride (AAC), Benzethonium chloride (BTC), cetrimonium bromide (CTMB), cetylpyridinium chloride (CPC), cetyltrimethyl ammonium bromide (CTAB), Benzalkonium chloride etc.

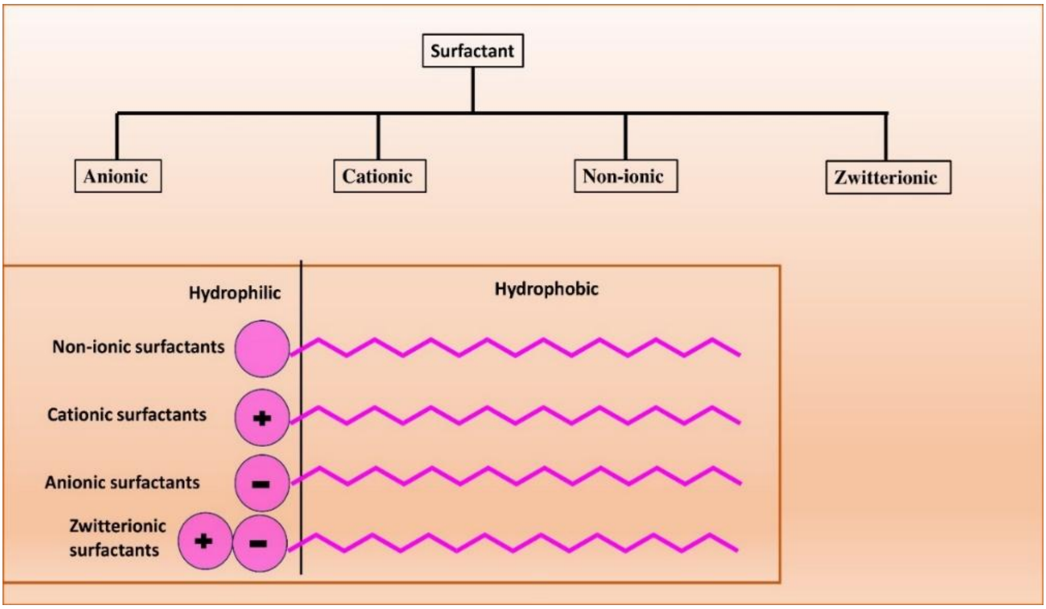


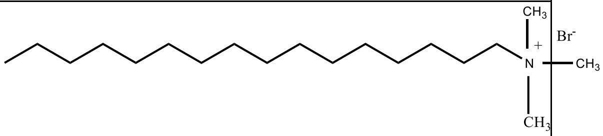
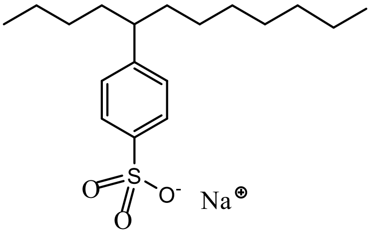
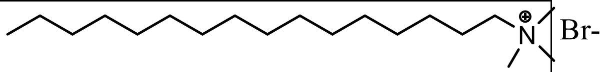
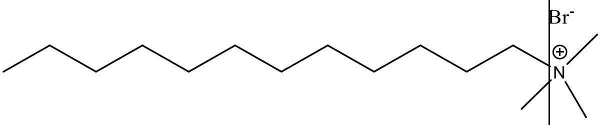
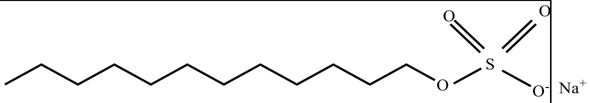
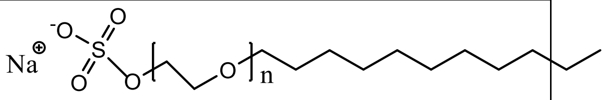
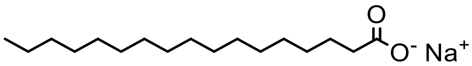
Figure 2.1 Types of surfactants and their molecular structure.

2.2.3 Non-ionic surfactants

Non-ionic surfactants contain hydrophilic elements that are not charged. These materials clean effectively and are unaffected by water. They come from groups like fatty alcohol polyglycosides and alcohol ethoxylates and are typically discovered in cleaning detergents. Long chain alcohols have certain surfactant characteristics (kawamara et al., 2023). Cetyl alcohol. stearyl alcohol, Fatty alcohols, cetostearyl alcohol (mostly made of stearyl alcohols and cetyl alcohols), and oleyl alcohol are the most prevalent types of these and its applications such as food emulsifiers, pharmaceutical formulations, cosmetics. Example of nonionic surfactants are alkyl phenol ethoxylate, fatty acid alkoxylate, triton x-100, cetyl alcohol, stearyl alcohol,Polyoxyethylene sorbitan esters (Tween), Alkyl polyglucosides etc.

2.2.4 Zwitterionic surfactants

A zwitterionic surfactant is made up of two groups (anionic and cationic) having diametrically opposed charges. Zwitterions are typically referred to as "amphoteric," yet both concepts are distinct. An amphoteric surfactant is one that undergoes a pH change from low to high and changes from a net cation to a net anion via Zwitterion. Only a small pH range allows the molecule to be Zwitterionic since neither the acidic nor basic sites are always charged. The physicochemical behaviour typically matches that of non-ionic surfactants at the isoelectric point (Gu et al., 1992). A continuous transition towards the cation or anion character occurs below and above the isoelectric point, respectively. Outstanding dermatological abilities are associated with a subgroup known as Zwitterion. Examples of surfaces and interfaces include the following: Interfaces between solids, liquids, and solid-liquid Liquid - Vapour (surface); they have a mild irritant effect on the skin and eyes. They are perfectly suited for usage in shampoo and other personal care (cosmetic) products. Surfactants that include both cation and anion centres attached to the same molecule are known as zwitterionic (amphoteric) surfactants and its applications as manufacturing for Baby shampoos, skincare products, pharmaceuticals. Example of zwitterionic surfactants is a cocoamido propyl betaine, glyceryl laurate,Cocamidopropyl betaine, Lecithin etc.

Surfactants		**Structures**
Cationic surfactants	Cetyltrimethylammonium bromide	
	4-(5-Dodecyl) benzenesulfonate	
	Cetrimonium bromide	
	Dodecyltrimethylammonium bromide	
Anionic surfactants	Sodium dodecyl sulfate	
	Sodium laureth sulfate	
	Sodium stearate	

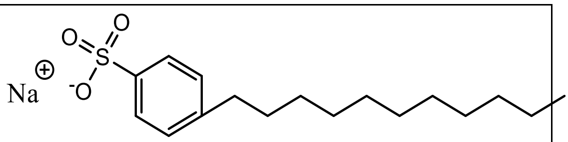
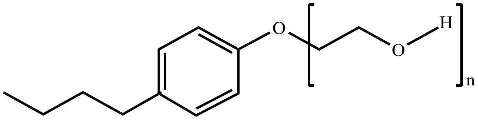
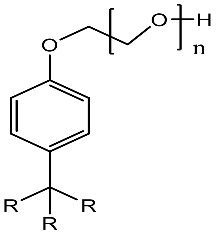
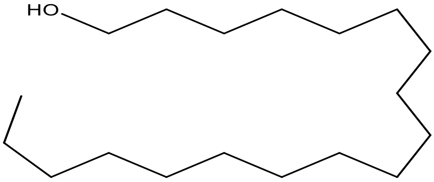
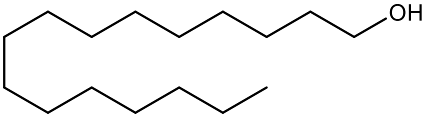
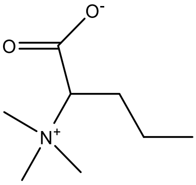
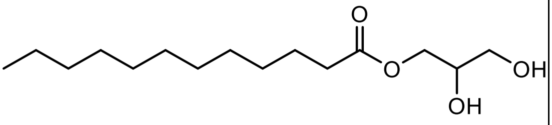
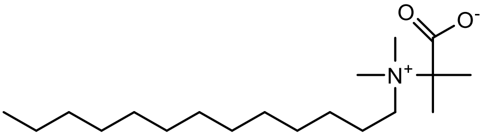
	Sodium Dodecylbenzene Sulfonate Surfactant	
Non-ionic surfactants	Triton-X 100	 n=9-10
	Alkyl phenol ethoxylate	
	Stearyl alcohol	
	Cetyl alcohol	
Zwitterionic surfactants	Propyl betaine	
	Glyceryl laurate	
	Dodecyl dimethyl betaine	

Figure 2.1 Molecular structure of surfactants.

2.3 Applications of the surfactants

The surfactant is a crucial component of emulsifying agent, foaming agent, cleaning agent, wetting agent, dispersing agent, and anti-foaming agents and is used in a wide range of goods, some of which are listed below:

2.3.1 Surfactants in crop protection
2.3.2 Surfactants in foods
2.3.3 Surfactant and wetting
2.3.4 Ore flotation
2.3.5 Surfactants and detergency
2.3.6 Surfactants in respiratory distress therapy
2.3.7 Surfactants for contact lens cleaning
2.3.8 Surfactants in hard gelatine capsules
2.3.9 Inhibition of Corrosion
2.3.10 Surfactantin Nanotechnology
2.3.11 Surfactants in health and personal care products
2.3.12 Foams in harsh environments

2.3.1 Surfactants in crop protection

Crop protection goods include insecticides, fungicides, herbicides, and pesticides. The formulation of pesticides has a major impact on their stability and efficacy. These days, crop protection products are being created to be more robust, user-safe, environmentally friendly, simpler to use, and more effective when applied. Interface and colloidal science affect all applications of sprayed materials. The pesticide either enters the leaf or comes into contact with the insect through the foliar deposit that is created when spray droplets first impact the leaf's surface (Otzen et al., 2011).

2.3.2 Surfactants in foods materials

Surfactants, which are also used in the preparation of many common meals, help to make a number of processes easier, including extracting cholesterol, solubilizing oils, emulsifying liquor, preventing component separation, and solubilizing vital nutrients. Ice cream, a partially frozen froth with 40.00–50.00% air (by volume), is a well-known example of Surfactants in the foods (Kurepa et al., 2019).

2.3.3 Surfactant and wetting

Liquid drop's surface tension is higher than the surface's critical surface tension, it will form a bead on the surface due to its poor affinity for the surface. However, if it has a strong affinity for the surface, it will spread and form a film. Surface tension of Teflon is 18 mN m^{-1}, whereas that of nylon is around 46 mN m^{-1}. Surfactants are frequently utilised as wetting agents, especially when applying the wetting liquid to a "wax-like" surface. In this context, the anionic surfactants are most frequently utilised (Wanguo et al., 2016).

2.3.4 Ore flotation

Surfactants can be used to modify the contact angle, which affects a solid particle's capacity to float on the liquid medium. Making a needle float on the surface of the water by coating it in wax is a common experiment in fundamental chemistry. The needle sinks when subsequent household detergent is introduced. The concepts are the same as those used in the flotation process, which treats raw mineral ores by adding a small amount of collector oil during the grinding and slurring stage. The collector oil, a cationic surfactant, anionic surfactants, or, non-ionic surfactant, affects the ore particles' capacity to hold moisture (Rosen et al., 1988). For oxide and carbonate ores, long-chain fatty acids are typically used, but for sulphide ores, thiophosphates and organic xanthates are frequently used. A foaming agent is frequently added to the suspension in practise in order to help the ore particles stick to the air bubbles when air is shot through it. When skimming is employed to extract the ore bits, they float to the surface. Sludge and effluents are purified using this type of flotation as well (Ahmed et al., 2016, Nitschke et al., 2021, Mc et al., 1912).

2.3.5 Surfactants and detergency

The ability of surfactants to adsorb at interfaces and reduce the energy required to complete the removal of foreign material from solid surfaces is known as their detergent action. At the appropriate interfaces, the best wetting agents frequently diffuse and adsorb rapidly. With a minimum of eight carbon atoms and a long history of use as a detergent, soap is a surface-active fatty acid salt. When fats and glyceride oils are saponified with KOH or NaOH in the past to make soap, glycerol is created as a by-product. Despite the fact that soaps are excellent deodorizers, they are sensitive to acidic pHs and the hardness (Ca^{2+} and Mg^{2+} ions) of the water, which leads to soap scum. Synthetic detergents have mostly replaced soaps, yet the use of detergent producers will make up for this drawback. The ingredients that are used to formulate commercial detergents account for the majority of the manufacturing of surfactants (Hakan et al., 1979).

2.3.6 Surfactants in respiratory distress therapy

Neonatal respiratory distress syndrome, commonly known as hyaline membrane disease, affects premature newborns, and is treated with surfactant formulations as a replacement therapy. This lung condition, which causes 5000 fatalities annually, affects 20% of the 250,000 preterm infants born in the US each year. The main factor contributing to the pathogenesis of respiratory distress syndrome is a severe deficiency of endogenous lung surfactant. Preparations of lung surfactants are used in conjunction with increased oxygen and mechanical ventilation to enhance gas exchange in order to prevent or treat neonatal respiratory distress syndrome. Exogenous surfactants can come from animal products or be manufactured artificially (Wu et al., 2019).

2.3.7 Surfactants for contact lens cleaning

Lipid, oil, and inorganic deposits that have collected on contact lenses are emulsified by surfactants, which act as cleansers. Surfactant agents are utilised in mechanical cleaning systems. To use one, apply a few drops of solution to the lens's surface and use your thumb and fingers to gently rub it back and forth. An alternative technique is to place the lens in the palm of your hand and use your fingertip to gently touch it for twenty to thirty seconds. These cleansers frequently contain non-ionic detergents, buffers, preservatives, and wetting agents as constituents.

2.3.8 Surfactants in hard gelatine capsules

Poorly soluble the benzoic acid was given as a loose powder by (Pennings et al., 2006), and the same powder was also incorporated to size zero and size one capsules. The size one capsule that had the most tightly packed powder broke down the least quickly. By adding 0.5% polyol surfactant to the mixture, this issue can be remedied. They demonstrated how this increased the rate of material disaggregation, which they used to show how the dissolving rate greatly increased as a result. If hydrophobic compounds must be included in formulations due to filling machine requirements, wetting agents, or surfactants, can be added at levels of 0.1-0.5% to prevent their adverse effects on drug release.

2.3.9 Inhibition of corrosion

Surfactants' promising prospective use as corrosion inhibitors has been thoroughly researched during the past few years. It is common knowledge that surfactants have a propensity to collect together at interfaces in solutions. The basic role of the surfactant functional group is to be adsorbed on the metal surface, which is essential for the suppression of corrosion. It was found that the surfactant's ability to adsorb onto the metal surface, which is what gives the metal its corrosion prevention, is closely related to the surfactant's ability to aggregate to form micelles (Barman et al., 2023, Yang et al., 1995). According to the polarisation technique examination, sodium dodecyl sulfate is an effective anodic inhibitor at low anodic overvoltage’s, and the inhibitor's adsorption followed the Langmuir isotherm.

2.3.10 Surfactant in nanotechnology

Surfactant molecules can self-assemble into a variety of nanostructures, including spherical/rod-shaped micelles and lamellar sheets. It is conceivable to design a surfactant package using surfactant nanotechnology that can solubilize significant amounts of oil. Surfactant mixer can be used to create in-situ oil-in-water microemulsions, enabling the wetting of surfaces. This might make it possible to get rid of dangerous chemicals (Rui et al., 2023, Pefrowski et al., 1973, Zhou et al., 2017, Damato et al., 2017).

2.3.11 Surfactants in health and personal care products

Detergents also use cationic quaternary ammonium surfactants (quats), which have strong germicidal activity, as fabric softeners. ditallow dimethyl ammonium chloride, a fabric softener and antistatic, is the most widely used. Germicides, such as *Benzalkonium chlorides*, frequently have a N-ADBAC structure, in contrast to emulsifiers, which frequently have a N-alkyl imidazoline chloride configuration or N-alkyl trimethylammonium chloride (N-ATAC). The following requirements—light detergency, good foaming, passable conditioning, adequately maintained—are frequently satisfied when making shampoo (Amelia et al., 2019, Olajire et al., 2014). The term "natural surfactant" can be used to describe a surfactant that was chemically synthesized from one as well as one that was extracted directly from a natural source. New emulsion formulation processes are essential for cosmetic formulations, especially for their preservation capabilities. The incredibly small droplet sizes and exceptional stability of the phase inversion temperature emulsion and microemulsion set them apart from other types of emulsions. A transparent, aesthetically pleasing O/W formulation can be made with the use of microemulsions (Miyazawa et al., 2021, Griese et al., 1999).

2.3.12 Foams in harsh environments

In order to restrict the fluids' movement after injection or to block particular zones or channels, foams can be injected into a petroleum reservoir. As a result, injected fluids are diverted into different sections of the reservoirA number of gases, including air/nitrogen, hydrocarbons, carbon dioxide, or steam, can be used to form acceptable foams for injection (Wang et el., 2023, Schramm et al., 2003, Barrantes et al., 2019, Banjare et al., 2024, Baghel et al., 2023).

2.4 Future aspects of surfactants

The study of biological systems, food, personal care and health products, mineral and petroleum processing, and even nanotechnology is among the practical application fields that are facilitated by surfactants. Surfactants have their many advantageous qualities; surfactants are almost necessary in daily living. The main uses of surfactants are in laundry detergents, dishwashing detergents, liquid soaps, cleaning goods, cosmetic hair care products, and personal care items. Surfactants are also among the most important substances found in these products (Rhein etal., 2006, Sun et al., 2019, Banajre et al., 2024, Banjare et al, 2024).

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Chapter 3: Properties of Surfactants

Manoj Kumar Banjare

Abstract

Surfactants are substances that, because of their architectures, possess both hydrophilic and hydrophobic qualities. They are utilized extensively in everyday life, numerous commercial goods, and electrochemical research. While the hydrophilic portions can have a wide variety of functional groups, the hydrophobic portions often consist of lengthy hydrocarbon chains. The surface tension in their aqueous solutions is decreased by these compounds, which are also known as surface active agents. As a result, they are utilized as detergents, solubilizers, and emulsifiers that also have antimicrobial qualities. Green surfactants, also known as biosurfactants, are being thoroughly researched despite the widespread usage of synthetic surfactants.In this chapter we discuss the different properties, interfacial parameter, thermodynamic parameter

Keywords: Surfactants, Properties, CMC, Interfacial parameters, Thermodynamic Parameters

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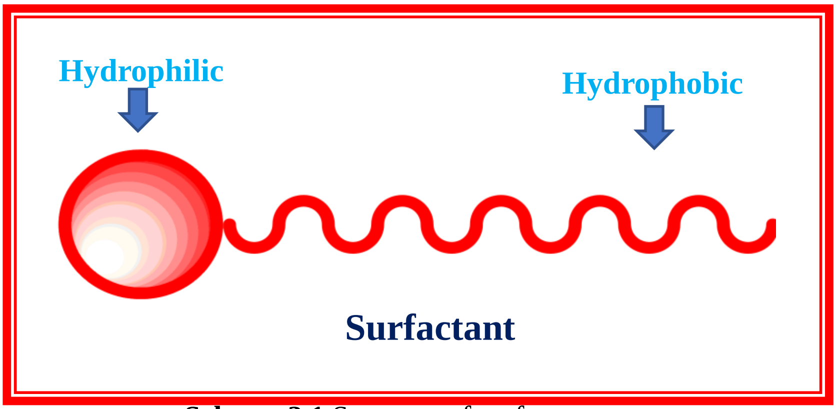
3.1 Introduction

The amphiphilic molecule has a tremendous role in society, nowadays mostly used in biological activities, food, personal care products, medicines, agrochemicals, and petro-chemicals (Kumar et al, 2022, Zhao 2019). These features can be enhanced by producing a sugar-based amphiphilic molecule system. These deals are good renewable alternatives to the conventional production of materials (Pandey et al., 2007). Surfactants are a type of amphiphilic component also known as surface-active agents illustrated in Scheme 3.1. It has several beneficial qualities, including wetting, cleaning, foaming, emulsifier splitting phases dropping surface and interfacial tension etc(Patel et al., 2008). It has special properties to adsorb at interfaces where it assembles in aqueous fluids as micelles of surfactant monomers. The phenomenon occurs at a critical micelle concentration (CMC) because of the dual nature of the surfactant, which generates numerous extended characteristics in the solution, including "self-assembly," also known as micelles. Many potential applications of surfactants including anti-corrosion, cosmetics, surface sciences, nanoscience, pharmaceuticals, medicine delivery, and agrochemicals (Bakshi et al., 2021).



Scheme 3.1 Structure of surfactant monomer.

3.2 Properties of surfactants

Water-repelling and water-loving molecules combine to form surfactants, sometimes referred to as surface-active agents. This amphiphilic chemical structure is shown the distinct characteristics. Surfactants play a critical role in processes involving liquids, solids, and gases because of their ability to change the properties of the contact. They are utilised in a variety of sectors and applications as a result. They are crucial in several activities, of pharmaceutical and pharmaceutical formulations to industrial and residential cleaning. When combined with oil, surfactants disperse and adsorb in water, either at the oil-water contact or the air-water interface (Hasan et al., 2018). All properties of surfactants are shown in Scheme 3.2.

Scheme 3.2 A systematic representation the properties of surfactants.

3.2.1 Amphiphilic nature

Surfactant molecules have polar, hydrophilic head groups and nonpolar, hydrophobic tail groups (Scheme 3.2). They may interact with both polar and nonpolar molecules at the same time according to their amphiphilic nature.

3.2.2 Surface tension reduction

Surfactants are reduce surface tension, allowing them to spread and moisten surfaces effectively. Surfactants are characteristic to assist water penetrating and remove dirt and oils in applications like surface activity. Surfactants are self-assembled to form micelles at maximum concentrations. Hydrophobic tails cluster inward to enclose hydrophobic molecules for solubilization in micelles which are colloidal formations (Jangde et al., 2022)

3.2.3 Emulsification, foaming, detergency, and wetting

Surfactants provide a border between immiscible substances, such as water and oil, to stabilise emulsions. Emulsions are a common ingredient in many goods, such as cosmetics, medicinal formulations, and salad dressings. Surfactants reduce the interfacial tension that separates the liquid and gas phases, which makes foam production smoother. Through the solubilization dispersion of oils, greases, and other hydrophobic materials in water, surfactants enhance the cleaning process. They also aid in avoiding the redeposition of dirt into surfaces. Surfactants improve wetting characteristics, enabling liquids to cover solid surfaces consistently. This helps with adherence and equal coverage in coating and painting applications.

3.2.4 Adsorption

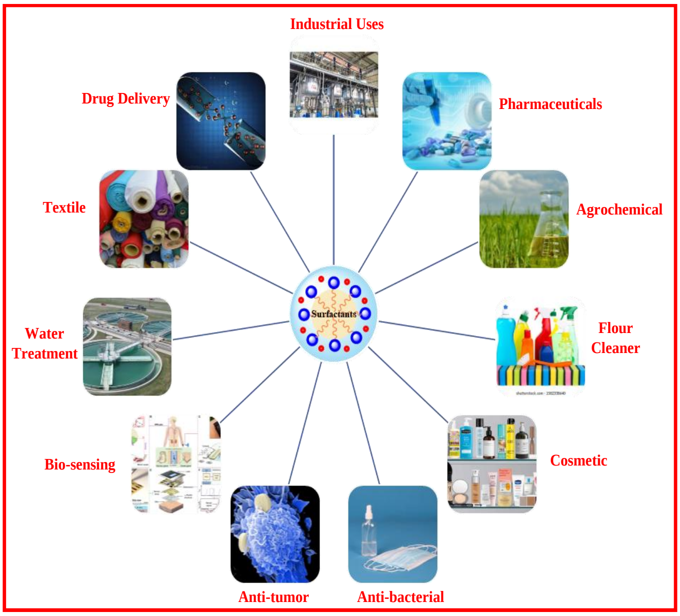
Surfactants generate monolayers that lower surface tension when they preferentially adsorb at interfaces. Processes like the stabilisation of foams and emulsions make use of this feature.

3.2.5 Variability

Surfactants come in several varieties, including non-ionic (no charge), cationic (positive charge), anionic (negative charge), and zwitterionic (both positive and negative charges). The characteristics and uses of various varieties vary. For instance, anionic and cationic surfactants are frequently employed in detergents and fabric softeners, respectively.

3.2.6 Biocompatibility

Used of many surfactants in pharmaceutical, cosmetic, food products is safe and biocompatible. Oral drugs, topical creams, and personal care products all include them (Woias et al., 2021).



Scheme 3.3 A systematic representation the application of surfactants.

3.2.7 Application of surfactants

The excellent qualities of surfactants have led to their application in the field of various development and significant number of medicinal additives in recent years. They are widely used in a variety of industries as emulsifiers and wetting agents. Surfactants are widely used in many sectors because of their special qualities. They reduce surface tension, which makes it easier for water and oil to combine and improves cleaning effectiveness in home goods like detergents and cleansers. They help with efficient distribution in medicines by enhancing drug solubility and bioavailability. Adjuvants, like as surfactants, are used in agriculture to improve the efficacy and dispersion of pesticides and herbicides (Sangwai et al., 2022). Their emulsifying and foaming qualities are used in cosmetics to help create lather and stability in the product. Surfactants are used in industrial processes including paint, coating, and lubricant applications because of their ability to disperse, moisten, and inhibit foaming. Surfactants are essential for efficiency and innovation in a variety of industries. Non-ionic surfactants are employed to stabilise proteins more frequently than ionic surfactants, albeit the reason for this is currently unknown. In bio-pharmaceutical goods, polysorbates are the non-ionic surfactants that are most often utilised illustrated in Scheme 3.3.

3.3 Critical micelle concentration (CMC)

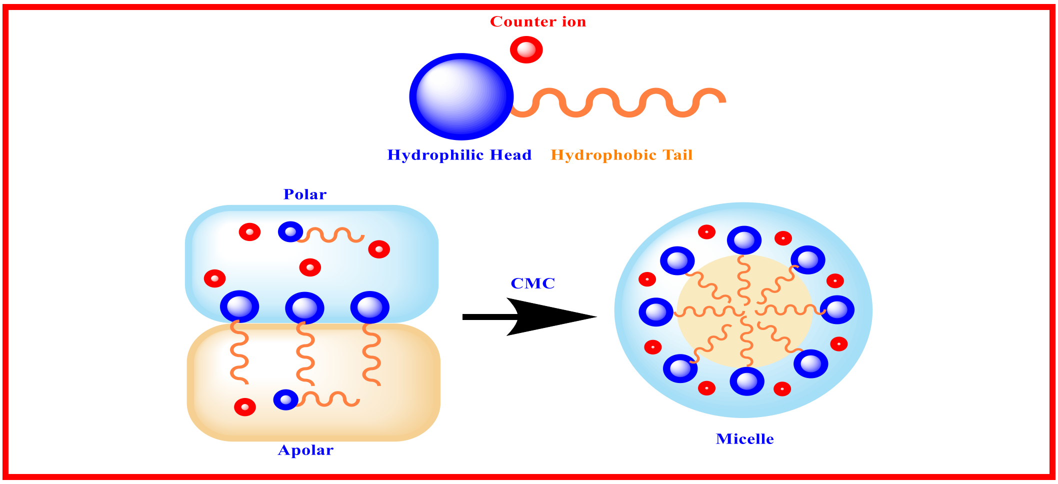
The critical micellar concentration (CMC) is the degree of micellar formation in a solution that contains surfactant molecules. The micelles consist of a hydrophobic core and a hydrophilic surface. The surfactant molecules exist as distinct molecules and below the CMC. The molecules start to group and form micelles above the CMC. The CMC is a crucial metric in the study of surfactants and has several uses. Detergents include micelles, which help clean surfaces and reduce water's surface tension. Hydrophobic compounds can be solubilized in micelles and above the CMC to aid in their passage across membranes (Guo et al., 2021).

Table 3.1 List of different techniques for the characterization of CMC.

S.N.	**Techniques**	**Characterization**
1.	Electron microscopy-Scanning (SEM)	Morphology
2.	Electron microscopy-Transmission (TEM)	Morphology
3.	Nuclear magnetic resonance (NMR)	CMC/ Intramolecular interaction
4.	Fourier transform infrared spectroscopy (FTIR)	Micelle characteristics
5.	Dynamic light scattering (DLS)	Distribution of sizes and zeta potential
6.	UV-Visible spectroscopy	Confirmed micelle formation
7.	X-ray photoelectron spectroscopy (XPS)	Micelle's elemental makeup

8.	X-ray diffractometry (XRD)	Crystallinity
9.	Small-angle neutron scattering	CMC
10.	Surface tension	CMC
11.	Colorimetry	CMC/CAC
12.	Conductometry	CMC
13.	Fluorescence	CMC
14.	Energy dispersive X-ray spectroscopy	Emission
15.	Loresta-GP MCT-T610 resistivity meter	Volume resistivity

Surface tension measurements, conductivity tests, dynamic light scattering (DLS), transmission electron microscope (TEM), scanning electron microscope (SEM), fluorescence spectroscopy, and other methods may all be used to estimate the CMC (Table 3.1). It is dependent upon the surfactant's chemical makeup as well as the solution's characteristics, including temperature, pH, and ionic strength. Typically, the CMC rises as the surfactant's hydrophobicity increases and falls as it becomes less hydrophobic.



Scheme 3.4 A systematic representation of micelle formation of the amphiphilic molecule.

3.4 Formation of micelle

Micelles are chemical structures in which the hydrophilic core is surrounded by a hydrophobic shell of amphiphilic molecules contained in a liquid form an aggregate of spherical or cylindrical shape, such as surfactants(Miller et al., 2021). This structure determines the proportion of hydrophobic molecules that become stabilised and soluble in aqueous solutions. The development of micelles is a complex process, driven by both hydrophobic and electrostatic interactions between amphiphilic molecules. When amphiphilic molecules are added to aqueous solutions, they form aggregates known as micelles shown in Scheme 3.4. These aggregates are composed of a hydrophobic core surrounded by a hydrophilic part. The hydrophilic portion of the amphiphiles is made up of their head groups that interact with the aqueous environment, whilst the hydrophobic core is made up of the hydrophobic tails of the amphiphiles(Edler et al., 2020).

When the amphiphiles molecules arranged themselves in a manner that minimizes the contact between the hydrophobic tails and the aqueous environment to formation of micelle. The quantity of amphiphilic molecules in the solution has an impact on the size of the micelles. When amphiphiles are present at low quantities, their individual molecules interact with one another to form tiny aggregates called primary micelles. The main micelles can interact and produce bigger aggregates known as secondary micelles at greater concentrations (Jadhav et al., 2015). The size of these micelles can range from a few nanometres to several hundred nanometres.

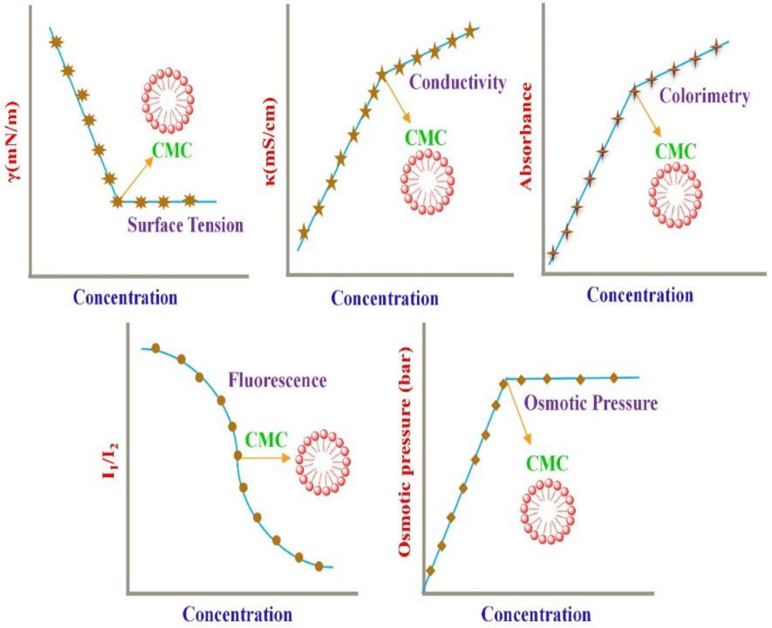


Fig. 3.5 Micelle formation of surfactants by using different techniques.

3.5 Characterization techniques of micelle formation

The CMC and micelle size in aqueous solutions may be measured using a variety of methods, comprising surface tension, fluorescence, conductometry, viscosity, light scattering, sound velocity, calorimetry, spectrophotometry, SANS, and dye solubilization etc. The most common technique is dynamic light scattering (DLS), which uses laser light to measure the Brownian motion of the micelle particles in solution. The DLS method enables the polydispersity and average size of the micelles to be measured. Electron microscopy- transmission (TEM), which enables direct micelle viewing, is an additional method that may be applied. The size, form, and surface charge of the micelles shown in Fig. 3.1 and Table 1.6 may be ascertained using this method.

3.6 Physicochemical properties of surfactants

The unique properties of surfactant molecules have prompted extensive study. Micelles are self-assembling of molecules that are formed by surfactants. To aid in the production of surfactants, they may also adsorb and form a monolayer at the air-water interface.

I) Interfacial properties

Interfacial properties are characteristics of the interface between two different materials, such as an aqueous solution and an organic phase. Interfacial properties include surface tension, wettability, surface energy, wetting, and spreading, adsorption, and adhesion etc. The force required to move a line of water over a surface is known as surface tension, and the wettability of a liquid is how readily it spreads across a surface. Surface energy is the quantity of energy required to produce a unit area of the surface, whereas wetting and spreading describe how a liquid will spread out over a surface. Adsorption is the process of an adsorbate being attracted to a surface, while adhesion is the force between two surfaces. Understanding interfacial properties are important for many industries, as they determine the effectiveness of interactions between materials.

a) Surface tension at CMC (γ_{CMC})

Surface tension is a fundamental physical property that is used in surface, interface, and colloid research and is shown by amphiphilic molecules such as ionic liquids and surfactants. A study looking at how surface tension affects the way amphiphilic molecules group together in various solvents, including water, sugar, its derivatives, and other organic solvents. Surface tension has consistently decreased in several solvents, when the molar ratio of amphiphilic compounds has grown. Eq. (3.1) was utilised to compute the surface tension (γ) of amphiphilic systems.

$$\gamma_{CMC} = \frac{\text{Drop of Water X 72}}{\text{Drop of Solution}} \dots\dots\dots\dots\dots\dots \qquad \mathbf{(3.1)}$$

b) The maximum surface excess concentration (Γ_{max})

A chemical species' the maximum concentration at the surface of a liquid or solid is known its the maximum surface excess concentration. In assessing a material's stability, solubility, and reactivity, it is a crucial characteristic. Measurements of molecule adsorption and desorption may also be made using it. Temperature, material type, and surface area available for adsorption can be used to define it. Eq. (1.2) was utilised to determine the maximum surface excess (Γ_{max}) of amphiphilic systems based on the slope ($d\gamma/d\log_{10}C$).

$$\Gamma_{max} = \left(\frac{1}{2.303nRT}\right)\left(\frac{d\gamma}{d\log_{10}C}\right)Tp \quad \text{..............................} \quad \textbf{(3.2)}$$

Where, the molar gas constant ($R = 8.314\ Jmol^{-1}K^{-1}$), the surfactant concentration (C), the absolute temperature (T) in Kelvin, and the pre-factor (n) values for the non-ionic surfactant (1), ionic liquids, cationic and anionic surfactants (2) have been obtained.

c) The minimum surface area per molecule (A_{min})

In the fields of chemistry and materials science, the idea of minimum surface area per molecule is crucial. It speaks about the smallest space that a molecule might possibly occupy on a surface. Using Eq. (3.3), the minimum areas per molecule (A_{min}) of amphiphilic systems have been determined.

$$A_{min} = \left(\frac{1}{\Gamma_{max}}\right)N_A \quad \text{.......................................} \quad \textbf{(3.3)}$$

Where, Γ_{max} is the maximum surface excess concentration ($mol.m^{-2}$) and A_{min} is the minimum area per molecule (m^2mol^{-1}). N_A is Avogadro's number ($6.022\times10^{23}\ mol^{-1}$).

d) Surface pressure at CMC (π_{CMC})

The force a surface applies to a body per unit area is measured to the surface pressure at CMC. In addition to determine the air density and air flow around an object. Surface pressure can also be affected by temperature and humidity. Using Eq. (3.4), the surface pressure at CMC (πCMC) was determined,

$$\pi_{CMC} = \gamma_0 - \gamma_{CMC} \quad \text{.....................................} \quad \textbf{(3.4)}$$

Where, γ_0 represents the surface tension of pure water, and γ_{CMC} represents the surface tension at CMC.

e) The efficiency of adsorption (pC_{20})

The degree to which a material is adsorbed into a surface is determined by the effectiveness of adsorption (pC_{20}). The quantity of substance adsorbed per unit area of the surface serves as the measurement. The higher value of pC_{20} is shown the more efficient in adsorption process. Generally, adsorption is more efficient when the surface has a large surface area or when the material being adsorbed has a higher affinity to the surface. The adsorption efficiency (pC_{20}) was determined by using Eq. (3.5).

$$pC_{20} = -\log_{10}C_{20} \quad \text{.................................} \quad \textbf{(3.5)}$$

I) Thermodynamic properties

The most important thermodynamic property of amphiphilic molecules is their tendency to self-assemble into ordered structures. This self-assembly is accelerated by the hydrophobic effect, which is brought on by the attractive interaction between the molecules' hydrophobic groups. The organization of amphiphilic molecules into ordered structures can be further stabilized by hydrogen bonding and other interactions between the molecules.

a) Degree of micellization (α)

When the degree of micellization is low, the amphiphilic molecules remain separate and the solubility and stability are lower. In general, while maximising a substance's solubility and stability, one must take into account the degree of micellization of an amphiphilic molecule. The slopes of the pre- and post-micellar curves of conductivity, it determines the degree of micellar ionisation (α) using Eq. (3.6).

$$\alpha = \frac{S_2}{S_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \mathbf{(3.6)}$$

Where S_1 and S_2 represent the pre- and post-micellar slopes of surfactant, respectively.

b) The standard Gibbs free energy of micellization (ΔG°_M)

The standard Gibbs energy of micellization (ΔG°_M) of the amphiphilic system has been computed by using Eq. (3.7).

$$\Delta G^\circ_M = (2-\alpha)RT\ln\frac{55.4}{CMC} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \mathbf{(3.7)}$$

Where, α is the degree of micellar ionisation, (2-α) for monomeric surfactants, T is the absolute temperature (299 K), R is the molar gas constant (8.314 $\mathrm{Jmol^{-1}K^{-1}}$), and 55.4 is the volume from one litre of water.

c) The standard Gibbs free energy of adsorption (ΔG°_{ads})

The standard Gibbs free energy of adsorption (ΔG°_{ads}) of amphiphilic molecules is calculate by using Eq. (1.8)

$$\Delta G^\circ_{ads} = \Delta G^\circ_M - \frac{\pi_{CMC}}{\Gamma_{max}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \mathbf{(3.8)}$$

Where, the maximum surface excess concentration is denoted by Γ_{max}, the surface pressure at CMC is represented by π_{CMC}, and the standard Gibbs free energy of micellization is represented by ΔG°_M.

d) The standard Gibbs energy of transfer (ΔG°_{trans})

The standard Gibbs energy of transfer (ΔG°_{trans}) is the energy released or absorbed when an amphiphilic molecule transfers from one medium to another. When studying how amphiphilic molecules behave in various settings and interact with their surroundings, ΔG°_{trans} is a useful tool. The standard Gibbs free energy of transfer (ΔG°_{trans}) was calculated by using Eq. (3.9).

$$\Delta G^\circ_{\mathrm{trans}} = \Delta G^\circ_{\mathrm{M(solvents\ mixed\ media)}} - \Delta G^\circ_{\mathrm{M(pure\ water)}} \quad \ldots\ldots\ldots \quad \mathbf{(3.9)}$$

Where, $\Delta G^\circ_{\mathrm{M\ (pure\ water)}}$ is pure water and $\Delta G^\circ_{\mathrm{M\ (solvents\ mixed\ media)}}$ is amphiphilic mixed media respectively.

e) The standard Gibbs free energy of the given air/water interface ($\Delta G^{(s)}_{min}$)

The standard Gibbs free energy of the specified air-water interface (ΔG(s)min) has been determined by using Eq. (3.10),

$$\Delta G^{(S)}_{min} = A_{min} . \Upsilon_{CMC} . N_A \quad \text{..........................} \quad \textbf{(3.10)}$$

Where N_A is the Avogadro number (6.022×10^{23} mol^{-1}), γ_{CMC} is the surface tension of the amphiphilic system at equilibrium, and A_{min} is the minimum surface area per molecule.

f) The standard Gibbs free energy of micellization per alkyl tail ($\Delta G°_{m,tail}$)

The standard Gibbs free energy of micellization per alkyl tail ($\Delta G^o_{m,\ tail}$) is used to calculate the energy required to form micelles from amphiphilic chemicals. It has to deal with the balance between the hydrophilic and hydrophobic parts of the molecule. This energy is dependent on size, shape, stiffness, and solvent characteristics of the amphiphilic molecules. It is also affected by temperature and the ionic strength in the solution. Eq. (3.11) has been utilised to compute the conventional Gibbs free energy of micellization per alkyl tail ($\Delta G^o_{m,tail}$) of amphiphilic systems.

$$\Delta G^{\circ}_{m,tail} = \frac{\Delta G^{\circ}_{M}}{2} \quad \text{....................................} \quad \textbf{(3.11)}$$

II) Critical packing parameter (*P*)

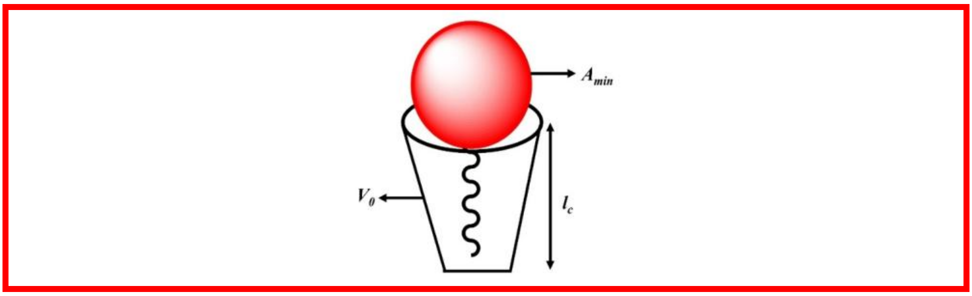
The critical packing parameter (CPP) (*P*) of amphiphilic molecules is calculate by using Eq. (3.12) and shown in Scheme 3.5 and Table 3.2 The critical packing parameter (*P*) and the minimum surface area of amphiphilic molecules was discovered by Israelachvili *et al.*, (Wang et al., 2013).

$$P = \frac{V_0}{A_{min} l_c} \text{.......................................} \quad \textbf{(3.12)}$$

$$V_0 = (27.4 + 26.9C_n)\text{Å}^3 \text{ per hydrocarbon chain ....} \quad \textbf{(1.13)}$$

$$l_c = (1.5 + 1.265C_n)\text{Å} \text{ per hydrocarbon chain ....} \quad \textbf{(1.14)}$$

The length of the long alkyl chain (hydrophobic tail) and the minimum area required for each amphiphilic molecule to aggregate in the systems were calculated using Tanford's(Banjare et al., 2018), where V_o, l_c, and A_{min} indicate the volume of long alkyl chain groups of the hydrophobic part of an amphiphilic molecule Eq. (3.13 and 3.14).

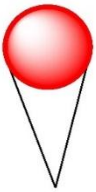
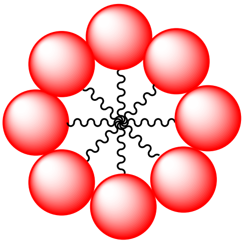


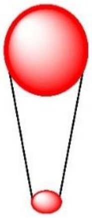
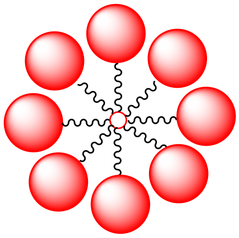
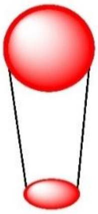
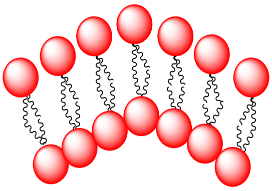
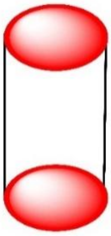
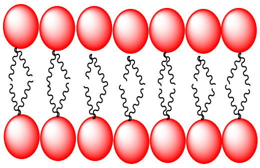
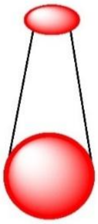
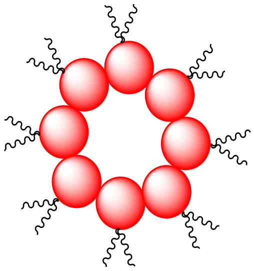
Scheme 3.6 A systematic representation of critical packing parameter.

III) Phase behaviours

It is possible to alter the surface characteristics of materials by exposing surfactants to varying pressure, temperature, and concentration. The phase behaviour of surfactants is an important factor in determining their adsorption of effectiveness and its applications. The phase behaviour of surfactants is largely determined by the degree of hydrophobicity and the molecular structure of the surfactants. At low temperatures, surfactants can form an isotropic liquid and an isotropic gel, or a lamellar phase. The higher temperature surfactants molecules are forming a reverse micellar phase, a micellar cubic phase, and then a micellar hexagonal phase. These stages have an impact on the solubilization capacity, interfacial tension decrease, and emulsion stability, all of which are important for a variety of applications, including increased oil recovery, detergents, and cosmetics.

Table 3.2 Different shapes of surfactant monomers and the corresponding shape of micelle.

Packing parameter value's	**Critical packing shape**	**Shape**	**Characteristics**	**Shape of Self-assembly entities**
***P* = < 0.33**		**Spherical Micelle**	Surfactants with a single-chain and substantial head group.	

***P* = 0.33 - 0.5**		**Cylindrical Micelle**	Surfactants with a single chain and tiny head groups.	
***P* = 0.5 - 1.0**		**Bilayer Vesicle**	Surfactants have two chains, each with a big head group and flexible chains	
***P* = 1.0**		**Lamellar Phase**	Small head groups on double-chain surfactants or inflexible, immovable chains	
***P* = > 1.0**		**Inverted / Reverse Micelle**	Surfactants having a double chain, big hydrophobic groups, and a tiny head group	

IV) Viscosity

The degree of the hydrophobicity-hydrophilicity balance of the molecule, the kind of media, the temperature, and the concentration of the molecule all have an impact on the viscosity of amphiphilic molecules. Additionally, the viscosity of amphiphilic molecules can be impacted by the presence of other molecules in the medium. varied amphiphilic systems have varied viscosity parameters, including relative, specific, decreased, and intrinsic viscosity.

i) Relative viscosity (η_r)

The higher relative viscosity is exhibited by molecules whose hydrophilic and hydrophobic components are more affixed to one another. This relative viscosity is also influenced by the dimensions of the molecules and the geometry of their hydrophobic and hydrophilic constituents. The relative viscosity (η_r) of all systems computed from Eq. (3.15) is expressed as:

$$\eta_r = \frac{\eta_s}{\eta_0} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \textbf{(3.15)}$$

Where $\eta_{r,}$ is the relative viscosity of the system, η_s is the viscosity of the solution, and η_o is the viscosity of the pure solvent.

ii) Specific viscosity (η_{sp})

Specific viscosity is a measure of how much a material's viscosity increases when it is exposed to a certain concentration of an amphiphilic molecule. The increase in viscosity is due to the amphiphilic molecules are ability to interact with and increase the viscosity of the material. The specific viscosity (η_{sp}) of all systems computed from Eq. (4.16) is expressed as:

$$\eta_{sp} = \eta_r - 1 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \textbf{(3.16)}$$

iii) Reduced viscosity (η_{red})

The reduced viscosity of amphiphilic molecules are that occurs when the molecules are aggregate/clusters, in an aqueous solution. When a molecule repels, its opposite end is drawn to water. This creates a structure in which the molecules arrange themselves in a way that reduces the overall viscosity of the solution. Reduced viscosity can also be used to improve the performance of industrial processes. The reduced viscosity (η_{Red}) of all systems are calculated from Eq. (3.17) and (3.18) is expressed as:

$$\eta_{Red} = \frac{\eta_{sp}}{C} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \textbf{(3.17)}$$

$$\eta_{sp} = \eta_r - 1 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \textbf{(3.18)}$$

Where η_{sp} is the specific viscosity, η_r is the relative viscosity and C is the concentration of the amphiphilic system respectively.

iv) Intrinsic viscosity [η]

The intrinsic viscosity values [η] for the amphiphilic system were calculated from Eq. (3.19).

$$[\eta] = \lim_{C \to 0} \frac{\eta_{sp}}{C} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \textbf{(3.19)}$$

V) **Mixed micelle**

Mixed micelles of two amphiphilic molecules (i.e., surfactants, ionic liquids, polymer, and co-polymer) represent a unique type of self-assembled structure in which the hydrophilic and hydrophobic moieties are arranged distinctly. Various researchers have proposed a number of ideas to forecast the interaction in binary amphiphilic systems.

(a) **Clint model**

The Clint's model is employed to assess the ideal micellar mole fraction of combined two surfactant systems, both of which clarify departures from ideality for researchers mixed systems. The Clint model of the predicted ideal mixing of CMC value is obtained from Eq. (3.20).

$$\frac{1}{CMC_{ideal}} = \frac{\alpha_1}{CMC_1} + \frac{\alpha_2}{CMC_2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \mathbf{(3.20)}$$

Where, CMC_1 and CMC_2 is the critical micelle concentrations of the two amphiphilic components are indicated. A molar percentage of amphiphilic molecules, α_1 and α_2, make up CMC_{ideal}, which is a combination of CMC.

(b) **Rubingh model**

The Rubingh model is the phase separation model of mixed micelles. This theoretical model was developed by Dutch physicist Peter Rubingh in the early 2000s. It is used to explain the properties of mixed micelles, which are aggregates of amphiphilic molecules such as lipids and surfactants. The model considers the interaction of hydrophobic and hydrophilic contacts as well as the impact of electrostatic charge interactions between the amphiphilic molecule to describe to the behavior of a specific mixed micelles systems. The model also considers how these interactions modify the mixed micelles' size and structure. The Rubingh model may be used to measure these interactions and forecast the stability and solubility of mixed micelles in a given solution. The Rubingh theory may be used to determine a mixture of CMC for non-ideal mixed micellization of amphiphilic components from Eq. (3.21).

$$\frac{1}{CMC_{mix}} = \frac{1}{f_1 CMC_1} + \frac{1}{f_2 CMC_2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \mathbf{(3.21)}$$

The activity coefficients of amphiphilic components denoted as f_1 and f_2, may be calculated using the following Eq. (3.22) and (3.23).

$$f_1 = exp[\beta(1 - X_1)^2] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \mathbf{(3.22)}$$

$$f_2 = exp[\beta(X_1)^2] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \mathbf{(3.23)}$$

The Rubingh model is used to calculate the micellar mole fraction of amphiphile 1:

$$\frac{(X_1)^2 \ln\left(\frac{\alpha_1 CMC_{mix}}{X_1 CMC_1}\right)}{(1-X_1)^2 \ln\left[\frac{(1-\alpha_1) CMC_{mix}}{(1-X_1) CMC_2}\right]} = 1 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \mathbf{(3.24)}$$

where X_1 is the mole percentage of component 1 of the mixed amphiphilic micelle; the X_1 equation may be solved by using Eq. (3.24 and 3.25).

$$X_1^{ideal} = \frac{\alpha_1 CMC_2}{\alpha_1 CMC_2 + \alpha_2 CMC_1} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad \mathbf{(3.25)}$$

The attractive or repulsive contact between two amphiphilic components is confirmed by the Rubingh model using the regular solution theory by an interaction parameter computed by Eq. (3.26).

$$\beta = \frac{\ln\left(\frac{\alpha_1 C_{mix}}{X_1 C_1}\right)}{(1-X_1)^2} \dots\dots\dots\dots \quad \textbf{(3.26)}$$

β is a sign of how much the two surfactants interact.

(c) Rosen model

The micellar fraction of moles of surfactant 1 (X^{α}) at the mixed adsorption layer may be iteratively determined using the Rosen model, which was estimated with the help of Eq. (3.27).

$$\frac{(X^{\alpha})^2 \ln\left(\frac{\alpha_1 CMC_{mix}}{X^{\alpha} CMC_1}\right)}{(1-X^{\alpha})^2 \ln\left[\frac{(1-\alpha_1) CMC_{mix}}{(1-X^{\alpha}) CMC_2}\right]} = 1 \dots\dots\dots\dots \quad \textbf{(3.27)}$$

Pure surfactants CMC_1 and CMC_2, respectively, are represented by C_{mix}, the mixed concentrations. The proportion of pure surfactant 1 in solution with a certain γ value and α_1 stoichiometric mole fraction. Eq. (3.28) was utilised to determine the value of X^{α}, which is the interaction parameter (β^{σ}) evaluated at the air/solution interface.

$$\beta^{\alpha} = \frac{\ln\left(\frac{\alpha_1 C_{mix}}{X^{\alpha} C_1}\right)}{(1-X^{\alpha})^2} \dots\dots\dots\dots \quad \textbf{(3.28)}$$

In the mixed micelle system, the activity coefficients (f_1 and f_2) of the two surfactants are connected to the interaction parameter (β^{σ}). Eq. (3.29) and (3.30) are used to calculate the activity coefficient.

$$f_1 = exp[\beta(1-X^{\alpha})^2] \dots\dots\dots\dots \quad \textbf{(3.29)}$$

$$f_2 = exp[\beta(X^{\alpha})^2] \dots\dots\dots\dots \quad \textbf{(3.30)}$$

(d) Motomura model

Motomura's method has been applied to determine the micellar mole fraction in the ideal condition by using Eq. (3.31).

$$X_{ideal} = \frac{\alpha_1 CMC_2}{\alpha_1 CMC_2 + (1-\alpha_2) CMC_1} \dots\dots\dots\dots \quad \textbf{(3.31)}$$

Making use of Eq. (3.32) to establish a connection between the activity coefficients and excess free energy of mixing.

$$\Delta G_{ex} = RT[X_1 . lnf_1 + (1-X_1) . lnf_2] \dots\dots\dots\dots \quad \textbf{(3.32)}$$

3.6 Conclusion

Ionic liquids and inositol must overcome these difficulties to fully realise their promise in a variety of applications and cures. To do this, it will take continuing research, innovation, and cooperation among scientists, engineers, healthcare providers, and regulatory organisations. It is more possible that goods will be incompatible or negatively impact the value of the components if more surfactant is needed in manufacturing. They are having great success substituting enzymes for chemicals in their formulations, as can be observed in the sector of household detergents. Many makers of surfactants have started researching and creating systems that combine surfactants with enzymes. There is also a need to find manufacturing methods and formulations that use less energy and resources overall. An example of this is crop protection in agriculture, which uses fewer active substances to get the same outcomes. Be accountable for conserving natural resources and energy at the same time. These challenges allow for an improvement in the way other substances interact with the surfactant, which subsequently creates new possibilities. Solutions to reduce materials or energy consumption are also important. Examples include low-temperature cleaning, water-efficient laundry technology, and energy-efficient manufacturing. The ability to innovate closely with customers and technology providers will be essential for surfactant suppliers to take advantage of these trends. As a method of creating and producing our products where there is a lot of activity on both the products and the biochemical production pathways, bio-surfactants may be seen as the next step in innovation rather than as a new class of surfactants or even chemicals. The production of surfactants has mostly been driven by environmental considerations. We produce more biodegradable products, employ renewable raw resources, and so on. But it's also important to consider the other two pillars of sustainability since it's becoming more and clearer that we need all three to meet our difficulties.

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Chapter 4: Application of Surfactant in Drug Delivery

Bhupendra Singh Banjare, Nitai Sarkar, Manoj Kumar Banjare

Abstract

Surfactants are essential for improving drug delivery systems because they provide remedies to problems relating to drug stability, solubility, and bioavailability. This chapter highlights the vital function that surfactants play in the delivery of drugs, emphasizing their special physicochemical characteristics that help with important pharmaceutical issues such as low drug solubility, stability, and bioavailability. As amphiphilic molecules, surfactants make it possible to create a variety of delivery systems that encapsulate hydrophobic medications and improve their therapeutic potential. These systems include solid lipid nanoparticles, liposomes, micelles, and nanoemulsions. They help drugs move across biological membranes, stabilize formulations, and stop aggregation. The chapter also demonstrates how surfactants help with targeted distribution and controlled drug release, which lowers systemic toxicity and increases site-specific effectiveness. The safety and efficacy of biocompatible surfactants, such as polysorbates and bile salts, in a variety of medicinal applications, are highlighted. Furthermore, surfactants continue to be essential for developing drug delivery systems, providing promising answers to contemporary therapeutic requirements.

Keywords: Surfactants, Drug delivery, Solubility, Amphiphilic molecules, Micelles.

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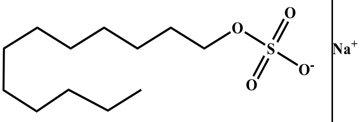
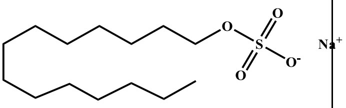
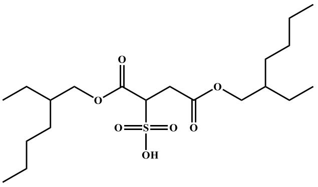
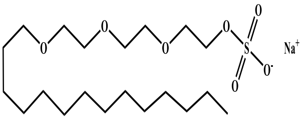
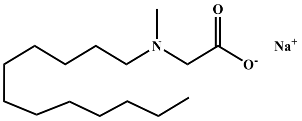
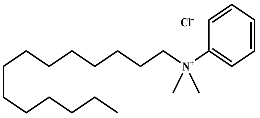
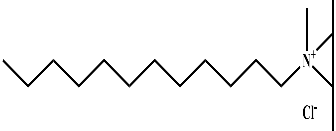
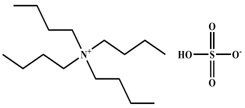
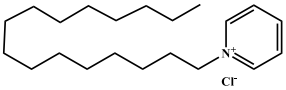
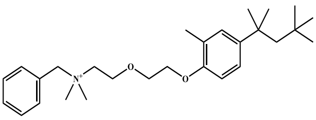
4.1. Introduction

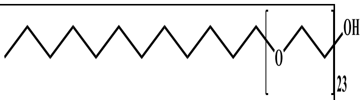
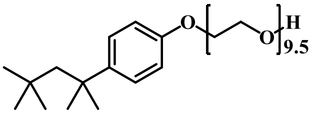
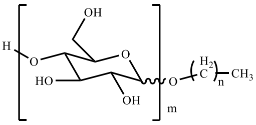
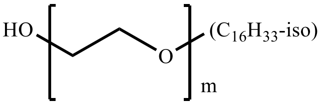
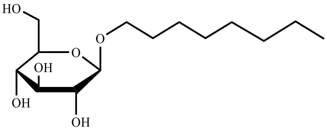
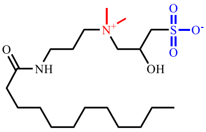
A surface-active agent (surfactant) is a chemical that decreases the surface tension between two substances (Ghosh et al., 2017; Ghosh et al., 2018). Water is attracted to the hydrophilic head while the hydrophobic head repels water. The dual nature of surfactants allows them to interact with both polar and nonpolar substances, enabling them to dissolve debris, emulsify oils, and stabilize mixes (Banajre& Banjare, 2024; Banjare & Banjare, 2024). The ionic nature of surfactants can be classified into four main groups: amphoteric (used in mild shampoos and personal care products; both positively and negatively charged); nonionic (used in food and cosmetics; no charge); cationic (used in fabric softeners and disinfectants; positively charged); and anionic (used in detergents; negatively charged). The use of these materials is extensive in many different industries, including petroleum, cleaning, cosmetics, medicine, and agriculture (Banjare & Banjare, 2024; Banjare & Banjare, 2023). A surfactant, such as pulmonary surfactant, is crucial in medicine because it lowers alveolar surface tension, which helps preterm babies' lungs work better. In some cases, synthetic surfactants are non-biodegradable, thus posing a threat to the environment (Table 4.1). Eco-friendly and biodegradable alternatives are being developed to reduce the impact on the environment (Banjare & Barman, 2024; Banjare & Tandon, 2024).

A drug is any chemical that, when given to the body, alters its composition or function. In addition to relieving symptoms, preventing illness, diagnosing, and treating diseases, drugs have many other uses (Banjare & Tandon, 2024; Ghosh et al., 2020;Karpichev et al., 2021) . The medications can be classified into three groups: prescriptions, over-the-counter medications, and recreational drugs. It is through the interaction of drugs with biological targets such as cells, enzymes, or receptors that drugs produce therapeutic effects (Ghosh et al., 2019; Ghosh et al., 2018). If medication is taken improperly, it can cause danger or adverse effects. Infections are treated with antibiotics, pain is treated with analgesics, and diseases are prevented with vaccinations (Table 4.2). Safety and efficacy are guaranteed when used properly (Ghosh et al., 2017; Ghosh et al., 2024; Banjare et al., 2020).

Surfactants are essential for drug delivery because they improve the solubility, stability, and bioavailability of medicinal substances (Ghosh et al., 2020; Ghosh et al., 2021). The inability of many medications to dissolve well in water restricts their effectiveness and absorption. By lowering surface and interfacial tension, surfactants make it possible to create stable emulsions, micelles, and liposomes that can hold hydrophobic medications and make distribution easier (Panda et al., 2020; Banjare & Baghel, 2023). Surfactants not only increase solubility but also enhance medicine stability by shielding active components from environmental deterioration, such as oxidation or hydrolysis (Banjare & Baghel, 2023). They also improve the permeability of biological membranes, which helps drugs be absorbed and targeted to certain cells or tissues(Karpichev et al., 2022; Ghosh et al., 2020). Injectable, topical, and oral medication formulations are among the many that employ surfactants. They make controlled-release systems and targeted distribution possible, for instance, in cancer treatment, when medications are administered to tumour cells only(Ghosh et al., 2020; Ghosh et al., 2021). Surfactants greatly enhance patient compliance and treatment results by optimising medication characteristics(Ghosh et al., 2019).

Table 4.1 Name and structure of different surfactants

Type of surfactants	**Name of surfactants** **Structures**
Anionic	Sodium dodecyl sulfate (SDS) 
	Sodium tetradecyl sulfate (STS) 
	Docusate 
	Sodium myreth sulfate (SMS) 
	Sodium lauryl sarcosinate (SLS) 
Cationic	Benzalkonium chloride 
	Dodecyl trimethylammonium chloride (DTAC) 
	Tetrabutylammonium hydrogen sulfate (TAHS) 
	Cetylpyridinium chloride (CPC) 
	Methylbenzethonium 
Non-ionic	Polyoxyethylene lauryl ether (Brij-35)

	
	Triton X-100 (TX-100) 
	Decyl polyglucose 
	Isoceteth-20 
	Octyl glucoside 
Zwitterionic	Cocamidopropyl hydroxysultaine 
	Lecithin

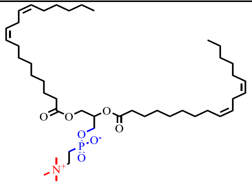
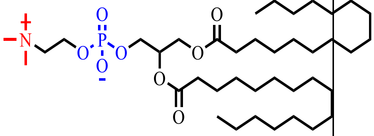
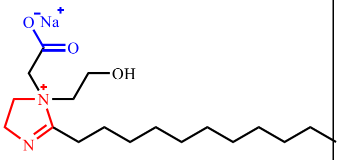
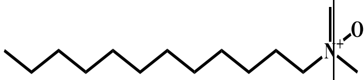
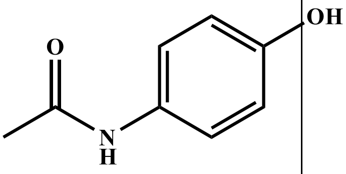
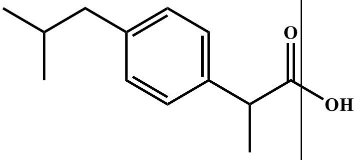
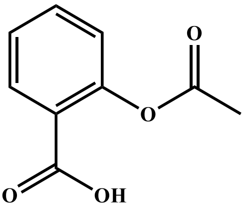
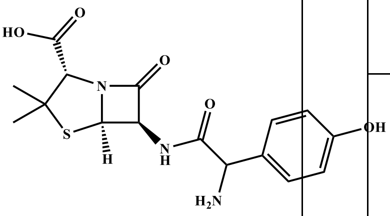
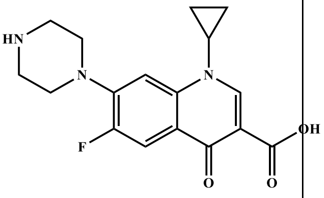
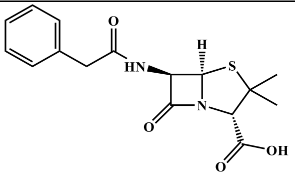
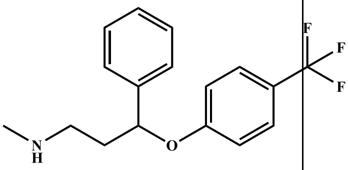
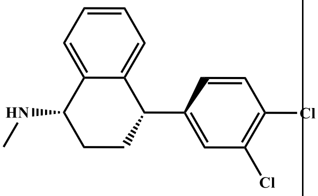
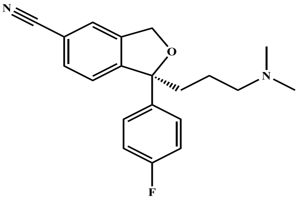
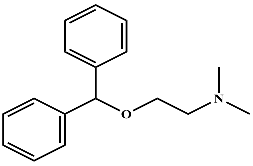
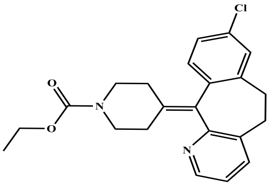
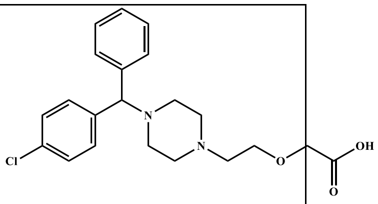
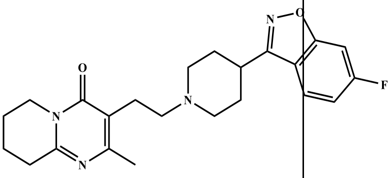
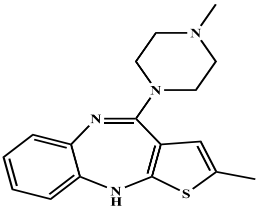
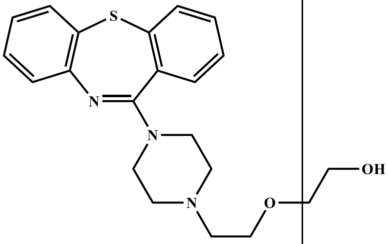
	
	Dipalmitoylphosphatidylcholine 
	Sodium lauroamphoacetate 
	Lauryldimethylamine oxide 

Table 4.2 Name and structure of different drugs.

Type of drugs	Name of drugs/ Structures
Analgesics	Paracetamol (PCM) 
	Ibuprofen (IBU) 
	Aspirin (ASP) 
Antibiotics	Amoxicillin (AMOX) 
	Ciprofloxacin 
	Penicillin 
Antidepressants	Fluoxetine 
	Sertraline 
	Escitalopram 
Antihistamines	Diphenhydramine 
	Loratadine 
	Cetirizine

	
Antipsychotics	Risperidone 
	Olanzapine 
	Quetiapine 

4.2. Drug delivery were studied using different surfactant-based vehicle

Sett et al. [2023] studied the administration of medication to the respiratory system using a surfactant vehicle. Surfactant-delivered medicinal compounds can mainly provide extra advantages, but they may also enhance surfactant function. This technology may find application in clinical settings.

Aydogan et al. [2018] studied the surfactant combinations made of dioctyl sulfosuccinate sodium salt (AOT) and dodecyltrimethylammonium bromide (DTAB) to effectively and efficiently disseminate drugs. When compared to the spreading performances of certain conventional surfactants, the DTAB/AOT mixes' constituents exhibit a synergistic interaction that has improved the formulation drop's spreading on the mucin and CF mucus models.

Gradzielski [2022] permormedthe aqueous polyelectrolyte-surfactant complexes (PESCs) typically consist of lengthy polyelectrolyte chains complexing hydrophobic micellar surfactant aggregates. For possible medication delivery uses, this makes them appealing.

Alara et al. [2023] reviewed the widespread use of magnetic surfactants in medication delivery and DNA compaction. Magnetic surfactants can also be used to transport medications to specific parts of the body. For hydrophobic drug delivery, magnetic surfactants have been employed as nano-carriers. One such magnetic surfactant is magnetic proline-based ionic liquid surfactant.

Chatterjee et al. [2024] performed the drugs with limited oral bioavailability can be produced using self-emulsifying drug delivery systems (SEDDSs) because of their high first-pass metabolism and low water solubility. According to an oral pharmacokinetic research conducted in a rat model, the relative bioavailability of FEN Lf-SEDDS was 1.3 and 5.5 times greater than that of the commercial product and pure medication, respectively. In self-emulsifying medication delivery systems, lactoferrin might be a considerable replacement for synthetic surfactants.

Carabadjac et al. [2024] studied the intravenous distribution of poorly soluble medications, micellar drug delivery systems (MDDS) employ a combination of lecithin and glycocholate (GC) micelles. to describe the competitive binding of human serum albumin (HSA) to GC and the medication substitute anilinonaphthalenesulfonate (ANS). According to the findings, ANS equilibrates between HSA and GC micelles for unbound GC above the CMC, although it strongly favours free sites on HSA.

Wen et al. [2019] reviewed the use of surfactant-based vesicles (Niosomes) as nanocarriers for medication administration because of their ability to provide tailored distribution. A thorough summary of niosomal research to date is given in this review, which also covers the formulation components, niosome types, effects of components on niosome formation, fabrication and purification techniques, niosome physical characterisation techniques, and recent applications.

Grinstaff et al. [2023] studied using a cobalt salen catalyst to create block copolymers of monomethoxylated polyethylene glycol and poly(glycerol carbonate) (mPEG-b-PGC) by ringopening polymerising benzyl glycidyl ether, monomethoxylated polyethylene glycol, and carbon dioxide. While the PTX-loaded nanoparticles are cytotoxic to lung, breast, and ovarian cancer cell lines, the mPEG-b-PGC polymer itself is noncytotoxic.

4.3. Physicochemical determination of surfactant in drug delivery

Several analytical methods are used to ascertain the physicochemical characteristics of surfactants in medication administration(Ghosh et al., 2020; Banjare & Barman, 2024). To assess emulsification efficiency, surface and interfacial tension are assessed using techniques such as the drop count method. Fluorescence spectroscopy, conductivity measurements, or surface tension mapping are used to determine the critical micelle concentration (CMC)(Aminabhavi et al., 2000). The size and shape of micelle or vesicle particles are examined using dynamic light scattering (DLS) and electron microscopy (TEM/SEM). Visual observations or differential scanning calorimetry (DSC) are used to evaluate thermal characteristics like Krafft and cloud points(Hoque et al., 2021; Peng et al., 2016).

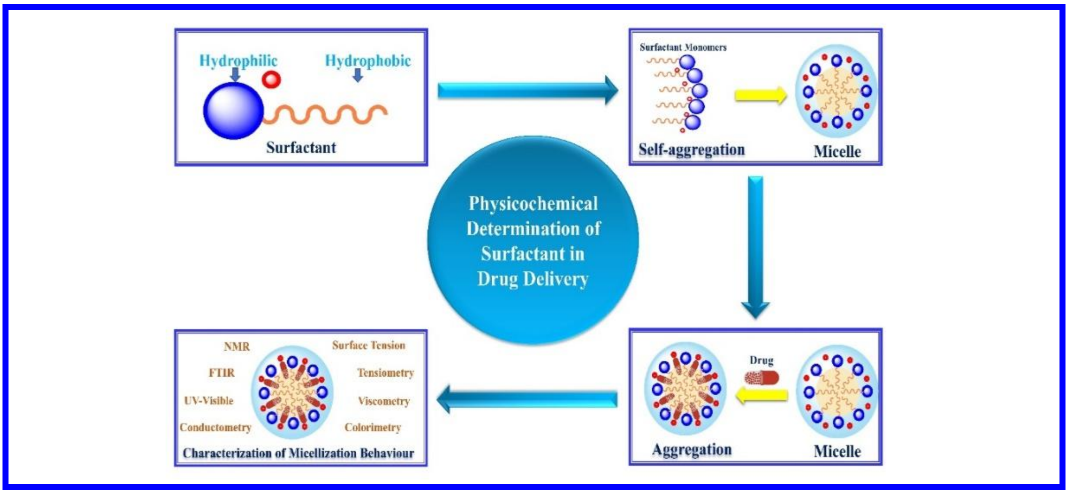


Figure 4.1 A systematic representation of physicochemical determination of surfactant in drug delivery.

Zeta potential analysis assesses colloidal stability, whereas UV-Vis spectroscopy or HPLC are used to estimate solubilization capability. For gel or cream compositions, viscosity is measured using rheometers(Tine et al., 2017). Molecular insights are provided by methods such as mass spectrometry, NMR, and FTIR (Figure 4.1). Cell viability assays are used to evaluate the surfactant's toxicity and biocompatibility, guaranteeing its safety for usage in pharmaceuticals(Peng et al., 2017; Guo et al., 2019). These techniques maximize the efficacy of surfactants in medication delivery systems(Soriyan et al., 2011).

4.4. Mechanism of surfactants in drug delivery

Surfactants are essential for drug administration because they lower interfacial tension and enhance drug solubility, stability, and bioavailability(Chadha&Kumar, 2015). These micelles improve the dispersion of medicinal molecules in aquatic settings by encasing them inside their hydrophobic cores. Micelle production not only improves medication solubility but also shields active components from deterioration(Chfaira&Abram, 2015; Delattre et al., 2015). By breaking down lipid bilayers and increasing membrane permeability, a surfactant can also help with controlled medication release. Emulsions and nanoparticles are stabilised as a consequence, guaranteeing consistent delivery and an extended period of circulation (Figure 4.2). Because they are amphiphilic, they may be included in formulations for a range of delivery methods(Rather et al., 2007; Parkes et al., 2012).

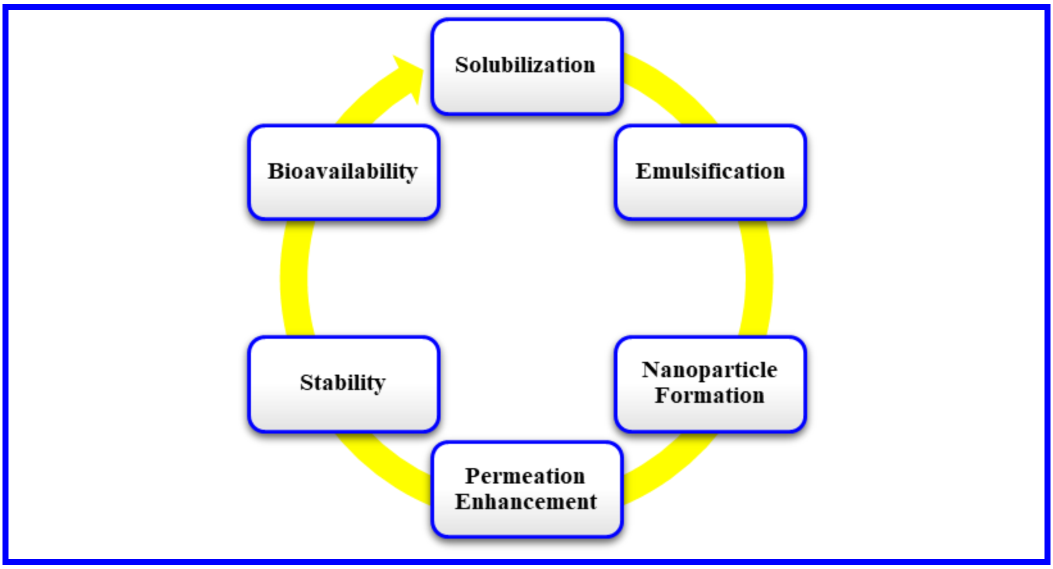


Figure 4.2 A systematic representation of the mechanism of surfactant in drug delivery.

4.4.1. Solubilization

Surfactants improve solubilisation in drug administration by generating micelles in aqueous solutions when their concentration surpasses the critical micelle concentration (CMC) (Wabaidur et al., 2021). Due to their hydrophilic exterior and hydrophobic core, these micelles can encapsulate medications that are not very soluble in water. This method makes hydrophobic medications appear more soluble in water(Hoque et al., 2019; Parkes et al., 2014). Surfactants also increase medication molecule dispersion by lowering surface and interfacial tension, which inhibits aggregation.

Surfactants are crucial for delivering hydrophobic pharmaceuticals in formulations including emulsions, liposomes, and nanosuspensions because of this solubilisation mechanism, which improves drug stability, bioavailability, and therapeutic effectiveness(Chandler, 2005; Ghosh & Baghel, 2008). An indicator of drug association with a micelle is its hydrophobicity (Figure 4.3). A drug molecule that has a black colour indicates a hydrophobic region and one that has a yellow colour indicates a hydrophilic region. Completely water-insoluble compounds can be integrated into the micelle core (case 5), and completely water-soluble compounds can be adsorbed into the micelle outer compartment (case 1). Drug compounds with an intermediate hydrophobic/hydrophilic ratio (cases 2 to 4) will interact with the micelle particle(Torchilin, 2001; Hegazy et al., 2008).

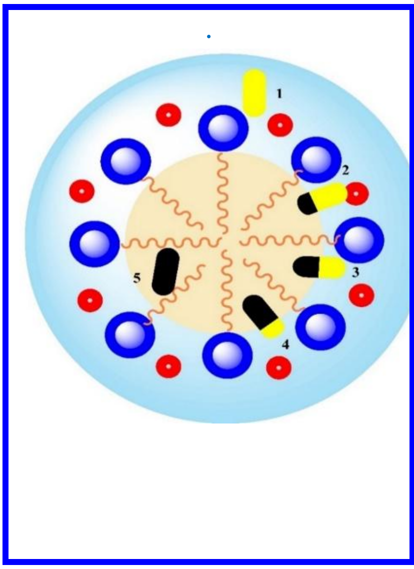


Figure 4.3 A systematic representation of drug solubility in micelle.

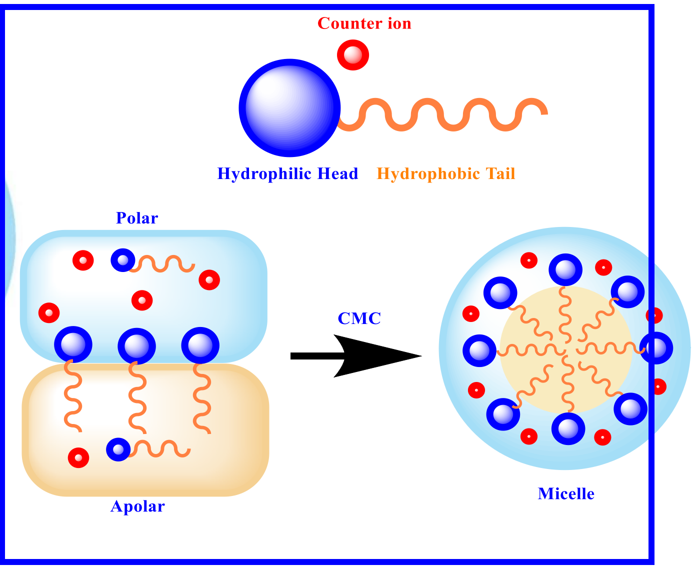


Figure 4.4 A systematic representation of micelle formation of surfactant

4.4.2. Emulsification

Surfactants help immiscible phases, such as water and oil, create stable emulsions by lowering the interfacial tension between them(Moulik et al., 2013). This makes emulsification easier in medication delivery. By adhering to the oil-water interface and creating a barrier around the droplets, surfactants stabilise these emulsions and stop them from coalescing. With hydrophilic and hydrophobic segments, their amphiphilic nature allows them to stabilise water-in-oil (W/O) or oil-in-water (O/W) emulsions, depending on the formulation(Kaur & Kumar, 2020; Kumari et al., 2013). Hydrophobic medications are made more soluble and bioavailable by this emulsification process, which also makes it possible for them to disperse uniformly in aqueous solutions (Figure 4.4). Along with protecting active ingredients and enhancing medication stability in emulsion-based delivery systems, surfactants help regulate drug release(Hu et al., 2010; Robards et al., 1998).

4.4.3. Nanoparticle formation

Surfactants are essential for the production of nanoparticles in drug administration because they stabilise and regulate their size. Surfactants stop drug particles from aggregating by lowering the surface tension at their contact with the surrounding liquid(Walker& Singh, 2006). They can adsorb onto the surface of nanoparticles due to their amphiphilic nature, creating an electrostatic or steric barrier that stabilises the particles(Shurdut et al., 2000). Surfactants help in emulsification during nanoparticle production, regulating the development and nucleation of nanoparticles. In delivery systems based on nanoparticles, this process guarantees consistent particle size, increases drug loading capacity, and improves the solubility, stability, and bioavailability of hydrophobic medicines(Rogers&Stringfellow, 2009).

4.4.4. Permeation enhancement

Surfactants improve medication distribution by breaking down biological barriers including cellular lipid bilayers and the stratum corneum(Cooper et al., 2013). They can interact with lipid membranes and fluidise them due to their amphiphilic nature, which increases permeability and decreases stiffness. Additionally, by altering the configuration of tight junctions between cells, surfactants can promote paracellular transport(Sharafi et al., 2017; Ghambarian et al., 2016). They guarantee a greater drug concentration at the absorption site and encourage diffusion by solubilising hydrophobic medications. Surfactants also lessen surface tension, which improves the way drugs enter tissues. This permeation-enhancing process is commonly utilised in transdermal, nasal, and oral drug delivery systems and enhances drug absorption, especially for less permeable medicines(Fernandez-Alba et al., 2018; Sharafi et al., 2015).

4.4.5. Stability

Surfactants improve stability in drug delivery by stopping drug molecules from aggregating, precipitating, and degrading(Jin et al., 2005). By adhering to the surface of drug particles or droplets, they create a barrier that lowers interfacial tension and stops flocculation or coalescence in dispersions such as emulsions and suspensions. Additionally, surfactants protect medications against environmental elements including oxidation, pH fluctuations, and enzymatic breakdown(Papadopoulou-Mourkidou et al., 2015). Throughout storage and usage, surfactants preserve the drug's therapeutic efficacy, guarantee homogeneity, and extend shelf life by stabilising formulations at the molecular and particle levels(Delattre et al., 2016; Aaron et al., 2015).

4.4.6. Bioavailability

Surfactants increase the solubility, permeability, and stability of medications, which in turn increases drug bioavailability(Tine et al., 2015). By creating micelles, which enclose hydrophobic drug molecules and allow for their dispersion in aqueous settings, they improve the solubilisation of medications that are poorly soluble in water. By rupturing lipid membranes or altering tight junctions, surfactants also increase permeability, which makes it easier for drugs to pass through biological barriers(Tine et al., 2014; Schafer et al., 2016). Furthermore, they prevent drug formulations from degrading, guaranteeing that more active medications enter the bloodstream. Surfactants facilitate uniform drug distribution and absorption by lowering surface and interfacial tension, which eventually raises the bioavailability of medications, particularly those with limited permeability or solubility(Wu et al., 2018; Wang et al., 2007).

4.5. Types of surfactants in drug delivery

The ability of surfactants to lower surface tension and enhance the solubility, stability, and bioavailability of medications makes them popular in drug delivery systems (Figure 4.5 and 4.6). Based on their ionic nature, the many kinds of surfactants employed in drug delivery can be divided into several categories(Huddleston et al., 2011; Sun et al., 2016).

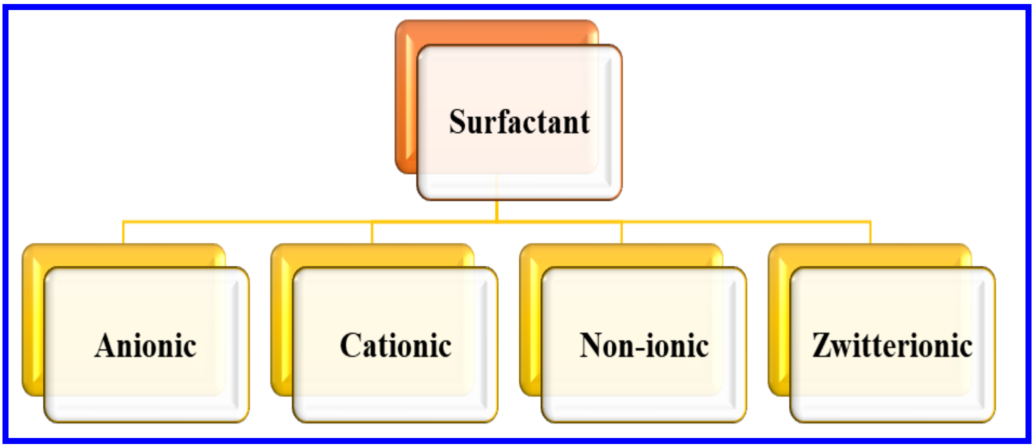


Figure 4.5 A systematic representation of types of surfactant.

4.5.1. Anionic surfactant

The anionic surfactants increase the solubility, stability, and bioavailability of medications that are not particularly soluble in water, they are essential for drug administration. The hydrophilic head of these surfactants is negatively charged, which allows them to interact with avariety of pharmacological compounds and biological membranes(Wang& Zhang, 2017; Korade&Fulekar, 2009). To efficiently encapsulate and distribute hydrophobic medications, they are frequently utilised in emulsion, micelle, and nanoparticle formulations. Notwithstanding their benefits, anionic surfactants require careful optimisation since they may be irritating and harmful at high doses(Tejada et al., 2017). More research is being done to create safer, biodegradable anionic surfactants so that they may be used in more sophisticated medication delivery systems. One typical example is the well-known anionic surfactant sodium lauryl sulphate (SLS), which is utilised in medicinal formulations(Silambarasan& Abraham, 2013). SLS stabilises and improves medication solubilisation in emulsions and dispersions. To enhance drug release characteristics, it is also utilised in parenteral, topical, and oral formulations(Barbosa et al., 2009).

4.5.2. Cationic surfactant

Cationic surfactants have a positive charge that allows them to interact strongly with negatively charged biological membranes and molecules like DNA or RNA, they are frequently used in medication delivery(Abraham& Silambarasan, 2016). They are very useful for gene transfer, transfection, and nanoparticle stabilisation because of this characteristic. Targeted delivery, cellular uptake, and medication solubility are all improved by cationic surfactants. However, as compared to non-ionic or anionic surfactants, cationic surfactants may show increased haemolytic activity and cytotoxicity(Lamus& Abdelghani, 2000; Zheng et al., 2016). Because of this, their utilisation necessitates careful formulation design in drug delivery applications to balance safety and effectiveness. One such example is the cationic surfactant cetyltrimethylammonium bromide (CTAB), which is frequently utilised in nanoparticle formulations. To encapsulate hydrophobic medications and improve their delivery effectiveness, CTAB helps create stable emulsions and liposomes.It is also used as a transfection agent in gene therapy to encourage cells to absorb genetic material(Aqil et al., 2016; Pal et al., 2014).

4.5.3. Non-ionic surfactant

Non-ionic surfactants are frequently utilised in drug administration because of their excellent biocompatibility, low toxicity, and formulation stabilising capabilities. Because they don't have a net charge, these surfactants are less prone to interfere with biological membranes(Zhang et al., 2014). In addition to creating micelles, emulsions, and nanoparticles, they are very good at improving the stability and solubility of hydrophobic medications. Non-ionic surfactants can be used in a wide range of medication delivery methods, such as parenteral, transdermal, and oral. They are perfect for novel medication administration methods, such as those based on nanotechnology, because of their low irritancy and wide variety of functions(Mehta et al., 2015;Müllertz et al., 2014). One well-known example is polysorbate 80, sometimes known as Tween 80, a non-ionic surfactant that is frequently used in pharmaceutical formulations.To increase drug stability and dispersion, polysorbate 80 is utilised in injectable medications, vaccinations, and lipid-based drug delivery systems. Additionally, it keeps proteins from clumping together in biopharmaceuticals, guaranteeing steady therapeutic effectiveness(Guan et al., 2015; Chourasia et al., 2016).

4.5.4. Zwitterionic surfactant

Zwitterionic surfactants have a net neutral charge because their hydrophilic head groups are both positively and negatively charged. They are ideal for drug delivery applications because of their special shape, which offers superior biocompatibility, minimal toxicity, and less interactions with biological membranes(Shakeel& Ramadan, 2010; Nicolosi et al., 2008). Zwitterionic surfactants have a reputation for being stable in intricate biological settings and having antifouling qualities. Because they can reduce immunological recognition and protein adsorption, zwitterionic surfactants are also becoming more popular in the creation of nanocarriers. This allows for longer circulation durations and better therapeutic effectiveness(Shafiq et al., 2008). Phosphatidylcholine, a naturally occurring zwitterionic surfactant often present in liposomes, is a noteworthy example. It is often utilised in the creation of lipid-based drug delivery systems, such as liposomal carriers for vaccinations, genetic treatments, and anticancer medications(Roessler et al., 2001; Roessler et al., 2001).The lipid bilayer is stabilised by phosphatidylcholine, which also makes it possible to encapsulate hydrophilic and hydrophobic medications, improving their solubility, stability, and targeted administration(Nicolosi et al., 2008).

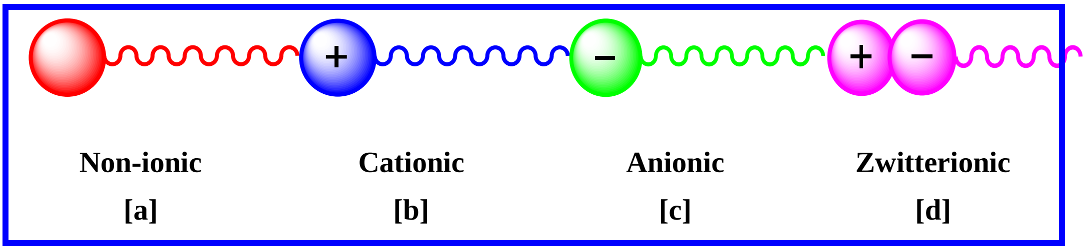


Figure 4.6 A systematic representation of surfactant molecules.

4.6. Surfactants in drug delivery

Surfactants are essential for drug administration because they increase the stability, solubility, and bioavailability of medications that are not particularly soluble in water(Nicolosi et al., 2011). They work by enhancing absorption, enabling drug dispersion, and lowering surface and interfacial tension. The four types of surfactants are zwitterionic (like lecithin), cationic (like cetyltrimethylammonium bromide), non-ionic (like Tween 80), and anionic (like sodium lauryl sulphate). Solid dispersions, micelle-forming systems, and self-emulsifying drug delivery systems (SEDDS) all often involve surfactants. Micelles are linked to polymeric and non-polymeric surfactants that are in a state of dynamic equilibrium with systemic monomers(Baker et al., 1999; Baker et al., 2002). As a result, its structure may be adjusted to suit variations in the medium. The process by which counterions are drawn to the micelle by electrostatic forces. According to Table 4.3, micelle size, shape, and additional phase change are significantly impacted by counter ion repulsion and its effects on hydration and subsequent solubilisation. Diblock copolymers and tri-block copolymers are the biodegradable polymers that make up the new-generation drug delivery micelle. For the majority of diblock copolymers, the insoluble portion of the block aggregates into the micelle's core side, while the soluble segment forms the outer side(Ahmad et al., 2017; Duan et al., 2009). Among them, non-ionic surfactants are favoured because of their superior compatibility and reduced toxicity. They improve medication solubility by encasing hydrophobic drug molecules in micelles. Certain surfactants influence tight junctions or cell membranes to increase intestinal permeability.To ensure that the surfactant is safe and effective for administration, however, cautious selection is necessary to reduce adverse effects including gastrointestinal discomfort(Baker et al., 2001).

4.6.1. Improving drug bioavailability

Surfactants are essential for improving medication bioavailability in drug delivery because they solve issues with many medicines' limited absorption and low solubility. They facilitate the dispersion of hydrophobic medications in gastrointestinal fluids by lowering surface and interfacial tension(Yilmaz& Borchert, 2005; Benita et al., 2010). Surfactants increase the apparent solubility and prevent degradation of lipophilic medicines by encasing them in micelles. Better dissolving rates result from this, which is crucial for raising bioavailability. Additionally, surfactants can alter intestinal permeability by interacting with cell membranes or releasing tight junctions, which makes it easier for drugs to pass through the intestinal epithelium(Guterres et al., 2007). Polysorbates (e.g., Tween 80) and other non-ionic surfactants are frequently utilised because of their compatibility with biological systems and reduced toxicity. In some formulations, anionic and cationic surfactants can work well, but they are less commonly utilised. To get the best possible therapeutic effectiveness through increased bioavailability, surfactants are crucial in contemporary drug delivery systems(Benita et al., 2012; Sheth et al., 2016).

4.6.2. Formulation of solid dosage forms

The goal of developing solid dosage forms using surfactants for drug administration is to increase the solubility, stability, and bioavailability of medications that are not highly soluble in water(Oh et al., 2016; Pathak et al., 2008). To improve medicine dispersion and absorption, surfactants are used into solidformulations including pills, capsules, and powders. Surfactants such as sodium lauryl sulphate (SLS) are employed as wetting agents in tablet formulations to help ensure that medication particles are distributed uniformly throughout gastrointestinal fluids(Kawaoka et al., 2012). Surfactants, like Tween 80, are mixed with oils and cosurfactants in self-emulsifying drug delivery systems (SEDDS) to create preconcentrates that are then enclosed in soft or hard gelatin capsules. When these systems come into touch with stomach fluids, they self-emulsify and create fine oil-in-water emulsions that enhance medication solubility(Myc et al., 2015). To improve dissolving rates and stabilise amorphous drug forms, solid dispersions include surfactants in the polymer matrix. Surfactants in solid dosage forms are essential for resolving issues with medication delivery's solubility and bioavailability(Amiji et al., 2016).

4.6.3. Nanocarriers

Surfactant-containing nanocarriers are novel drug delivery methods intended to increase the therapeutic effectiveness and bioavailability of medications that are not highly soluble in water. Solid lipid nanoparticles (SLNs), micelles, nanoemulsions, and nanostructured lipid carriers (NLCs) are examples of nanocarriers that depend on surfactants to improve intestinal permeability, stability, and solubilisation(Pidaparthi& Suares, 2016; Sanjula et al., 2016). By lowering interfacial tension and inhibiting particle aggregation, surfactants serve as stabilising agents in these systems. Surfactants such as lecithin and polysorbates (like Tween 80) encapsulate hydrophobic medications in micelles and nanoemulsions, enhancing their solubility and shielding them from enzymatic breakdown. Surfactants like sodium lauryl sulphate (SLS) or Pluronics aid in stabilising the lipid matrix and facilitating drug loading in SLNs and NLCs(Kumar& Jain, 2016; Boche&Pokharkar, 2016). By altering the permeability of intestinal membranes or encouraging lymphatic transport, surfactants can also improve medication absorption. For the delivery of poorly soluble medications with enhanced bioavailability and regulated release patterns, surfactant-based nanocarriers are very successful due to these characteristics(Sanjula et al., 2016).

4.7. Challenges and limitations of surfactants in drug delivery

Surfactants have drawbacks and restrictions even though they have several advantages in medication administration. They may be poisonous and irritating, especially at large dosages or after extended usage, which is a big worry(Alonso et al., 2006; Tiwari& Amiji, 2006). Some surfactants might cause inflammation or hypersensitivity by rupturing cellular membranes or triggering immunological reactions. Cationic surfactants, for example, are often more cytotoxic than their non-ionic counterparts. Stability of medication delivery systems based on surfactants is another issue. Drug release or degradation may occur sooner if micelles, emulsions, or nanoparticles become unstable due to environmental conditions such as pH, temperature, and ionic strength. Problems with compatibility with other formulation elements might also occur, which would impact the total effectiveness(Cabral et al., 2012).Furthermore, it might be challenging to attain consistent therapeutic results due to surfactants' variability in drug encapsulation efficiency and release characteristics (Figure 4.7). Because strict testing and quality control are necessary to guarantee the safety, scalability, and repeatability of surfactant-based systems, regulatory obstacles are also substantial(Shridharan et al., 2012). Last but not least, the broad use of biocompatible, biodegradable surfactants is hindered by their high manufacturing costs and scarcity. Advanced research on safer, more effective surfactants and creative formulation techniques are essential to overcoming these obstacles and realising their full promise in drug delivery systems(Ali et al., 2007).

Table 4.3 Drug delivery using micelles of surfactants

Surfactant	Size (nm)	Drug	Ref.
Non-polymeric micelles			
SDS	200	Diphenhydramine, Tetracaine, Camptothecin (CPT)	122, 123, 124
Polysorbate 80	-	Itazigrel	125
Cremophor	-	Paclitaxel (PTX)	126
Polymeric micelles			
Methoxy(PEG)-block-poly(5-benzyloxy-trimethylene carbonate)	96	Ellipticine	127
PEG-PE (phosphatidyl ethanolamine)	-	Anticancer drug	128
Poly(p-Dioxznone-co-L-Lactide)-b-PEG(PPDO/PLLA-b-PEG)	60-165	β-Glactosidase	129
PEG-block-poly(phenylalanine)(PEG-b-PPhe)	55-58	Paclitaxel (PTX)	130
Methoxy(PEG)-poly(caprolactone/trimethylene carbonate) Diblock PEG-poly(CL-co-TMC)	-	Risperidone	131
Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide)(PEO-PPO-PEO)	50	Fentanyl	132
Poly(caprolactone)-b-poly(ethylene oxide)(PCL-b-PEO)	500-600	Dihydrotestosterone (DHT)	133
Poly(epsilon-caprolactone)(poloxamer 188), Poly(ethyleneoxide)-b-PBLA(PEO-b-PBLA)	-	Amphotericin B (AMB)	134, 135
Cholesterol end capped PEO-b-Cholesterol-end-capped poly(2-methyacryloyloxyethyl phosphorylcholine)(CEPEO-b-CMPC)	-	Adriamycin (A DR)	136

4.8 Future perspectives and innovations

Surfactants' future in drug delivery depends on improving their functioning, design, and use to get beyond current obstacles. Creating biocompatible and biodegradable surfactants is a major priority to reduce toxicity and negative responses(Ahmad et al., 2011). For increased safety and effectiveness, researchers are investigating both natural surfactants, such as phospholipids, and synthesised ones with specific characteristics. There are potential advancements in surfactant-based systems thanks to nanotechnology. The production of nanostructured carriers such as solid lipid nanoparticles, liposomes, and micelles depends heavily on surfactants. By enabling precise medication targeting and regulated release, these devices improve therapeutic results while reducing adverse effects(Zhang et al., 2011; Ghorab et al., 2016). Furthermore, there are efforts underway to produce smart surfactants that react to pH, temperature, or enzymes, enabling on-demand medication release in certain settings, including cancer locations or inflammatory tissues (Figure 4.8). Additionally, surfactant-based carriers are being combined with cutting-edge medication delivery strategies including gene therapy and RNA-based treatments. These methods enhance cellular absorption and safeguard genetic material, creating new treatment options for illnesses that were previously incurable(Lal et al., 2016; Jia et al., 2016). Future developments will also concentrate on economical formulations and environmentally friendly production techniques to increase the accessibility of surfactant-based medication delivery systems on a worldwide scale(Abd El-Gawad et al., 2016). By combining cutting-edge materials science and bioengineering, surfactants' full promise to transform contemporary medicine is probably going to be realised(Au et al., 1999).

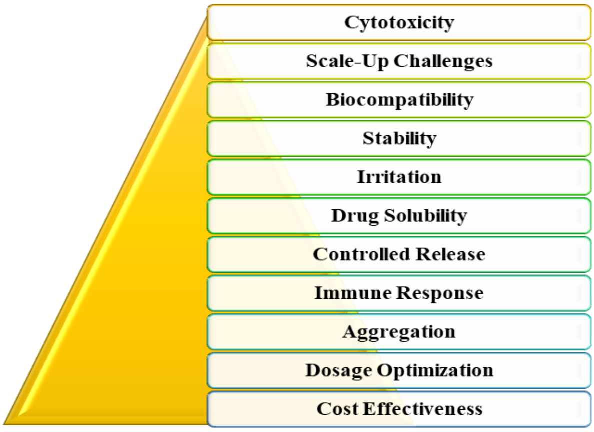


Figure 4.7 A systematic representation of challenges and limitations of surfactant in drug delivery.

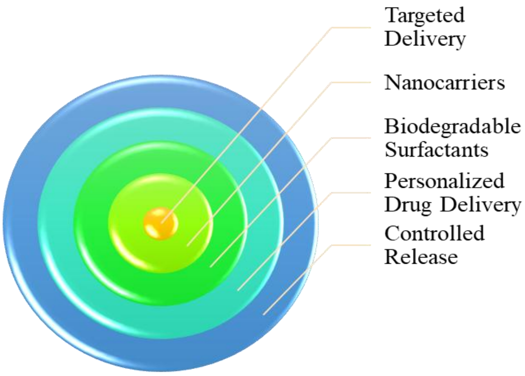


Figure 4.8 A systematic representation of future perspectives and innovations.

4.8 Conclusions

In drug delivery systems, surfactants are essential because they improve the solubility, stability, and bioavailability of medications that are not particularly soluble in water. Hydrophobic medications can be delivered thanks to these amphiphilic compounds' ability to lower surface tension and promote the production of micelles, emulsions, and nanoparticles. Surfactants are used in several medication delivery methods, such as parenteral, transdermal, and oral. Additionally, they help with better medication targeting, controlled drug release, and fewer adverse effects. Catalytic surfactants like cetyltrimethylammonium bromide, anionic surfactants like sodium lauryl sulphate, and non-ionic surfactants like polysorbates are all often utilised. To sum up, surfactants are essential to contemporary pharmaceutical formulations because they provide effective and efficient drug delivery. Through the optimisation of medication stability and solubility, they tackle important issues in drug development. Drug delivery might be revolutionised by further research into innovative surfactant-based systems, especially in targeted treatment and nanomedicine, which will improve patient outcomes and therapeutic efficacy.

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Chapter 5: Application of Surfactants in Personal Care Products Formulation

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Abstract

As a responsive ecosystem that interacts with the environment to promote general health, the human skin is essential to the immune system. Because of its capacity to lower surface tension, emulsify oils, wash, and produce foam, surfactants are frequently employed in cosmetic compositions. They are essential components of many different kinds of products, including face cleansers, body washes, shampoos, and lotions. Cosmetics and customised care items that contain surfactants can help protect and nourish the skin. Surfactants are surface-active substances that have a unique physical property that enables them to adsorb at the contact. Micelles are formed when surfactant monomers assemble in liquids. Research and development of personal care cosmetics with surfactant-based ingredients are funded by a global marketplace for items pertaining to personal care formulations. The study looks at the active chemicals or raw materials that come from surfactant systems and are used in cosmetics and personal care products. Face masks, gel-based leave-on skin care products, and face washes are among the products used in this study. formulations that combine antioxidants (AO) with multifunctional active ingredients. Without causing product degradation, the successful combinations were able to endure difficulties. By carefully choosing multifunctional actives, antioxidants, and chelators for the formulation, self-preserving cosmetics and personal care products can be created that are just as effective as preserved ones.

Keywords: Personal care products, Surfactants, Formulation science, Emulsification, foaming agents, Cleansing agents.

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5.1 Introduction

The efficacy of personal care products, such as skincare and haircare formulas, is largely dependent on surfactants. These amphiphilic molecules facilitate the mixing of water and oil phases and reduce surface tension, which is essential for the formation of foam, emulsions, and detergency. Because of growing consumer awareness and regulatory concerns, there is a greater need for mild, environmentally friendly surfactants.Cosmetics are products designed for "cleansing, beautifying, promoting attractiveness, or altering" the appearance without affecting the body's structure or functions (Attwood et al., 1983, Barman et al., 2024). They are widely used for skincare, haircare, and personal grooming, with formulations tailored to various needs and preferences (Azarmi et al., 2015). Surfactants are essential ingredients in many cosmetic and personal care products (Banjare et al., 2024). They play a crucial role in formulations due to their unique molecular structure, which allows them to reduce surface tension between two substances, such as oil and water. Cosmetics are as a face wash is a skincare product designed to cleanse the face by removing dirt, oil, makeup, and impurities from the skin's surface (Barman et al., 2024). It is an essential part of a daily skincare routine and is formulated for various skin types and concerns, other is shampoo is a haircare product designed to cleanse the scalp and hair by removing dirt, oil, sweat, and product buildup. It is a fundamental part of hair hygiene and is formulated to cater to different hair types, concerns, and styling preferences and Face cream is a skincare product designed to hydrate, nourish, and protect the skin. It forms a critical part of daily skincare routines and caters to various skin concerns, including dryness, aging, and sensitivity etc.

Review of Literature

The function of surfactants in personal care formulations has been the subject of several investigations. According to research, sulfate-free alternatives have been developed because anionic surfactants, such as SLS, offer superior washing but may irritate skin (Smith et al., 2021). Developments in biodegradable surfactants have also helped create environmentally friendly formulations without sacrificing effectiveness (Karsa et al., 2012).In contrast, nonionic and amphoteric surfactants have shown less risk for irritation while yet having good cleaning qualities (Salomon et al., 2022).Synergistic formulations, which combine surfactant combinations to maximise washing effectiveness while minimising any irritation, have also been studied recently. For example, it has been demonstrated that adding amphoteric surfactants to formulations that contain anionic surfactants improves mildness without compromising foaming capacity(Lechuga et al., 2025).Furthermore, new formulations using enzyme-modified surfactants from natural sources are demonstrating the growing popularity of green chemistry and biodegradable surfactants. These developments meet customer demand for eco-friendly personal care products that strike a balance between effectiveness and environmental responsibility(Hossein et al., 2023).According to the literature, there is an increasing trend towards multifunctional, gentle, and sustainable surfactants that satisfy both consumer and regulatory requirements. The future of the personal care sector will probably be shaped by novel formulation techniques that use bio-based and low-irritancy surfactants as research progresses.

5.2History

In ancient time various region had used different natural products as a cosmetic for enhance their beauty such region as a: In Egypt, Ancient Egypt was among the first societies to employ cosmetics, with both men and women using makeup to improve their looks (Chaudhari et al., 2011). In Egypt, cosmetics were initially used 5,000 years ago. Women used white to shield their faces from the sun, and incense oils were used to soften the skin and provide a nice scent (Scottet al al., 2016). Additionally, the Egyptians were the first to apply eyeliner using black paint based on antimony. Additionally, they would crush flowers to produce a natural blush (Lucas et al., 1930).The ninth century C.E., women from the Sakalava and Vezo tribes of Madagascar started donning masonjoany, a beautiful paste made from powdered wood (Blanco et al., 2000). In addition to serving as sunscreen and insect repellant, ladies use it to decorate their faces by using white and yellow pastes to paint flowers, leaves, and stars. The custom stems from the cultural interaction between Malagasy and Arab traders near the island's northwest coast.Royal family ladies of Mongolia painted red dots directly beneath their eyes, in the middle of their cheeks. But the reason remains a mystery. They said that a joyful queen's rosy cheeks, or face blush, were the cause. Blusher lifts the cosmetic appearance by highlighting the cheekbones and improving the contour of the face. Beauty products are now widely accessible and utilised by both men and women to treat their own skin and bodies in the twenty-first century. Even though women have historically worn most contemporary makeup, more and more men are increasingly utilising traditionally feminine cosmetics to accentuate their own facial characteristics.

5.3Emerging Trends and Sustainable Alternatives: Biodegradability and sustainability are the main topics of recent developments in surfactant technology. Bio-based surfactants provide gentler and more environmentally friendly alternatives as they are made from renewable resources like sugar and coconut oil. Formulations without sulphates are becoming more and more popular since they are less likely to cause irritation. Furthermore, enzymatically produced surfactants that provide enhanced performance with no environmental effect are the result of developments in green chemistry.

5.4Impact on Skin and Hair: Although surfactants are necessary in formulations for personal care products, it is important to take into account how they affect skin and hair. Dryness and discomfort can result from the removal of natural lipids by harsh surfactants like SLS. To lessen these effects, formulators frequently combine mild surfactants or add conditioning ingredients. Skin compatibility is further improved by humectants and pH changes.

5.5 Cleansing action of soap and detergents

The cleansing action of detergents is due to their ability to:

Reduce surface tension: Detergents can reduce the surface tension of water.

Emulsify oil and grease: Detergents can emulsify oil and grease.

Suspend oil and grease in water: Detergents can keep oil and grease suspended in water.

Detergents work by forming micelles, which are clusters of detergent molecules that help dissolve dirt (Jayarathne et al., 2024).

Here's how detergents work:

Micelle formation: When detergent is dissolved in water, the detergent molecules gather together to form micelles (Tsurtsumia et al., 2021).

Dirt attachment: When dirty clothes are dipped in the detergent solution, the dirt particles attach to the hydrocarbon part of the detergent molecules (Johnson et al., 1999).

Washing: When the clothes are agitated in the detergent solution, the dirt particles are washed away in the water. Detergents are effective in hard water because they don't form insoluble calcium or magnesium salts. Soaps, on the other hand, are not suitable for hard water because they do form these salts. Show in fig.5.1.

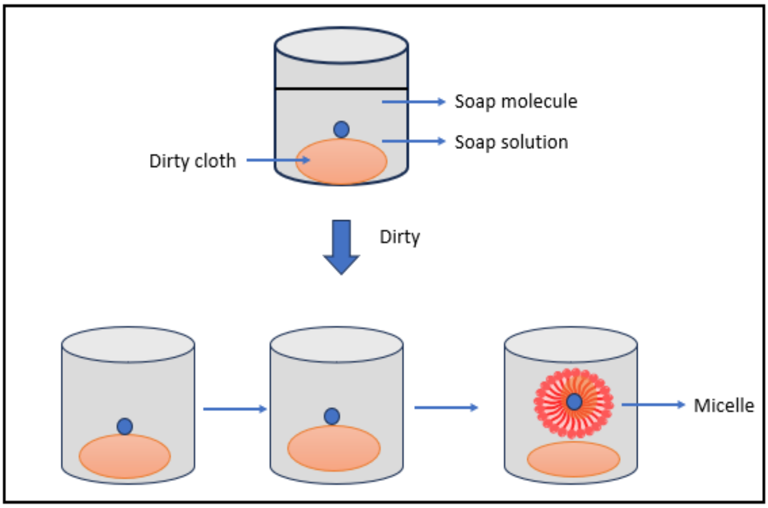

Figure 5.1. Cleansing action of soap or detergents

5.6 Surfactants in health and personal care products

Detergents also use cationic quaternary ammonium surfactants (quats), which have strong germicidal activity, as fabric softeners. ditallow dimethyl ammonium chloride, a fabric softener and antistatic, is the most widely used. Germicides, such as Benzalkonium chlorides, frequently have a N-ADBAC structure, in contrast to emulsifiers, which frequently have a N-alkyl imidazoline chloride configuration or N-alkyl trimethylammonium chloride (N-ATAC) (Miller et al., 1991).The following requirements—light detergency, good foaming, passable conditioning, adequately maintained—are frequently satisfied when making shampoo. The term "natural surfactant" can be used to describe a surfactant that was chemically synthesized from one as well as one that was extracted directly from a natural source (Gu et al., 1992). New emulsion formulation processes are essential for cosmetic formulations, especially for their preservation capabilities. The incredibly small droplet sizes and exceptional stability of the phase inversion temperature emulsion and microemulsion set them apart from other types of emulsions. A transparent, aesthetically pleasing O/W formulation can be made with the use of microemulsions.

5.7 Surfactants and detergency

The ability of surfactants to adsorb at interfaces and reduce the energy required to complete the removal of foreign material from solid surfaces is known as their detergent action. At the appropriate interfaces, the best wetting agents frequently diffuse and adsorb rapidly (Wanguo et al., 2016). With a minimum of eight carbon atoms and a long history of use as a detergent, soap is a surface-active fatty acid salt. When fats and glyceride oils are saponified with KOH or NaOH in the past to make soap, glycerol is created as a by-product. Despite the fact that soaps are excellent deodorizers, they are sensitive to acidic pHs and the hardness (Ca^{2+} and Mg^{2+} ions) of the water, which leads to soap scum. Synthetic detergents have mostly replaced soaps, yet the use of detergent producers will make up for this drawback (Bain et al., 1912). The ingredients that are used to formulate commercial detergents account for the majority of the manufacturing of surfactants.

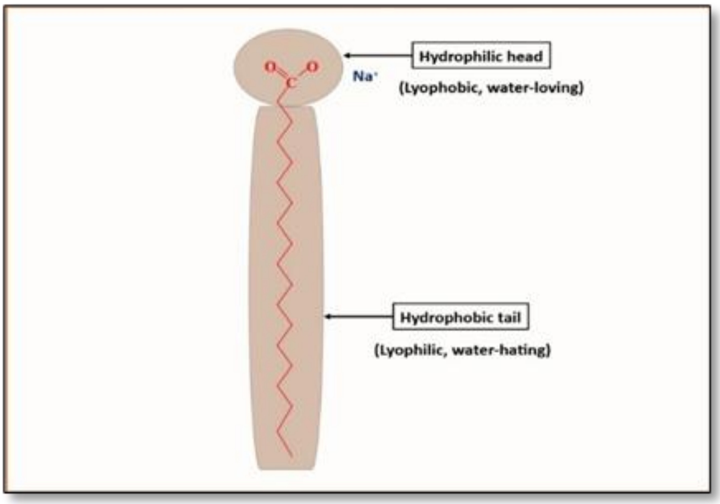

Figure 5.2 Structure of surfactant molecule

5.8 Types of surfactants in cosmetics

Surfactants are available in many forms, and are generally classified based on charge of the surface-active molecules such as anionic, non-ionic, cationic. Fig.5.2 show thestructure of surfactant molecule and Fig.5.3show the types of surfactants and their molecular structure.

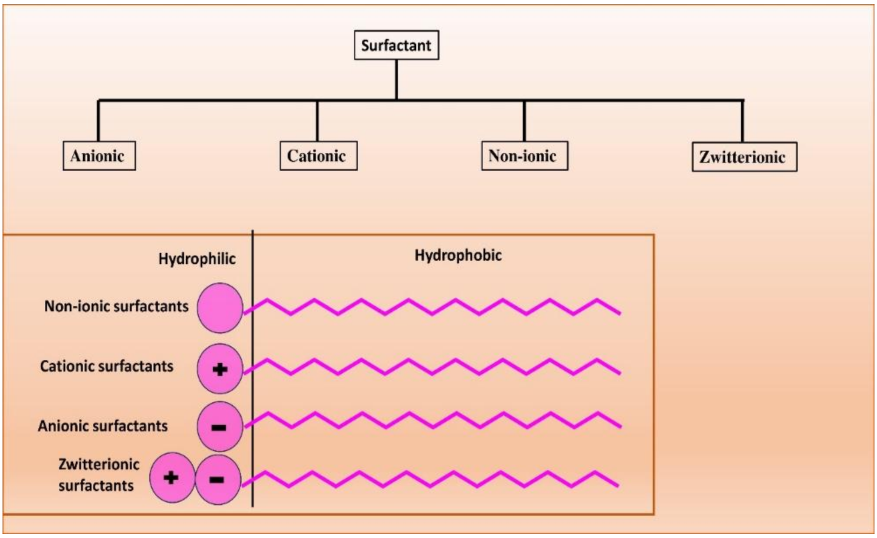

Figure 5.3 Types of surfactants and their molecular structure

5.8.1 Anionic surfactants

Anionic surfactants are made up of anionic functional groups like sulphate, sulfonate, phosphate, and carboxylate. Soaps are anionic surfactants produced by saponifying natural fats and oils, making them the most prevalent type of surfactant(Wang et al., 2023). The metal salt of an alkali carboxylic acid [R-COOH] that was originally generated from plant- or animal-based fats is referred to as "soap" in this context. The bulk of the time, the base of soap bars is a mixture of tallow and coconut fatty acids. Excellent cleansing and foaming properties. Common examples: Sodium lauryl sulfate (SLS), Sodium laurethsulfate (SLES), Alpha Olefin Sulfonates (AOS) etc.

5.8.2 Cationic surfactants

In this category, the hydrophilic element is positively charged. It sticks to surfaces and may have soil-repelling, antistatic, softening, antibacterial, or corrosion-inhibiting properties despite the fact that this group doesn't have any wash activity. In many typical uses, they serve as softeners (fabric softeners) and antistatic. Used in conditioners for their antistatic and conditioning properties. example of cationic surfactants is Behentrimonium chloride (BTAC), cetyltrimethyl ammonium bromide (CTAB) etc.

5.8.3 Non-ionic surfactants

Non-ionic surfactants contain hydrophilic elements that are not charged. These materials clean effectively and are unaffected by water. They come from groups like fatty alcohol polyglycosides and alcohol ethoxylates and are typically discovered in cleaning detergents. Non-ionic surfactants Mild and used in emulsions. Common examples: Polysorbates, Decyl glucoside etc.

5.8.4 Zwitterionic surfactants

A zwitterionic surfactant is made up of two groups (anionic and cationic) having diametrically opposed charges. Zwitterions are typically referred to as "amphoteric," yet both concepts are distinct. An amphoteric surfactant is one that undergoes a pH change from low to high and changes from a net cation to a net anion via Zwitterion. Mild and compatible with other surfactants. Common examples: Cocamidopropyl betaine, Lauramidopropyl betaine etc.

5.9 Micelles

Surfactant molecules have a drive to assemble above the cmc to create micelle-like structures. Usually, 10-100 of surfactant molecules make up a micelle. The amount of surfactant monomers in a micelle can be determined by its aggregation number(Arai et al., 1966). The molecular weight of the surfactant monomer by the aggregation number, one can determine the molecular weight of a micelle. Conversely, micelles grow and spread in milliseconds. But as the surfactant concentration and the surfactant's size and properties change, these time scales drastically alter. Micelle aggregates can take the forms of vesicles, rod-like or cylindrical micelles, spherical micelles, hemimicelles, plate-like micelles, and more, fig.5.4 shown micelle molecule. The arrangement of the surfactant's hydrocarbon chain in a micelle is what determines its shape(Rosen et al., 2004) (Barman et al., 2024).

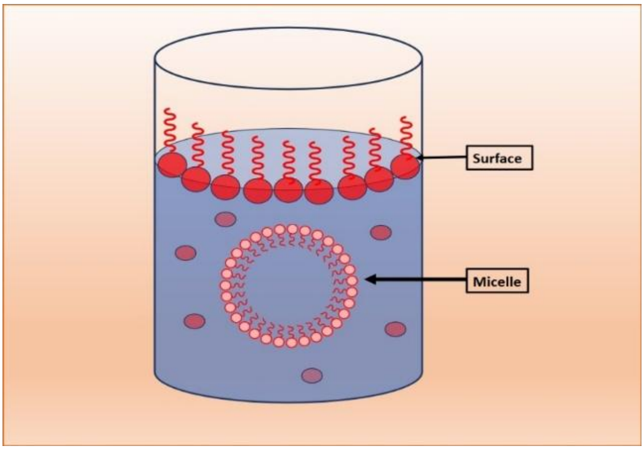

Figure 5.4 Schematic representation for the formation of micelle

5.10 Functions of Surfactants in Cosmetics

Several chemical surfactants are capable for several actions such as Removing dirt from the body surface, removing dirt from the body surface, Emulsification of non-compatible liquids, enhancing lather foaming in shampoos, Moisturizing and wetting the skin and hair, Conditioning the skin and hair(Ross et al., 1988). Functions of Surfactants in Cosmetics such as:

Cleansing Agents: Surfactants trap and remove dirt, oil, and impurities from the skinand hairs. Cleansing agents found in shampoos, body washes, and facial cleansers.

Foaming Agents: They help create lather, enhancing the sensory experience during use. Foaming agents found in shaving creams and bath gels.

Emulsifiers: Enable the mixing of oil and water, forming stable emulsions. Emulsifiers found in creams, lotions, and makeup.

Conditioning Agents: Some surfactants provide a smooth and soft feel on the skin or hair. Conditioning agents found in conditioners and leave-in treatments.

Solubilizers: Help dissolve ingredients like fragrances and essential oils in water-based products. Solubilizers found in micellar water and sprays.

5.11 Common Cosmetic Formulations with Surfactants

5.11.1 Shampoo: Shampoo is a hair care product, typically in the form of a viscous liquid, that is used for cleaning hair(Pedro et al., 2019). Less commonly, shampoo is available in solid bar format. Shampoo is used by applying it to wet hair, massaging the product into the scalp, and then rinsing it out. Some users may follow a shampooing with the use of hair conditioner.

Shampoos are of the following types:

Ingredients:

Primary surfactant: SLES or SLS (10-15%), Secondary surfactant: Cocamidopropyl betaine (2-5%), Conditioning agents: Polyquaternium, silicones, Thickening agents (e.g., salt), preservatives, fragrance, colour.

Process:

Initially the detergent is converted into a solution form. By dissolving surfactants in water.

To amount of surfactant is added and dissolved by stirring or heating gently. Then amount of perfume is added and dissolved. Add conditioning and functional ingredients. Colours and preservatives are dissolved separately in sufficient volumes of water and then added to the main solution. The whole solution is mixed well by gentle stirring. After than Adjust viscosity and pH (usually ~5.5).

5.11.2Face Cleanser

Face washing, often referred to as facial cleanliness or face cleansing, is a method of washing that may involve the use of soap or another cleaning solution together with water in order to get rid of debris, oil, grime, and other undesirable substances from the face(Lourith et al., 2009) (Barman et al., 2024). These contaminants or undesirable materials from the environment and cosmetics are scarcely soluble in water. By dissolving unwanted substances into smaller particles, face cleansing solutions can be added to regular face washing to aid in their efficient removal.

Ingredients:

Mild surfactants: Decyl glucoside, Lauryl glucoside (5-10%), Emollients: Glycerin, Propylene glycol. Soothing agents: Aloe vera, Panthenol.

Process:

Adding all of the ingredients together before incorporating the gum phase into the product means that all of the water in the product hydrates evenly which reduces lumps and bubbles. Mix surfactants in water phase. Incorporate emollients and active ingredients. Add the preservative to the blend and stir. Measure the pH of the product and check that it is within the correct range for the preservative you are using. Adjust if needed using a pH solution such as our suggested lactic acid at 80% dilution. Check the pH again and adjust if needed. The pH of our product is 5.2 which is fine for a wash-off cleanser. Adjust pH (5.0-6.0).

5.11.3Body Wash

A vital part of our everyday hygiene regimen, body wash—also known as shower gel—helps cleanse the skin of debris, oils, and pollutants while providing a pleasurable bathing experience. In order to create solutions that successfully cleanse, nourish, and protect the skin without irritating or drying it out, the science underlying body wash composition is crucial.

Ingredients:

Primary surfactant:

Ammonium Lauryl Ether Sulphate (AESA), Sodium Lauryl Sulphate (SLS), Sodium Lauryl Sulphate (SLES), Sodium LauroylSarcosinate, Sodium Cocoyl Glycinate, and other SLES or AOS (8–12%)

Secondary surfactant:

Cocamide DEA (CDEA), Cocamidopropyl Betaine (CAPB), Cocamidopropylamine Oxide (CAO), and Alkyl Polyglucoside (APG) are examples of Cocamidopropyl Betaine (2-4%).

Emulsifiers: - Glyceryl oleate, Polyglyceryl-4 laurate, Ceteareth-20

Moisturizers: - Shea butter, Glycerin.

Fragrance: - Fragrances and Essential oils Lavender, peppermint, eucalyptus, and citrus oils and color.

Conditioning agents: -Guar Hydroxypropyltrimonium Chloride, Quaternium-80, Hydrolyzed proteins

Preservatives: - Phenoxyethanol, benzyl alcohol, ethylhexylglycerin

Formulation Process

Dissolve surfactants in water while stirring to create a homogenous base. Adding Active Ingredients: Incorporate moisturizers, emollients, and conditioning agents while maintaining gentle mixing to prevent foam formation. Adjusting Viscosity: Add thickeners and stabilize the formulation(Guin et al., 2022). Then Add fragrance and colorants in the final stages to avoid evaporation or degradation during mixing. And Check and adjust the pH using citric acid or sodium hydroxide. After then Add preservatives to protect the product from microbial contamination. And Test for stability, pH, and skin compatibility before bottling the product.

5.11.4Lotions

A liquid or semi-liquid emulsion that contains more water than oil is called a lotion. A topical medication with a low viscosity that is meant to be applied to the skin is called lotion. Creams and gels, on the other hand, are more viscous, usually because they contain less water. Applying lotions to the outside of the body can be done with cotton wool, bare hands, a brush, or a clean cloth. Lotion examples Sunscreen lotions, face and hand moisturisers, and body lotions (Goodman et al., 2009) (Barman et al., 2023).

Ingredients:

1. Water Phase (Acts as the base and provides hydration):Purified water, Aloe vera juice, Hydrosols (e.g., rose water)
2. Oil Phase (10–20% of the formulation): Provides moisture and nourishment.
3. Natural oils (e.g., coconut oil, almond oil, jojoba oil), Esters (e.g., isopropyl myristate for alighter feel), Butters (e.g., shea butter, mango butter)
4. Emulsifiers (2–6%): Combine the water and oil phases to form a stable emulsion.Emulsifying wax (Cetearyl alcohol + Polysorbate 60), Glyceryl stearate, Lecithin
5. Thickeners (0.5–2%): Provide the desired viscosity and texture.Xanthan gum, Carbomer, Cetyl alcohol (also acts as a co-emulsifier)
6. Humectants (3–5%): Attract and retain moisture in the skin.Glycerin, Propylene glycol, Hyaluronic acid
7. Active Ingredients (1–10%): Address specific skin concerns.Vitamins (e.g., Vitamin E, Vitamin C), Botanical extracts (e.g., green tea extract, calendula),Anti-aging agents (e.g., peptides, niacinamide)
8. Preservatives (0.5–1%): Prevent microbial growth and extend shelf life.Phenoxyethanol, Potassium sorbate, Ethylhexylglycerin
9. Fragrance or Essential Oils (0.1–1%): Add scent and enhance the sensory experience.Lavender oil, Peppermint oil, Fragrance oils (skin-safe)
10. pH Adjusters (as needed): Maintain a skin-friendly pH (around 4.5–6.5).Citric acid, Sodium hydroxide

Formulation Process

Prepare the Water Phase: Heat the water and dissolve water-soluble ingredients (e.g., glycerin, humectants) in it. Prepare the Oil Phase: Heat oils, butters, and emulsifiers until fully melted (typically around 70°C). Emulsification: Slowly add the oil phase to the water phase while stirring continuously with a homogenizer or hand blender. Continue mixing until the mixture becomes uniform and starts to cool. Add Active Ingredients: Once the lotion cools to 40°C or lower, add temperature-sensitive ingredients like vitamins, extracts, and preservatives. Adjust the pH: Test the pH of the lotion and adjust if necessary, using citric

acid or sodium hydroxide.

Fragrance and Packaging: Add fragrance or essential oils and mix thoroughly. Transfer the lotion into clean, sterilized containers. and in last pH Adjuster: As needed(Banjare et al., 2024) (Banjare et al., 2023).

5.12 Conclusions

Surfactant plays a vital role either in cosmetic and non-cosmetic field. Anexhaustive study of its role and mechanism towards cosmetic technology delivery system wouldreveal a wide range of its potential in usage. Narrowing the research on each and every surfactantwould certainly benefit the field of cosmetic science towards revealing the inner beauty of mankind. Due to their ability to cleanse, froth, and emulsify, surfactants are essential in personal care compositions. But because of their effects on the environment and skin health, softer and more sustainable substitutes must be created. The future of personal care products will probably be shaped by ongoing research and innovation in green surfactants, which will be in line with customer preferences and legal requirements.

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Chapter 6: Application of Surfactants in Host-Guest Chemistry

Rupendra Kumar

ABSTRACT

Host-guest chemistry involving macrocyclic hosts is one of the most promising research areas in chemistry, materials science, and biochemistry in recent years. It is also called inclusion complexes, which are supramolecular structures whose components are maintained by noncovalent interaction in a reversible manner. Macrocyclic molecules such as cyclodextrins, crown ethers, cyclophanes, cryptands, and cyclopeptides are generally used as host molecules. In contrast, as guest molecules, various molecules such as ionic liquids, surfactants, amino acids, and many more are used. Ionic liquids are exist as liquid at room temperature. Surfactant consists of a hydrophobic tail and a hydrophilic head, both are amphiphilic compounds. The host centers are bonded together by non-covalent interactions such as hydrogen bonds, van der Waals bonds, or coordinate bonds. The polar heads of conventional ILs can therefore be adapted to act as surfactants by attachment of long hydrophobic chains to their hydrophobic ends. This chapter briefly describes the physicochemical properties, preparation method, and mechanism of host-guest complexes. In addition, we also highlight the characterization methods of synthesized host-guest complexes and their various applications, especially in amphiphilic molecules like surfactants, ionic liquids, and surface active ionic liquids.

Keywords: Host-Guest Chemistry, Amphiphilic Molecules, Surfactants, Ionic Liquids, Surface Active Ionic Liquids.

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6.1. INTRODUCTION

Host-guest chemistry involving macrocyclic hosts is one of the most promising research areas in chemical science, materials science, and biochemistry in recent years. Host-guest chemistry can be defined as a process of forming unique structural complexes via non-covalent interactions between molecules or ions [Ma & Zhao, 2015; Khan & Lee, 2021]. It is also called inclusion complexes, which are supramolecular structures whose components are maintained by non-covalent interaction in a reversible manner [Aleškovićan et al., 2024; Lee et al., 2020; Banjare et al., 2017]. The principles of supramolecular host-guest chemistry are increasingly being applied to complex systems, especially those assembling on solid surfaces, despite their development in organic and aqueous solutions [Teyssandier et al., 2016; Khan et al., 2021]. Macrocyclic molecules such as cyclodextrins, crown ethers, cryptands, and cyclophanes are generally used as host molecules and their structure are illustrsated in fig. 1. In contrast, as guest molecules, various molecules such as ionic liquids, surfactants, amino acids, and many more are used.

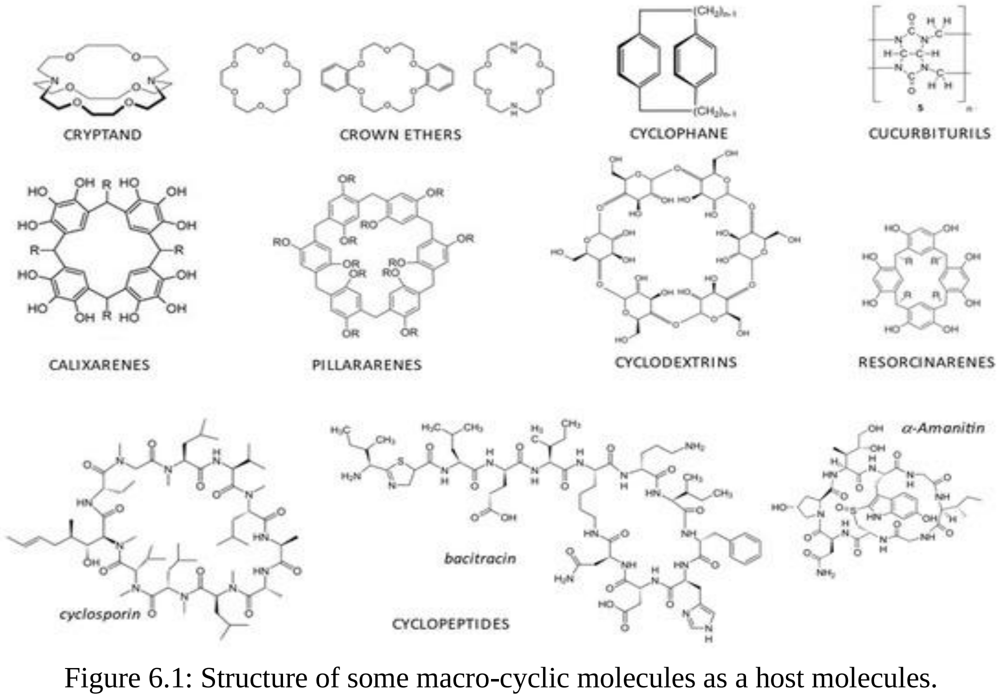
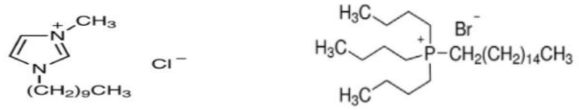


Figure 6.1: Structure of some macro-cyclic molecules as a host molecules.

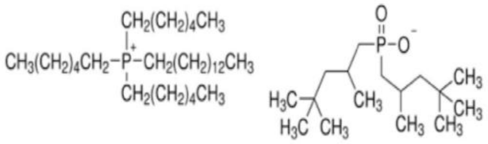
Cyclodextrins are water-soluble macrocyclic host molecules consisting of 6 glucopyranose units (α-CD), 7 glucopyranose units (β-CDs), and 8 glucopyranose units (γ-CDs) [Assaf et al., 2016; Banjare et al., 2020]. Cyclodextrins host molecules exhibit a remarkable molecular structure, with an outer layer that includes hydrophilic hydroxyl groups. This makes them highly water-soluble, and hydrophilic compounds are favoured [Poulson et al., 2022; Sandilya et al., 2020]. Although inner layers are hydrophobic in nature. As a guest molecule ionic liquids are widely used which is also known as surface-active ionic liquids (SAILs) i.e. tributyl(hexadecyl)phosphonium bromide [Buettner et al., 2022]. Structure of some surface active ionic liquids (SAILs) are illustrated in fig. 2. These ionic liquids (ILs) have long alkyl chains and are considered amphiphiles. Surface activity and self-aggregation are attributed to their charged head group and long hydrophobic tail [Ghosh et al., 2020].

This chapter we have briefly introduced on the synthesis method of host-guest complexes, mechanism of host-guest complexes, characterisation method of host-guest complexes, and applications of host-guest complexes.



1-Decyl-3-methylimidazolium chloride

Tributyl(hexadecyl)phosphonium bromide



Trihexyl(tetradecyl)phosphonium bis(2,4,4-trimethylpentyl) phosphinate

Figure 6.2: Structure of some amphiphilic molecules as a guest.

6.2. METHODS OF SYNTHESIS OF HOST-GUEST COMPLEXES

Host-guest complexes can be prepared by a variety of methods; however, there is no universal method.Depending on the properties of the guest molecules, host complexes should be prepared using the appropriate method [Mejuto et al., 2022].

6.2.1 Coprecipitation Method

Co-precipitation method is a most familiar method to prepare host-guest complexes with its main advantage of efficiency and simplicity [Periasamy et al., 2016; Sharma et al., 2017]. In this method a known quantity of CD host was properly dissolved in pure water and guest was dissolved in ethanol separately. Now the guest solution was slowly added into host solution in drop wise with constant stirring. In order to complete the process of encapsulation of guest in to CD host, the solution was equilibrated for 24 h with constant stirring. Then solution was placed in a lyophilizer for approximately 24 hours to obtain a consistent mass. During cooling, precipitation and crystallization was occurred. Once the inclusion complex had been formed, it was washed and dried [Sherje et al., 2017; Periasamy et al., 2020].

6.2.2 Kneading Method

The kneading method is perfect for guests that are poorly water-soluble because their dissolution is slow during the formation of the complex. This method is also called paste method. Although it provides a very high inclusion yield, it cannot be used at large scales. Slurry of CDs and dissolved solids or liquid guests are mixed in a mortar and kneaded until a paste is formed. To remove free particles that adhere to the cyclodextrin surface, the obtained solid must be washed with solvent and dried under vacuum. It has been reported that kneading of ibuprofen encapsulation produces inclusion complexes from cyclodextrins [Pereva et al., 2022; Zhou et al., 2022].

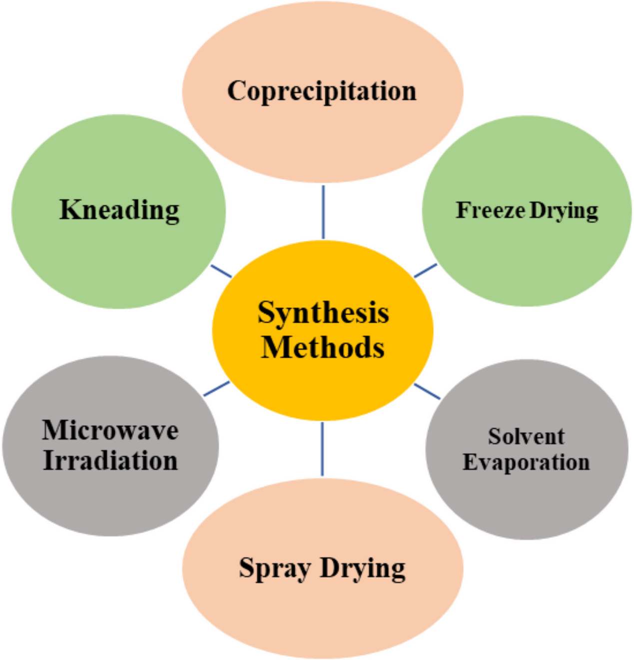


Figure 6.3: Synthesis methods of host-guest complexes.

6.2.3 Solvent Evaporation Method

Yallapu et al. studied inclusion complexation between β-Cyclodextrin-curcumin using solvent evaporation, in which cyclodextrin (host) was dissolved in deionized water in a 20 mL glass vial containing a magnetic bar. The solution was stirred at 400 rpm, after two mg (5%), four mg (10%), eight mg (20%), and twelve mg (30%) of curcumin was added. Acetone was evaporated by stirring without a cap. After stirring overnight, centrifugation at 1000 rpm for 5 minutes, and freeze drying of the supernatant, highly water-soluble cyclodextrin-curcumin inclusion complexes were recovered. Until further use, the CD-CUR inclusion complexes were stored at 4 degrees Celsius [Yallapu et al., 2010].

6.2.4 Freeze Drying Method

In order to improve the stability of compounds, freeze-drying is commonly used. The freeze-drying method involves dissolving guest molecules in water, adding CDs and stirring thoroughly, then freezing the mixed solution to obtain inclusion compounds [Zhou et al., 2022]. Some other methods e.g. microwave irradiation, spray drying, and super critical carbon dioxide method are also used by researchers.

6.3. MECHANISM OF HOST-GUEST COMPLEXES

Formation of the host-guest complex is usually a spontaneous process, in which host and guest molecules maximize their respective interactions [Yu et al., 2019]. Banjare et al. studied the molecular interactions between cyclodextrin and amphiphilic molecules i.e. ionic liquid and characterized by using 1H NMR. Host molecules can create inclusion complexes (ICs) of various guest molecules due to their hydrophobic cavity and truncated shape. Accordingly, it was shown that the cavity of the β-CD contained only the long alkyl chain molecules. As a result, the stronger IC is mostly formed by the longer alkyl chain molecules. The final result suggested that two types of inclusion complexes were formed, one was formed by feasible inclusion, and another was formed by restricted inclusion (shown in fig. 4) [Banjare et al., 2018].

6.4. CHARACTERISATION METHOD OF HOST-GUEST COMPLEXES

Host-guest complexes are characterised by various spectroscopic techniques such as Nuclear Magnetic Resonance (NMR), UV-visible Spectroscopy, Fourier Transform Infra-Red Spectroscopy, and other techniques i.e. X-ray Diffraction (XRD) etc.

6.4.1 Nuclear Magnetic Resonance Spectroscopy

The wide range of applications of nuclear magnetic resonance spectroscopy, from structural elucidation of structures to intra/intermolecular investigations, makes it one of the most complete spectroscopy techniques available in chemistry [Charisiadis et al., 2014; Yunfei et al., 2021]. Banjare and co-workers reported that the host–guest complexation of 1-Butyl-3-methylimidazolium octylsulfate [BMIM][OS] within α-cyclodextrin and β-cyclodextrin. Their host–guest complexes were characterized by ^{1}HNMR. Using this method, guest molecules were encapsulated in the β-CD cavity, thereby observing changes in the chemical shift of protons. Both the [BMIM] [OS] and the chemical shifts of the host molecules were modified by inserting the IL into the hydrophobic hole of the host. In this experiment, hydrophobic forces are observed between IL protons H2 and H3 and CDs protons H3 and H5. It was confirmed by electrostatic interactions of the outer parts of the cyclodextrins protons H1 and H3 with the protons H4 and H5 of the IL, that the IL chain portion is encased within the hydrophobic cavity of the CD [Subramaniam et al., 2010].

6.4.2 Fourier Transform Infra-Red Spectroscopy

An important aspect of the FTIR technique is that it can be used to analyze inclusion complex (IC), such as the ILs and the cyclodextrin complexes [Hui et al., 2020]. The FTIR technique can be used to detect the presence of the host molecule and the guest molecule in a complex. FTIR analysis identifies hydrogen bonds and electrostatic interactions by identifying changes in vibrational frequencies and intensities of functional groups. In general, FTIR spectroscopy plays an important role in the characterization of inclusion complexes as it provides information on molecular interactions, structural changes, and confirms the presence of inclusions [Cid-Samamed et al., 2022]. Baghel and group studied the synthesis of host-guest complexes between surface active ionic liquid Trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl) phosphinate (THTDPP) and β-cyclodextrin by using job's plot method. It was charaterised by using FTIR technique. Researchers used FTIR spectroscopy to demonstrate the IC's formation. It was found that in the FTIR absorption peaks of β-CD and [THTDPP] IC , O–H stretching of the IC changed, C–H stretching changed, C = O stretching band altered and C = C stretching also altered, Which proves host guest complex formation. Barman et al. [32] investigated 1-hexyl-3-methylimidazolium chloride [HMIm]Cl, 1-benzyl-3-methylimidazolium chloride [BMIm]Cl, host-guest complexes formed with α-CD,β-CD. It was characterized by FTIR technique. The result shows that the comparison of the different frequencies of pure CD, pure SAIL, and the corresponding complexes supports the inclusion phenomenon [Baghel et al., 2023].

6.4.3. UV-visible Spectroscopy

One method for describing the host-guest complexation between cyclodextrins and surface-active ionic liquids is UV-visible absorption spectroscopy [Barman et al., 2018]. The stoichiometry and stability constant of the host-guest are ascertained using this method. Ghosh et al. investigated the UV-visible spectra of host-guest complexes of α-cyclodextrin and long chain ionic liquid i.e. 1-decyl-3-methylimidazolium tetrafluroborate [Dmim][BF_4]. They were show the 1:1 stochiometry of the inclusion complexes (ICs) [Dmim][BF_4]:α-CD.They were employed external probe methyl orange (MO) because the α-CD did not show a UV-visible peak in the 300-500nm wavelength range. The formation of ICs was indicated by the UV-visible response, which also reveals the the formation of two isebestic points i.e. 465nm and 453nm [Ghosh et al., 2020].

6.4.4 X-ray Diffraction (XRD)

X-ray diffraction is a widely used technique in studying inclusion complexes (ICs) to assess and determine their structure [Kou et al., 2024]. Zheng et al. investigated the synthesis of host-guest complexes with ionic liquid (IL) surfactant, 1-dodecyl-3-methylimidazolium hexafluorophosphate (C12mimPF6) and β-CD. The findings of research paper reveals that at different urea concentrations , there was no significant difference between the patterns before and after adding urea, which was shown by XRD patterns of the powder, which also indicates that the β-CD-C12mimPF6 ICs still have channel type structure, and hydrogen bonding between CDs does not significantly contribute to channel stability [Li et al., 2007]. Subramaniam et al. studied synthesis of the inclusion complex of dicationic ionic liquid and β-cyclodextrin and characterised by using XRD, which further evidence that complexes were formed.

Researchers were found that the three main types of CD complex crystal structures: channel-type, cage-type, and layer-type. Based on the results obtained, it could be said that the inclusion complex obtained is a fine crystalline powder, and that the XRD pattern obtained with the β-CD-TetraPhimBr shows that the inclusion complex forms head-to-head channels between the molecules [Subramaniam et al., 2010].

6.5. APPLICATIONS OF HOST-GUEST COMPLEXES

In host-guest chemistry, amphiphilic molecules are crucial, especially when designing and modifying molecular systems that require the creation of inclusion complexes [Khan et al., 2021]. In host-guest chemistry, a "host" molecule, which typically fits within the cavity or receptor, interacts with a "guest" molecule, which is usually smaller and fits within the host's binding site [Lbáñez et al., 2023]. In this context, amphiphilic molecules have been used by researchers in the following ways:

(i) Controlled Drug Delivery

From the very beginning of the administration, host-guest complexation provides the best method for releasing a toxic drug without unexpected side effects. Sarkar et al. investigated three benzimidazolium-based ionic liquids (surface-active) containing bromide anion and cation, bearing long alkyl chains such as decyl- ([C_{10}CFBim]Br), octyl- ([C_8CFBim]Br), and hexyl- ([C_6CFBim]Br) were created and produced as antimicrobial medications. β-cyclodextrin has been used to create host-guest complexes of the investigated ILs; taking these conjugations into account should increase the ILs safety and make them viable options for controlled drug release. ILs based on benzimidazolium serve as a potential solution for biomedical applications such as controlled drug delivery. This work provides proof of concept for this theory [Sarkar et al., 2021].

(ii) Environmental remediation

The green cyclodextrin (CD) derivatives can be used to support innovative environmental remediation strategies, including the extraction of pesticides and heavy metals. A CD derivative offers a versatile and sustainable option for remediation of pesticides and heavy metals and presents a significant opportunity for mitigating environmental contamination [Fouda-Mbanga et al., 2025].

(iii) Food industry

Due to their hygroscopic properties, CDs are used primarily in foods to encapsulate compounds of interest and improve water retention. In recents years, CDs have gained a lot of popularity in the food industry because they inhance antioxidant activity and bioavailability. In addition, CDs are also used as food preservatives and packaging materials. According to Siró et al., complexed tocopherol is released from active package in a controlled way, providing a long-lasting antioxidative effect [Siró et al., 2006]. Various studies have shown that encapsulating CDs and forming ICs extends the shelf life of a wide range of foods [Liu et al., 2022].

(iv) Pharmaceuticals

Researchers was found that the Cyclodextrins host molecules are used for several purposes in pharmaceutical industry [Esteso et al., 2024]. Pereira et al. was explored that as drug formulation agents, CDs can enhance bioavailability and solubility, reduce hemolysis and adverse effects, prevent admixture incompatibilities, and act as excipients. In addition to improving the solubility of drugs, the compound will have a greater therapeutic efficacy, and it will be necessary to use smaller doses. In addition several CDs-based anticancer drugs were currently being evaluated in clinical trials [Pereira et al., 2021].

6.5. FUTURES SCOPES

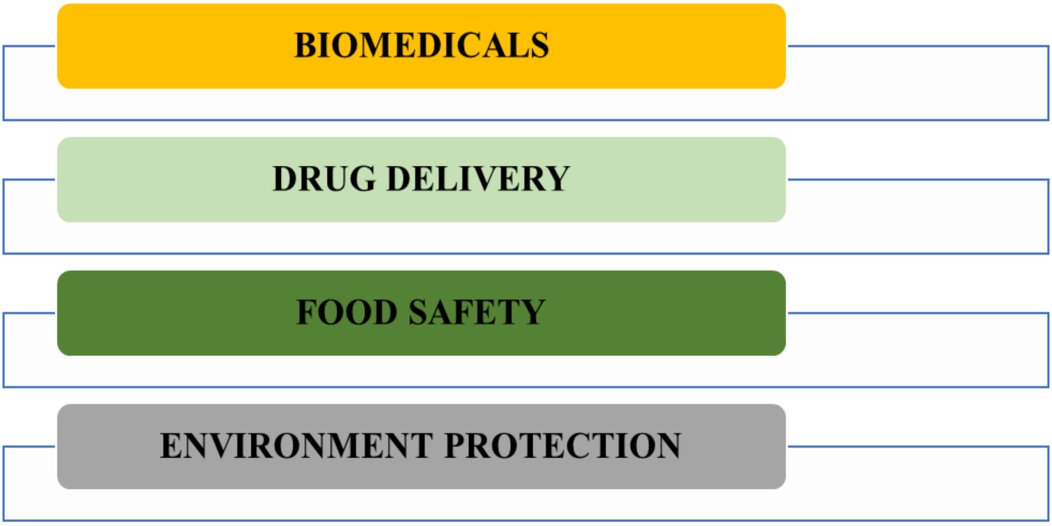


Figure 6.4: Future scopes of host-guest complexes.

6.6. CONCLUSION

A highly interdisciplinary and rapidly expanding area of study in biology, chemistry, and materials science is host-guest chemistry utilising macrocyclic hosts [Sayed et al., 2021]. In which cyclodextrin host molecules are increasingly attracting the attention of researchers due to their intrinsic structural features [Zhou et al., 2022]. In summary, this chapter aims to explore the synthesis method of host-guest complexes, the mechanism of host-guest complexes, characterization techniques, and the application of host-guest. This chapter highlights amphiphilic molecules as a guest molecule with cyclodextrins molecules as host molecules in the field of pharmaceuticals, drug delivery, and environment. In addition, cyclodextrins have shown great potential in several areas of biomedical and food safety applications.

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Chapter 7: Application of Surfactants in Micellar Systems

Benvikram Barman, Manoj Kumar Banjare, Amit Kumar Chaturwedi

Abstract

Amphiphilic compounds known as surfactants reduce surface tension and create micelles in solutions. Micellar systems are essential in many industries, such as food, detergents, cosmetics, medicines, and environmental applications. The categorisation, creation, and uses of micellar systems are examined in this work, with an emphasis on how they contribute to improved chemical reactions, emulsification, and solubilisation. Future directions in surfactant research are also covered, as well as difficulties including toxicity and environmental issues. The surfactant is a crucial component of emulsifying agent, foaming agent, cleaning agent, wetting agent, dispersing agent, and anti-foaming agents and is used in a wide range of goods. Surfactant molecules have a drive to assemble above the critical micelle concentration (CMC) to create micelle-like structures. Usually, 10-100 of surfactant molecules make up a micelle. The amount of surfactant monomers in a micelle can be determined by its aggregation number. The arrangement of the surfactant's hydrocarbon chain in a micelle is what determines its shape. Surfactants they lower surface tension and promote micelle self-assembly in aqueous or non-aqueous mediums, surfactants are essential to micellar systems. Micelles are aggregates of colloidal size that are created when the concentration of surfactant molecules above the critical micelle concentration (CMC). Because of their low toxicity, biodegradability, ease of handling, and one-step process, micellar systems—which are based on the use of surfactant solutions—are a viable alternative to organic solvents for the extraction of contaminants. Because these systems can change interfacial characteristics and solubilise hydrophobic materials, they have a wide range of uses.

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Keywords:
Micelles, Surfactants, Self-assembly, Critical micelle concentration (CMC), Hydrophilic-lipophilic balance (HLB), Emulsification, Micellar solubilization, Detergency, Drug delivery, Nanotechnology, Polymeric micelles, Cosmetics and personal care, Microemulsions.

7.1 Introduction

Surface-active agents, or surfactants, are compounds that have both hydrophilic (loving water) and hydrophobic (repelling water) components(Saxena et al., 2023). Because of their dual nature, they can lower interfacial and surface tension, which causes micelle production in aqueous solutions(Hargreaves et al., 2007). When the concentration of surfactant surpasses the Critical Micelle Concentration (CMC), micelles—aggregates of surfactant molecules—self-assemble.Micellar systems are widely used because of their capacity to improve solubility, stabilise emulsions, and provide regulated delivery of drugs, micellar systems are extensively employed in both industrial and scientific domains. Enhancing detergent, cosmetic, medicinal, and environmental remediation formulations require an understanding of surfactant behaviour and micelle production.Amphiphilic substances known as surfactants are essential to micellar systems because they have a major impact on the solubilisation, emulsification, and stabilisation processes. Their applications in a variety of industries, including as medicines, cosmetics, environmental remediation, and increased oil recovery, have been the subject of several research. The purpose of this review of the literature is to provide an overview of the major discoveries in the field of surfactants and their micellar applications.Surface-active agents, surfactants possess a special physical characteristic that allows them to adsorb at the interface (Najim et al., 2023). The polar head group and non-polar hydrophobic tail make form surfactants. Surfactant monomers have the ability to aggregate in liquids to form micelles, or colloidal-sized clusters (CSCs) with a diameter of 1–100 nm. The range of surfactant concentrations known as the CMC is where micelle production takes place. Below this concentration, the surfactant monomers disperse in the solution(Banjare et al. 2023). The many uses of surfactants, include as lubricants for cars, detergents for cleaning procedures, electronic printing, biotechnology, cosmetics, petroleum industries, pharmaceuticals, and colloidal sciences, among others (Barman et al., 2024, Adetunla et al., 2023).

Review of Literature

Surface-active agents, often known as surfactants, are amphiphilic compounds with hydrophilic (which attracts water) and hydrophobic (which repels water) head groups. (study Saini et al. 2024). These molecules self-assemble into micelle-like structures in aqueous solutions at a certain concentration known as the critical micelle concentration (CMC). (Study Serravalle et al. 2024). The hydrophobic effect is what propels this self-assembly, in which the hydrophilic heads interact with the surrounding aqueous environment and the hydrophobic tails group together to reduce their exposure to water, creating a core. (Xiao et al. 2024).

7.2Types of surfactants

Surfactants are available in many forms, and are generally classified based on charge of the surface-active molecules such as anionic, non-ionic, cationic and amphoteric. Show in fig. 3.1-3.2.

7.2.1 Anionic surfactants

Anionic surfactants are made up of anionic functional groups like sulphate, sulfonate, phosphate, and carboxylate(Dutta et al. 2019). The majority of detergent formulations contain anionic surfactants, which we use more frequently than any other kind of surfactant. The best detergency is provided by alkyl and alkyl-aryl chains with a length of C12–C18 (Swarup et al., 1993). Soaps are anionic surfactants produced by saponifying natural fats and oils, making them the most prevalent type of surfactant. The metal salt of an alkali carboxylic acid [R-COOH] that was originally generated from plant- or animal-based fats is referred to as "soap" in this context. The bulk of the time, the base of soap bars is a mixture of tallow and coconut fatty acids. Example of anionic surfactants are ALS, SLS, SDS, AEP, SDBS etc and its applications is Soaps, shampoos, detergents, industrial cleaners.

7.2.2 Cationic surfactants

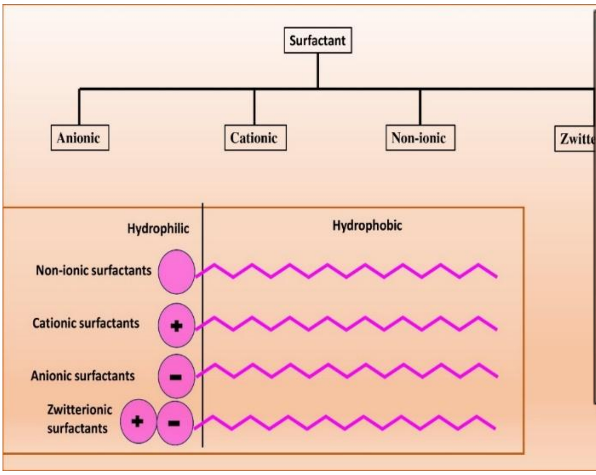
In this category, the hydrophilic element is positively charged. It sticks to surfaces and may have soil-repelling, antistatic, softening, antibacterial, or corrosion-inhibiting properties despite the fact that this group doesn't have any wash activity. In many typical uses, they serve as softeners (fabric softeners) and antistatic. The counter ion of cat$^+$ surfactants is often a halide or methyl sulphate (Wu et al., 2019). The pH affects the primary, secondary, or tertiary amines. Example of cationic surfactants are alkyl ammonium chloride (AAC), Benzethonium chloride (BTC), cetrimonium bromide (CTMB), cetylpyridinium chloride (CPC), cetyltrimethyl ammonium bromide (CTAB) and its applications is fabric softeners, disinfectants, personal care products.

7.2.3 Non-ionic surfactants

Non-ionic surfactants contain hydrophilic elements that are not charged. These materials clean effectively and are unaffected by water. They come from groups like fatty alcohol polyglycosides and alcohol ethoxylates and are typically discovered in cleaning detergents. Long chain alcohols have certain surfactant characteristics (Shenyuan et al., 1995). Cetyl alcohol. stearyl alcohol, Fatty alcohols, cetostearyl alcohol (mostly made of stearyl alcohols and cetyl alcohols), and oleyl alcohol are the most prevalent types of these. Example of nonionic surfactants are alkyl phenol ethoxylate, fatty acid alkoxylate, triton x-100, cetyl alcohol, stearyl alcohol, and its applications: Drug delivery systems, food emulsifiers, cosmetics.

7.2.4 Zwitterionic surfactants

A zwitterionic surfactant is made up of two groups (anionic and cationic) having diametrically opposed charges. Zwitterions are typically referred to as "amphoteric," yet both concepts are distinct. An amphoteric surfactant is one that undergoes a pH change from low to high and changes from a net cation to a net anion via Zwitterion. Only a small pH range allows the molecule to be Zwitterionic since neither the acidic nor basic sites are always charged. The physicochemical behaviour typically matches that of non-ionic surfactants at the isoelectric point. A continuous transition towards the cation or anion character occurs below and above the isoelectric point, respectively. Outstanding dermatological abilities are associated with a subgroup known as Zwitterion. Examples of surfaces and interfaces include the following: Interfaces between solids, liquids, and solid-liquid Liquid - Vapour (surface); they have a mild irritant effect on the skin and eyes(Barman et al., 2024). They are perfectly suited for usage in shampoo and other personal care (cosmetic) products. Surfactants that include both cation and anion centres attached to the same molecule are known as zwitterionic (amphoteric) surfactants. Example of zwitterionic surfactants is a cocoamido propyl betaine, glyceryl laurate and its applications: Protein purification, specialized detergents.



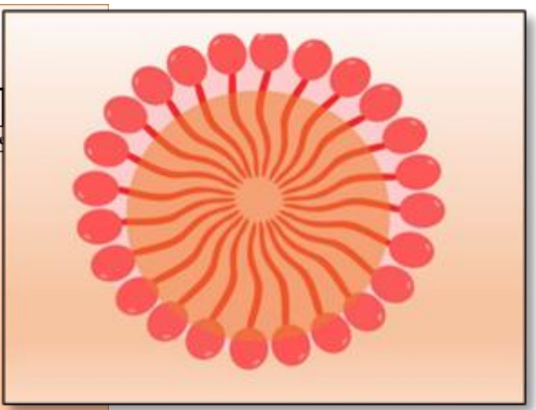
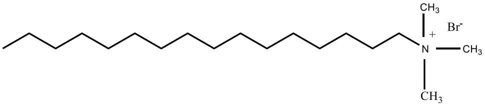
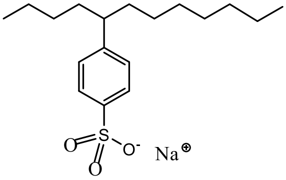
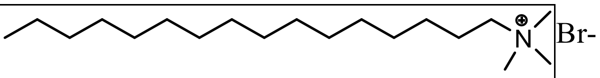
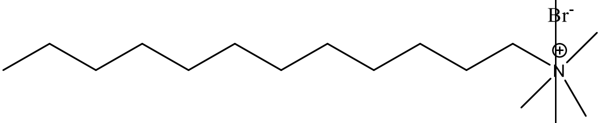
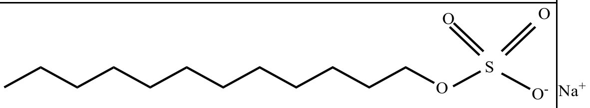
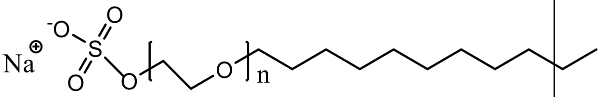
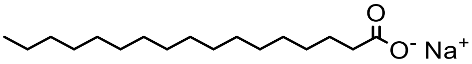
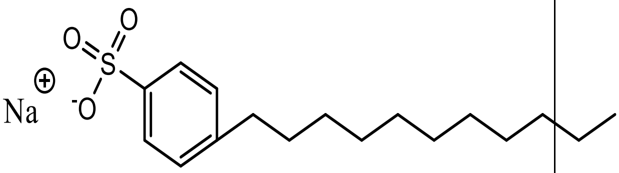
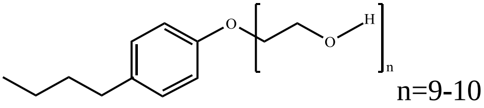
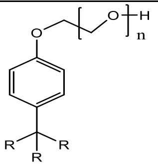
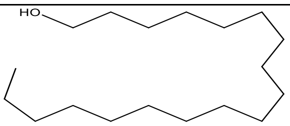
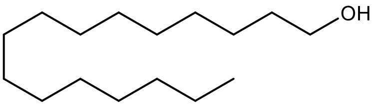
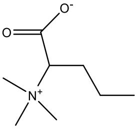


Figure 7.1 Types of surfactants and their molecular structure

Figure 7.2 Structure of micelle

Surfactants		Structures
Cationic surfactants	Cetyltrimethylammonium bromide	
	4-(5-Dodecyl) benzenesulfonate	

	Cetrimonium bromide	
	Dodecyltrimethylammonium bromide	
Anionic surfactants	Sodium dodecyl sulfate	
	Sodium laureth sulfate	
	Sodium stearate	
	Sodium Dodecylbenzene Sulfonate Surfactant	
Non-ionic surfactants	Triton-X 100	
	Alkyl phenol ethoxylate	
	Stearyl alcohol	
	Cetyl alcohol	
Zwitterionic surfactant	Propyl betaine	

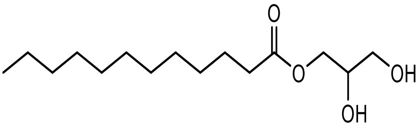
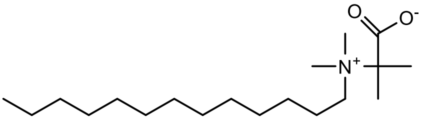
s	Glyceryl laurate	
	Dodecyl dimethyl betaine	

Figure 3.2 Molecular structure of surfactants

7.3 Micellar Systems

When the concentration of surfactant above the Critical Micelle Concentration (CMC), micelles are formed(Rui et al., 2023). While the hydrophilic heads stay open to the surrounding aqueous environment, the hydrophobic tails congregate in the centre.Micelle formation is the process by which surfactant molecules self-assemble into spherical, cylindrical, or lamellar structures when their concentration above the critical micelle concentration (CMC) (Maulik et al. 2024). Micelle stability and functioning are significantly influenced by the hydrophilic-lipophilic balance (HLB) (Das et al. 2014). Recent research has demonstrated that micellar structures may be tuned by altering the ionic strength, pH, and surfactant content (Gerola et al. 2017).Surfactant molecules have a drive to assemble above the cmc to create micelle-like structures. Usually, 10-100 of surfactant molecules make up a micelle. The amount of surfactant monomers in a micelle can be determined by its aggregation number. The molecular weight of the surfactant monomer by the aggregation number, one can determine the molecular weight of a micelle. Conversely, micelles grow and spread in milliseconds. But as the surfactant concentration and the surfactant's size and properties change, these time scales drastically alter. Micelle aggregates can take the forms of vesicles, rod-like or cylindrical micelles, spherical micelles, hemimicelles, plate-like micelles, and more, fig.3.3 shown micelle molecule. The arrangement of the surfactant's hydrocarbon chain in a micelle is what determines its shape.

7.4 Critical micelle concentration

The concentration of surfactants over which micelles form is known as the critical micelle concentration. Micelle nanoparticles are 5 to 100 nm in size. These molecules begin to form the micellar structure at this concentration thanks to the reduction in free energy driving assembly(Gray et al., 1973). Temperature, pressure, and (in some cases strongly) the presence and concentration of additional surface-active compounds and electrolytes all are affect in CMC value for a specific dispersant in a given medium. The formation ofCMC has shown in fig.3.4. Only at temperatures over the crucial micelle or Kraft temperature do micelles develop(Zhou et al., 2017). Micelles cannot form below the Kraft temperature.

7.5 Applications of surfactants in micellar systems

The surfactant is a crucial component of emulsifying agent, foaming agent, cleaning agent, wetting agent, dispersing agent, and anti-foaming agents and is used in a wide range of goods, some of which are listed below:

7.5.1 Drug Delivery Systems

Surfactants play a crucial role because they improve the solubility, stability, and bioavailability of hydrophobic medications, surfactants are essential components of drug delivery systems(Shinoda et al., 1963). The capacity of micellar drug delivery systems to encapsulate poorly soluble medications and provide regulated and targeted release has been the subject of much research. The use of Pluronic block copolymers to create polymeric micelles has demonstrated encouraging outcomes in terms of enhancing drug transport across biological membranes. Furthermore, surfactant-based nanoemulsions are used to improve the effectiveness and absorption of medicinal substances. The goal of ongoing research is to create surfactants that are both biocompatible and biodegradable for safer medication delivery applications(Hait et al., 2001).

Encapsulation: Micelles can encapsulate hydrophobic drugs, increasing their solubility and bioavailability in aqueous environments.

Targeted Delivery: Functionalized surfactants allow for site-specific drug release, minimizing side effects.

Sustained Release: Surfactant-based micelles enable controlled release of active pharmaceutical ingredients.

7.5.2 Enhanced Oil Recovery (EOR)

In enhanced oil recovery (EOR), surfactants are frequently employed to increase the extraction efficiency of crude oil. They facilitate the easier displacement of trapped oil inside reservoir rocks by lowering the interfacial tension between water and oil. Additionally, surfactants change the reservoir surfaces' wettability, which encourages more oil mobilisation. Numerous studies have shown that foam-based techniques, microemulsions, and surfactant-polymer flooding greatly increase oil recovery rates. In order to optimise EOR processes, recent developments have concentrated on creating surfactants that are both economical and ecologically benign.Surfactant micellar systems reduce interfacial tension between oil and water, mobilizing trapped oil in porous reservoirs.They enhance oil recovery by emulsifying oil and altering wettability.

7.5.3 Cosmetic and Personal Care Products

Surfactants are essential ingredients in personal care and cosmetics because they help with foaming, emulsification, and cleaning (Hayes et al. 2019). To reduce skin irritation and environmental effect, recent developments have concentrated on creating gentle and biodegradable surfactants (Tyagi et al. 2013).

Cleansers: Micelles in surfactant-based formulations (e.g., micellar water) remove dirt and oils from the skin.

Stabilization: Micellar systems help solubilize hydrophobic ingredients in creams, lotions, and shampoos.

7.5.4 Environmental Remediation

surfactants are frequently employed because they increase the solubility and mobility of hydrophobic contaminants, surfactants are important in environmental remediation because they make it easier to remove them from polluted soil and water. They are employed in oil spill cleanup, groundwater remediation, and soil cleaning. Research has demonstrated that the microbial breakdown of hydrocarbons and other persistent organic pollutants may be improved by surfactant-enhanced bioremediation. In order to maximise remediation process efficiency and reduce environmental effect, recent research has focused on creating biodegradable and non-toxic surfactants(Fuguet et al., 2005).

Pollutant Removal: Surfactants in micellar systems can solubilize hydrophobic contaminants, aiding in soil washing and wastewater treatment.

Oil Spill Cleanup: Micelles emulsify oil, facilitating its dispersion in water.

7.5.5 Food and Beverage Industry

The food and beverage sector makes considerable use of surfactants to improve shelf life, texture, and stability. In a range of items, such as dairy, baked goods, confections, and drinks, they serve as emulsifiers, foaming agents, and stabilisers. In order to increase the bioavailability of bioactive substances like vitamins, antioxidants, and essential oils, micellar systems are required for their encapsulation and regulated release. In order to satisfy growing consumer demand for clean-label and sustainable ingredients, recent developments have concentrated on the creation of natural and food-grade surfactants(Torchilin et al., 2001).

Emulsification: Surfactants stabilize oil-water emulsions, improving the texture and consistency of food products.

Encapsulation: Hydrophobic flavors and nutrients are encapsulated in micelles for improved **solubility and stability.**

7.5.6 Nanotechnology

In nanotechnology, surfactants are crucial for stabilising nanoparticles, regulating their size, and improving their dispersion over a range of substrates. They are essential to the production of nanomaterials, including as micelles, liposomes, and nanoemulsions, which are utilised extensively in coatings, electronics, and medication delivery. Surfactants promote the creation of highly ordered nanostructures by facilitating self-assembly processes. Designing surfactants that improve the functionality and efficiency of nanotechnology applications while maintaining environmental sustainability is the main focus of recent research(Lu et al., 2014).

Synthesis of Nanoparticles: Micelles serve as templates for the controlled synthesis of nanoparticles with specific sizes and morphologies.

Drug Conjugation: Nanomicelles enhance the delivery of poorly soluble drugs and therapeutic agents.

7.5.7 Chemical Synthesis and Catalysis

surfactants are frequently employed because of their special amphiphilic character, which enables them to alter surfaces, stabilise processes, and affect reaction dynamics, surfactants are important in chemical synthesis and catalysis(Liao et al., 2021). Here are a few important uses:

Micellar Catalysis: Surfactant micelles act as microreactors, concentrating reactants and enhancing reaction rates for organic and inorganic processes.

Green Chemistry: Micellar systems offer eco-friendly reaction media, reducing the need for organic solvents.

7.5.8 Detergency

The main active components of detergents, surfactants are essential to the cleaning process since they aid in the removal of stains, oils, and grime from textiles and surfaces. They work well in cleaning applications because of their amphiphilic nature, which enables them to interact with both water and grease. Surfactant micelles in detergents solubilize oils, grease, and particulate matter, making them essential for cleaning and laundry applications.

7.5.9 Biotechnology and Biochemistry

Surfactants are used extensively in biochemistry and biotechnology to help in cell membrane research, protein purification, and enzyme stabilisation. They are extensively employed in chromatography, electrophoresis, and the synthesis of recombinant proteins. In order to analyse the structure and function of membrane proteins, surfactants aid in their solubilisation. They also help with the separation and purification of biomolecules using bioseparations. In an effort to improve process efficiency while preserving biocompatibility, recent developments investigate the creation of non-toxic and biodegradable surfactants for biotechnological applications(Massarweh et al., 2020).

Protein Solubilization: Micellar systems solubilize and stabilize membrane proteins for structural and functional studies.

DNA Delivery: Surfactant micelles are used for gene delivery in molecular biology applications.

7.5.10 Analytical Applications

Chromatography: Micellar systems are employed in micellar electrokinetic chromatography (MEKC) for separating complex mixtures.

Spectroscopy: Micelles enhance the solubility of analytes, improving spectroscopic measurements.Surfactants in micellar systems are indispensable across industries due to their versatility, tunability, and ability to create microenvironments for diverse applications.

7.6 Advancements in Sustainable Surfactants

Growing environmental concerns, the need to lessen dependency on petroleum-based raw materials, and the goal of enhancing the biodegradability and safety profiles of surfactants have all made the development of sustainable surfactants a priority in both research and industry (Barman et al., 2024). Recent years have seen a number of significant developments in surfactant design and use. The following are a few of the most noteworthy developments:

7.6.1 Biodegradable Surfactants

Ensuring that surfactants break down into non-toxic, ecologically friendly compounds after usage is one of the primary objectives of sustainable surfactant development (Banjare et al., 2024). The development of more biodegradable surfactants that decompose swiftly and securely in natural settings is the result of advancements in surfactant chemistry.

Ex. Linear alkylbenzene sulfonates (LAS) are an example of an anionic surfactant that has been reformulated to increase its biodegradability. AndNatural sources of cationic surfactants, such plant oils' quaternary ammonium compounds (QACs), have been produced to have superior biodegradability.

7.6.2 Green Chemistry and Sustainable Synthesis

Enzyme-Catalyzed Processes: More environmentally friendly surfactant production techniques have been made possible by developments in green chemistry. Compared to conventional chemical synthesis techniques, enzyme-catalyzed procedures are more environmentally friendly, selective, and energy-efficient.

Ex.In commercial applications, surfactants produced by biocatalysis—enzymes such as lipases and esterases—are becoming more and more common (Barman et al., 2024, Barman et al., 2023).

7.6.3 Surfactants for Green Energy

Additionally, surfactants are being used in the creation of green energy technologies, like the manufacturing of biofuels. To increase energy production and cut waste, they can aid in the extraction of biofuel, emulsification, or even the processing of biomass.

7.6.4 Biosurfactants

Naturally occurring surfactants called biosurfactants are produced by microorganisms like yeast, fungus, and bacteria. Their biodegradability, low toxicity, and efficient performance in a range of applications (such as oil spill remediation, food processing, and medicines) make them a possible substitute for synthetic surfactants (Banjare et al., 2023, Barman et al., 2023).

Ex. of biosurfactants include rhamnolipids, sophorolipids, and lipopeptides.

7.6.5 Reduced Toxicity

Contemporary surfactants are being developed to reduce toxicity and skin irritation while preserving or enhancing their emulsifying or cleaning capabilities. This is especially crucial in the personal care and cosmetics sectors, where product safety is a major worry.

7.7 Challenges and Future Directions

The increasing demand for sustainable products and the ongoing developments in green chemistry are anticipated to propel the widespread adoption of these innovations in the upcoming years, despite the fact that significant progress has been made. These challenges include ensuring adequate performance for industrial applications, improving the cost-effectiveness of bio-based and biosurfactant production, and further reducing environmental impacts.

7.8 Conclusions

Micellar systems and surfactants are essential in a variety of applications, including environmental protection and medicines. Improvements in micelle research have enhanced cleaning effectiveness, medication administration, and solubilisation. However, the creation of environmentally friendly surfactants is required due to environmental concerns. Future developments will probably concentrate on responsive, biodegradable, and multipurpose surfactants, propelling long-term progress across several sectors. Thanks to developments in materials science and nanotechnology, the use of surfactants in micellar systems is spreading throughout a variety of sectors. Optimising micelle design for increased safety, sustainability, and efficiency is the goal of ongoing research. Future research should concentrate on creating eco-friendly surfactants and investigating cutting-edge micellar uses in cutting-edge industries like nanomedicine and biotechnology.

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Chapter 8: Application of Surfactant in Agricultural Science

Benvikram Barman, Dolly Baghel, ManojKumar Banjare

Abstract

Surfactants are crucial to modern farming practices because they increase the efficacy and sustainability of pesticide treatments. Recent studies emphasise the trend towards the usage of biosurfactants, which are ecologically friendly alternatives to traditional chemical surfactants. The improved surface activity of biosurfactants, which are generated from microorganisms, increases the solubility and dispersion of hydrophobic agrochemicals and decreases the interfacial tension of immiscible liquids. Additionally, biosurfactants have antibacterial properties that make them promising as biopesticides against pests, fungi, and diseases while enhancing plant resistance. Research highlights their contribution to sustainable agriculture, including enhancing trace element bioavailability and maintaining soil moisture levels for optimal crop growth. To improve soil texture, improve nutrient uptake, and reduce environmental toxicity, these substances are increasingly being used in soil amendments, pesticide formulations, and herbicides. Additionally, the cost of generating biosurfactants is decreasing and their scalability is growing due to advancements in biotechnological production, such as microbial fermentation and genetic engineering. According to these findings, biosurfactants are an essential component in reducing chemical residues in crops and ecosystems, which is consistent with global efforts to address environmental and food security concerns. Their adaptability makes them crucial for sustained agricultural growth, especially in light of climate change and growing food demands.

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Keywords: Surfactants, Agrochemical, Biosurfactants, Antibacterial, Pesticide, Environmental toxicity.

8.1 Introduction

Surface-active agents (SAAs), often known as surfactants, are essential to agricultural research because they improve soil conditions, increase the effectiveness of agrochemicals, and help plants absorb nutrients more effectively. To maximise their efficacy, they are frequently included in fertilisers, soil amendments, insecticides, and herbicides(Azarmi et al., 2015, Banajre et al., 2024). Surfactants' capacity to lower surface tension makes it possible for agricultural chemicals to spread, penetrate, and adhere more effectively, improving crop yields and sustainability(Barman et al., 2024, Cortes et al., 2021).

8.2 Review of Literature

Numerous studies have shown how surfactants may increase agricultural sustainability and efficiency. Studies have shown that adding surfactants to agrochemicals can greatly improve their effectiveness.

8.2.1 Role of Surfactants in Herbicide Efficiency

According to studies by (Bao et al. 2023, Bhardwaj et al., 2021), adding surfactants to glyphosate formulations can boost weed control effectiveness by as much as 40%. This is because greater spreading and penetration allow herbicides to be absorbed more effectively and decrease chemical waste.

8.2.2 Surfactants in Pesticide Applications

Nonionic surfactants enhanced pesticide adherence and absorption on plant surfaces, increasing pest control effectiveness by 30%, according to research by (Green & Foy 2004). Another study by (song et al., 2022) highlighted how organosilicone surfactants let insecticides penetrate plant tissues more effectively, improving the efficacy of pest management.

8.2.3 Seed Treatment and Germination Enhancement

According to research by (Madsen et al. 2016), surfactants in seed coats increased water absorption, which in turn increased germination rates in crops including wheat and barley. Faster and more consistent seedling emergence was made possible by the use of wetting agents.

8.2.4 Surfactants in Soil and Water Management

According to research by (DeBanoet al., 2000), surfactants assist sandy soils retain and infiltrate water, which reduces the need for irrigation by over 25%. This has important ramifications for dry regions' sustainable agriculture.

8.2.5 Environmental and Safety Aspects of Surfactant Use

Interest in biosurfactants has grown as a result of worries about the effects of synthetic surfactants on the environment. The potential of microbial and plant-derived surfactants as biodegradable and environmentally acceptable substitutes for conventional chemical surfactants is highlighted by research by (Banat et al., 2010).

8.3 Types of Surfactants Used in Agriculture

Surfactants are classified according to their ionic nature and chemical composition(Kralova et al., 2009). The following are the main categories of surfactants utilised in agriculture:

8.3.1 Nonionic Surfactants: Nonionic surfactants are frequently utilised in agricultural applications since they don't have an electrical charge. They enhance absorption and aid in the uniform distribution of agrochemicals across plant surfaces. Alkyl polyglucosides(APGs) and ethoxylated alcohols are two examples.

Example: Ethoxylated nonylphenol is commonly used in pesticide formulations to enhance adhesion and effectiveness, ensuring even distribution on plant surfaces.

8.3.2 Anionic Surfactants: These surfactants are frequently used in conjunction with other surfactants to enhance dispersion and emulsification because they are negatively charged(Gayathiri et al., 2022). The anionic surfactants phosphates, sulphates, and sulfonates are frequently found in fertilisers and herbicides.

Example: Sodium lauryl sulfate(SLS) is used in agricultural sprays to help distribute pesticides evenly across large crop fields.

8.3.3 Cationic Surfactants: Having a positive charge, cationic surfactants are less frequently utilised in agriculture because of the possibility of plant toxicity(Castro et al., 2013). Nonetheless, they are occasionally found in some pesticide formulations and soil additives.

Example: Quaternary ammonium compounds are applied in soil treatments to prevent fungal growth and bacterial infections in crops.

8.3.4 Amphoteric Surfactants: The pH of the solution determines whether amphoteric surfactants behave as cationic or anionic. Speciality formulations that call for pH-dependent qualities employ these surfactants(Barman et al., 2024).

Example: Betaines are used in some biopesticide formulations to improve solubility and stability.

8.4 Applications of Surfactants in Agriculture

Surfactants are essential to agriculture because they increase the efficacy of soil treatments, fertilisers, insecticides, and herbicides. They improve agricultural chemicals' adhesion, penetration, and spreading by lowering surface tension.

The following are some important uses:

8.4.1 Pesticide and Herbicide Efficiency

In order to provide greater coverage and more constant action against weeds and pests, surfactants aid in the even application of pesticides and herbicides on plant surfaces. Surfactants facilitate the chemicals' more efficient penetration of the plant cuticle by lowering surface tension(Sachdev et al., 2013).

The performance of insecticides and herbicides is frequently enhanced by the use of surfactants. They help in:

8.4.1.1Better spreading: On waxy plant surfaces, water-based sprays often create droplets that bead up. By lowering surface tension, surfactants enable the spray to disperse uniformly throughout the leaf.

8.4.1.2Enhanced penetration: In order to reach interior tissues, systemic insecticides and herbicides (like glyphosate) have to penetrate plant cuticles. Surfactants make this absorption easier.

8.4.1.3Reduced runoff: Pesticides may run off leaves in the absence of surfactants, contaminating the environment and decreasing their effectiveness.

Used Surfactants

- **8.4.1.3.1Silicone-based surfactants**: Permit insecticides and herbicides to enter plant tissues more deeply.
- **8.4.1.3.2Non-ionic surfactants** (e.g., ethoxylated alcohols): used to improve penetration of systemic herbicides like as glyphosate.
- **8.4.1.3.3Anionic surfactants**: They are frequently utilised in insecticide formulations and enhance the spread of pesticides.

8.4.2 Fertilizer Absorption and Nutrient Uptake

Surfactants are utilised to improve fertiliser nutrient absorption, particularly when foliar feeding is being employed. They guarantee that fertilisers remain on the plant long enough to be absorbed by increasing the wetness of leaf surfaces and decreasing evaporation.

When liquid fertilisers are applied to plant leaves (foliar fertilisation), surfactants enhance absorption(Silva et al., 2024).

They:

- **8.4.2.1Enhance root zone penetration**: Surfactants make it possible for plant roots to absorb nutrients from the soil more efficiently.
- **8.4.2.2Help fertilizers stick to leaves**: Nutrient solutions may bead up and roll off leaves in the absence of surfactants, which would decrease nutrient absorption.
- **8.4.2.3Improve solubility**: Consistent application is ensured by surfactants, which aid in the uniform dissolution of fertilisers in water.

8.4.3 Soil Wetting and Water Retention

Water is repelled by some soils, particularly those that are sandy and hydrophobic. Surfactants increase the retention of water in soil by:

- **8.4.3.1Breaking hydrophobic barriers**: They prevent water from collecting on the surface by improving the ability of water to percolate dry soils.
- **8.4.3.2Enhancing irrigation efficiency**: By distributing water more uniformly across the soil, dry patches are lessened and root hydration is enhanced.
- **8.4.3.3Reducingwaterwastage**:Surfactants improve agricultural yields and conserve resources by preventing excessive water runoff.

8.4.4 Seed Treatment and Germination Enhancement

Surfactants are used in seed coatings to:

8.4.4.1Increase seedling vigor: Surfactants promote in the establishment of stronger root systems in seedlings by increasing early moisture availability.

8.4.4.2Ensure uniform coating: They help with the uniform application of microbial inoculants, insecticides, and fungicides on seeds.

8.4.4.3Improve water absorption: Hydrophilic surfactants help seeds imbibe, which makes it possible for them to take water more effectively and germinate more quickly.

8.4.5 Foam Control in Agricultural Sprays

In agricultural sprayers, excessive foam generation can:

8.4.5.1 Reduce the accurateness of chemical application.

8.4.5.2 Cause delays in field operations.

8.4.5.3 Lead to loss of active ingredients.

How Surfactants Help

- To prevent foam formation, anti-foaming chemicals (AFCs) are added to spray solutions.
- Existing foam is broken down with defoamers.
- Fatty alcohols and silicone-based surfactants are common anti-foaming agents.

8.4.6 Post-Harvest Applications

Surfactants are used after harvest to:

8.4.6.1Improve disinfection efficiency: To keep harvested crops from spoiling, aid in the more efficient dissemination of antimicrobial medicines (AMMs).

8.4.6.2Remove pesticide residues: used to clean fruits and vegetables before they are sold in produce washing.

8.4.6.3Enhance wax coatings: Assist in applying protective coatings on fruits, such as citrus and apples, to prevent moisture loss and preserve freshness.

8.4.7 Biopesticide and Biostimulant Formulations

Biological pesticides (biopesticides) and biostimulants often require surfactants to:

8.4.7.1Ensure even dispersion: helps in the uniform distribution of plant extracts or beneficial microorganisms on plant surfaces.

8.4.7.2Stabilize microbial formulations: inhibits helpful microorganisms from gathering in one place.

8.4.7.3Enhance contact with pests: makes certain that, for efficient pest management, biological agents such as Bacillus thuringiensis (Bt) stick correctly to leaves.

8.4.8Enhancement of Pesticide Efficacy: Surfactants increase the capacity of pesticides to penetrate and distribute, which enhances their effectiveness. Surfactants decrease surface tension, which improves coverage and lowers runoff by ensuring that pesticides stick to plant surfaces [28].

Example: Organosilicone surfactants are widely used in insecticides to enhance penetration into plant tissues, making them more effective in controlling pests like aphids and whiteflies.

8.4.9Herbicide Performance Improvement: Surfactants are frequently needed by herbicides to increase their efficacy. Systemic herbicides are frequently used with nonionic surfactants to improve plant absorption. For instance, surfactants are commonly included in glyphosate formulations to aid with absorption(Banjare et al., 2024).

Example: The addition of polyethoxylated tallow amine in glyphosate-based herbicides enhances weed control by increasing the penetration of the active ingredient.

8.4.10Fertilizer Efficiency Enhancement: Liquid fertilisers use surfactants to enhance soil penetration and nutrient delivery. They ensure that plants acquire enough nutrients by assisting fertilisers in dispersing evenly and minimising leaching.

Example: Humic acid-based surfactants are used in foliar fertilizers to enhance nutrient uptake in crops like wheat and corn.

8.4.11Soil Conditioning and Moisture Retention: Surfactants help in altering the characteristics of soil to improve permeability and water retention. In sandy soils where water tends to drain rapidly, they are very helpful. Soil surfactants promote improved plant development by preventing water repellency and improving water distribution(Castro et al., 2014).

Example: Polyacrylamide-based surfactants are used in drought-prone areas to retain soil moisture and reduce water runoff in crops like rice and cotton.

8.4.12Seed Treatment: To enhance germination and early plant development, surfactants are included into seed coats. They aid in the even administration of seed treatments and promote water absorption.

Example: Seed-applied wetting agents, such as polysorbates, are used in maize and soybean cultivation to enhance seed hydration and uniform germination.

8.4.13Post-Harvest Applications: In post-harvest procedures, surfactants are used to lessen spoiling and increase the effectiveness of preservatives. They prolong the shelf life of agricultural products by improving the dispersion of antibacterial compounds.

Example: Lecithin-based surfactants are used in fruit coatings to reduce moisture loss and maintain freshness during transportation.

8.4.14Fungicide Delivery: When fungicides are applied, surfactants aid in the breakdown of the waxy coats of plant leaves, which improves the fungicides' ability to reach their intended targets.

8.4.15Water Retention and Distribution: Water in soil is better distributed and retained when surfactants are present. They can be used to irrigation systems to provide more equal water penetration, avoiding waterlogging or uneven distribution of soil moisture(Cirelli et al., 2010).

8.4.16Biodegradable Surfactants: The usage of biodegradable surfactants is growing in popularity as a result of the growing need for sustainable farming methods. These are environmentally friendly substitutes that break down organically, lessening their negative effects on the environment(Barman et al., 2024).

To conclude, the use of surfactants in agricultural research improves the effectiveness of agricultural goods, resulting in higher yields, improved crop protection, and more economical use of resources.

8.5 Mechanism of Action of Surfactants in Agriculture

Surfactants work by changing the way liquids and solids interact and their surface characteristics(Shukla et al., 2019). Among the primary mechanisms are:

8.5.1 Reducing Surface Tension: As a result, agrochemical treatments may cover plant surfaces more evenly.

8.5.2 Increasing Wettability: Surfactants increase absorption by making it easier for water-based solutions to moisten plant surfaces.

8.5.3 Enhancing Penetration: Surfactants help transport active chemicals into plant tissues by dissolving obstacles like waxy cuticles on leaves.

8.5.4 Improving Dispersion: By avoiding aggregation and settling, surfactants aid in maintaining the suspension of solid particles in liquid compositions.

8.5.5 Reducing Drift: By altering droplet size and enhancing spray deposition, some surfactants lessen spray drift.

8.6 Environmental and Safety Considerations

Although surfactants have many advantages in agriculture, their usage needs to be carefully controlled to avoid hazards to the environment and human health.

8.6.1 Biodegradability and Eco-Toxicity

To reduce the impact on the environment, biodegradable surfactants are recommended. Pollution of soil and water can result from the buildup of non-biodegradable surfactants in the environment(Poapst et al., 1994).

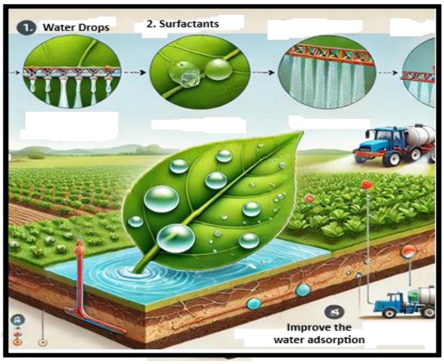

Figure 8.1. Showing how surfactant work in agriculture

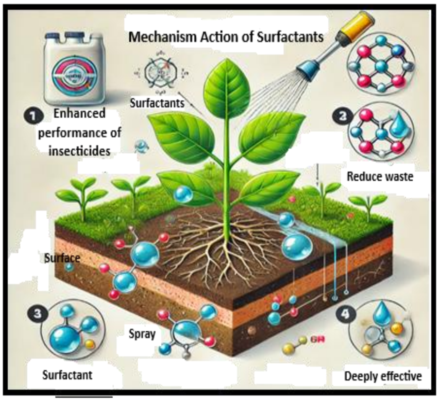

Figure 8.2. Mechanism of Action of Surfactants in Agriculture

8.6.2 Impact on Soil Microorganisms

Overuse of surfactants can upset the microbial balance in the soil, which can impact soil health and nutrient cycling.

8.6.3Residue Concerns

Food safety may be impacted by surfactant residues left on crops. Regulatory requirements and appropriate application methods must be adhered.

8.6.4Regulatory Compliance

To guarantee safety and effectiveness, surfactant usage is governed by agricultural standards. Environmental and agricultural authorities have established criteria that farmers and agricultural experts must follow (Knoche et al., 1994).

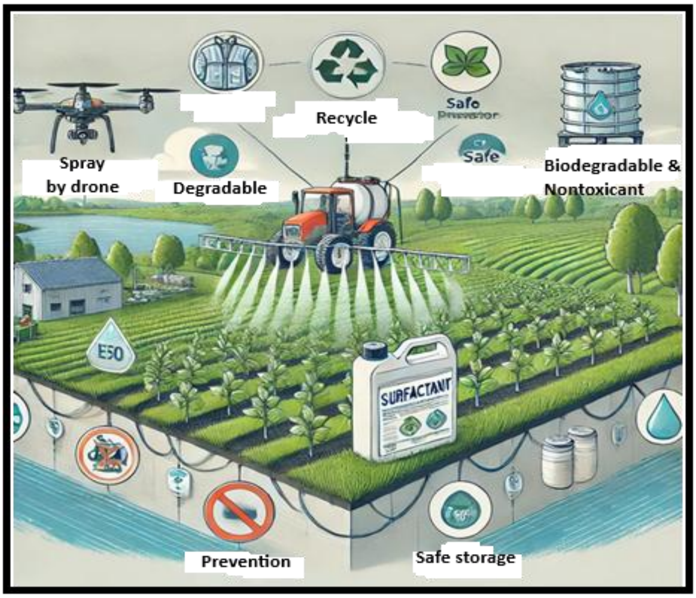

Figure 8.3. Environmental and Safety Considerations

8.7 Recent Advances in Agricultural Surfactants

The production of more efficient and ecologically friendly surfactants (EFSs) is the result of recent research and technical advancements(Barman et al., 2024).

8.7.1 Smart Surfactants

Smart surfactants are made to react to environmental factors like pH and temperature, maximising their effectiveness in particular situations(Chmieleska et al., 2019).

8.7.2 Biosurfactants

Biosurfactants, which are derived from natural sources like bacteria and plants, provide a sustainable substitute for synthetic surfactants. They are less harmful to the environment and biodegradable(Jibrin et al., 2021, Kirkwood et al., 1993).

8.7.3 Nano-Encapsulated Surfactants

The creation of nano-encapsulated surfactants (NESs), which enhance pesticide delivery and efficacy while lessening their environmental impact, has been made possible by nanotechnology(Barman et al., 2024).

8.7.4 Sustainable Formulations

The manufacturing of surfactants from renewable raw resources is becoming more and more common. The goal of green chemistry (GC) techniques is to lower the carbon footprint associated with the production of surfactants(Banjare et al., 2023).

8.8 Conclusion

Surfactants they increase the efficacy of fertilisers, insecticides, herbicides, and soil treatments, surfactants are essential to contemporary agriculture. Higher agricultural output is a result of their capacity to improve wetting, penetration, and dispersion. However, surfactant usage requires careful management of its safety and environmental effects. The agriculture industry has a chance to strike a balance between environmental responsibility and efficiency thanks to the development of sustainable and biodegradable surfactants. Innovative surfactant technologies can help agriculture move towards more efficient and sustainable agricultural methods.

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Chapter 9: Application of Surfactants in Pesticides

Namrata Tamboli

Abstract

Surfactants are vital to improving the efficacy of pesticides by facilitating their dispersion, adhesion, and penetration on cell surfaces. Surfactants function as adjuvants by reducing surface tension, which facilitates the even distribution of pesticide formulations on plant surfaces and enhances surface area. Their capacity to enhance the solubilization of hydrophobic active ingredients allows for the creation of more effective formulations, especially for pesticides with low water solubility. Surfactants improve the absorption of active ingredients into plant tissues by disrupting cuticular barriers, thereby enhancing systemic action. Recent advancements in surfactant technology include the development of biodegradable biosurfactants and polymeric surfactants, which aim to mitigate environmental persistence and toxicity issues, thereby providing sustainable alternatives to traditional surfactants. Responsive surfactants, engineered to activate under defined environmental conditions, offer targeted control in agricultural applications. The incorporation of surfactants in pesticide formulations leads to less amount requirement which contributes to decreased environmental contamination and expanded pest control effectiveness. Therefore, promoting sustainable agricultural practices with surfactants is crucial. This book chapter addresses This chapter includes the recent developments in surfactant chemistry, their significance in pesticide formulation, and emerging trends focused on eco-friendly and effective pest management solutions.

***Keywords**:* Surfactants, Pesticide, Hydrophobic Active Ingredient, Biosurfactants, Novel Surfactants, Sustainable Agriculture, Pest Management

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9.1. Introduction

Surfactants, or surface-active agents, are vital components in the formulation of pesticides, significantly improving their performance, stability, and delivery efficiency in agricultural practices (Silva et al., 2024). These amphiphilic molecules, comprising hydrophobic (waterrepelling) and hydrophilic (water-attracting) segments, reduce surface and interfacial tensions (Jain et al., 2023). This property facilitates better interaction between pesticide formulations and plant surfaces, pest targets, and environmental interfaces. Their functionality in wetting, emulsification, dispersion, and adhesion underscores their indispensable role in modern pesticide applications (Mustafa and Hussein, 2020). One primary role of surfactants is as wetting agents, reducing the surface tension of pesticide solutions. This ensures uniform spreading on the hydrophobic surfaces of plant leaves, optimizing coverage and enhancing penetration into the target areas. For instance, glyphosate, a widely used herbicide, relies on nonionic surfactants for effective weed control by penetrating the waxy cuticle of plants (Green &Beestman, 2007). Emulsifiers, another category of surfactants, stabilize oil-in-water emulsions for hydrophobic pesticides, preventing phase separation during storage and application (Hazen, 2000). Dispersants facilitate the uniform distribution of solid pesticide particles, avoiding aggregation and ensuring consistent activity in suspension formulations. Additionally, surfactants act as adhesion enhancers, improving pesticide retention on plant surfaces and minimizing loss due to rain or irrigation (Mustafa and Hussein, 2020). Moreover, surfactants enhance bioavailability and target specificity. They promote pesticide solubility, improve absorption through plant cuticles, and reduce drift during application. Advanced formulations, such as nanoemulsions, incorporate surfactants to achieve controlled pesticide delivery, minimizing environmental contamination and off-target effects (Wang et al., 2007). The development of biodegradable and eco-friendly surfactants is an emerging focus to address environmental concerns. These innovations aim to balance efficiency with sustainability, highlighting the pivotal role of surfactants in the future of agricultural pest management (Mustafa and Hussein, 2020). The research paradigm surrounding surfactants in pesticides focuses on their role in enhancing pesticide efficacy, stability, and environmental safety. Current studies emphasize optimizing surfactant properties, such as wetting, emulsification, dispersion, and adhesion, to improve pesticide delivery and minimize off-target effects (Green &Beestman, 2007). Innovations include the development of nanoemulsions and biodegradable surfactants to address environmental concerns while maintaining effectiveness (Wang et al., 2007). Additionally, research explores the interactions between surfactants, active ingredients, and plant surfaces to enhance bioavailability and target specificity (Mustafa and Hussein, 2020). This multidisciplinary approach drives sustainable advancements in agricultural pest management.

The incorporation of surfactants in pesticide formulations also has significant environmental and economic implications. By enhancing the efficacy of active ingredients, surfactants enable lower application rates, reducing the overall chemical load in the environment. Additionally, surfactants improve the targeting of pesticides, minimizing off-target effects and reducing the risk of contamination in non-target areas.For example, the use of biodegradable surfactants, such as alkyl polyglucosides, addresses environmental concerns associated with conventional surfactants. These biodegradable options maintain the functional properties of wetting, emulsification, and dispersion while reducing the ecological footprint of pesticide applications (Mustafa and Hussein, 2020). Furthermore, the improved efficiency provided by surfactants translates into cost savings for farmers, making pest management more affordable and sustainable.Recent advancements in surfactant technology have focused on developing novel formulations that address specific challenges in pesticide applications. Nanoemulsion-based surfactants, for instance, offer enhanced stability, bioavailability, and target specificity. These surfactants improve the penetration and retention of pesticides on plant surfaces Bby reducing droplet size to the nanoscale (Bao et al., 2023). Another innovation is the use of functionalized surfactants that combine multiple functionalities, such as wetting, emulsification, and adhesion, in a single molecule. These multifunctional surfactants simplify formulation design and improve overall performance. Additionally, the integration of surfactants with controlled-release technologies enables the gradual release of active ingredients, extending the duration of pest control and reducing the frequency of applications (Green &Beestman, 2007).

9.2. Role of surfactants in pesticide

Surfactants, also known as surface-active agents, are indispensable components of modern pesticide formulations due to their ability to optimize the physical, chemical, and biological properties of active ingredients. By reducing surface tension and enhancing interactions between the pesticide and its target, surfactants play a pivotal role in ensuring effective pest control. Their functionalities, including wetting, emulsification, dispersion, and adhesion, contribute to enhanced efficiency, improved stability, and reduced environmental impact of pesticide applications.

9.2.1. Wetting agents

Wetting agents are a subclass of surfactants designed to reduce the surface tension of pesticide solutions, enabling better coverage and penetration. Many plant surfaces, particularly the leaves, are hydrophobic, making it challenging for aqueous pesticide solutions to spread uniformly. Wetting agents address this limitation by promoting the spreading of the solution across the leaf surface, ensuring maximum contact with the target pest or pathogen. For instance, nonionic surfactants like alkylphenol ethoxylates and polyethylene glycol ethers are commonly used as wetting agents in pesticide formulations. Studies have shown that these surfactants significantly enhance the efficacy of herbicides like glyphosate, allowing the active ingredient to penetrate the cuticle and reach the site of action (Stock & Holloway, 1993). Similarly, in insecticide applications, wetting agents improve the adhesion and spread of solutions, increasing their effectiveness against pests with waxy cuticles. Another example is the use of Tween 20, a nonionic surfactant, in fungicide formulations. When added to solutions targeting fungal pathogens like *Botrytis cinerea*, it facilitates even distribution on plant surfaces, ensuring consistent fungicide efficacy (Bao et al., 2023). This illustrates the critical role of wetting agents in bridging the gap between pesticide chemistry and biological efficacy.

9.2.2. Emulsifiers

Emulsifiers are surfactants that stabilize mixtures of immiscible liquids, such as oil and water. Many pesticides are hydrophobic and require oil-based formulations to ensure stability and delivery (Feng et al., 2018). However, these formulations often face challenges such as phase separation during storage or application. Emulsifiers address this by stabilizing oil-in-water or water-in-oil emulsions, maintaining homogeneity and preventing coalescence e.g., sorbitan esters and polysorbates are widely used as emulsifiers in pesticide formulations. In oil-in-water emulsions, these surfactants form a protective layer around oil droplets, preventing aggregation. This stabilization ensures that hydrophobic pesticides, such as organophosphates and pyrethroids, remain uniformly dispersed in the spray solution, improving their effectiveness (Knowles, 2008). One notable application is in the formulation of chlorpyrifos, a hydrophobic insecticide. The inclusion of emulsifiers like Span 80 ensures the formation of a stable emulsion, allowing for consistent application and enhanced pest control in agricultural fields (Henao-Ardila et al., 2024; Green &Beestman, 2007). Emulsifiers thus play a crucial role in addressing formulation challenges, ensuring the stability and bioavailability of hydrophobic pesticides.

9.2.3. Dispersants

Dispersants are surfactants that facilitate the uniform dispersion of solid particles in liquid media, preventing sedimentation and aggregation. In suspension concentrates and wettable powders, dispersants ensure that pesticide particles remain evenly distributed, enabling consistent application and reducing clogging in spray equipment. Anionic surfactants, such as sodium lignosulfonate and alkylbenzene sulfonates, are commonly used as dispersants in pesticide formulations. These surfactants adsorb onto the surface of solid particles, imparting a negative charge that prevents particle aggregation through electrostatic repulsion (Mustafa and Hussein, 2020). This property is particularly important in the formulation of contact fungicides like mancozeb and systemic herbicides like atrazine. Sodium lignosulfonate often used in suspension concentrates of copper-based fungicides to ensure uniform dispersion of copper particles. It enhances the fungicide’s coverage and efficacy against diseases like downy mildew and blight (Cahill et al., 2018). Dispersants thus contribute significantly to the performance and reliability of pesticide formulations, ensuring uniform delivery of active ingredients.

9.2.4. Adjuvants

Adjuvants are auxiliary substances, often surfactants, added to pesticide formulations to enhance their performance. In the context of surfactants, adjuvants improve the adhesion, retention, and rain fastness of pesticides on plant surfaces. By forming a film or increasing the viscosity of the solution, they prevent wash-off by rain or irrigation, ensuring prolonged contact with the target. Silicone-based surfactants, such as organosilicon compounds, are widely used as adjuvants in pesticide formulations. These surfactants reduce surface tension to extremely low levels, enabling the formation of thin, uniform films on plant surfaces. Research has shown that silicone-based adjuvants enhance the adhesion and retention of systemic insecticides like imidacloprid, improving their uptake and translocation within plants (Stevens et al., 1993). Silwet L-77 is a silicone-based surfactant that is used in formulations that target aphids and whiteflies. It improves the spreading and adhesion of the pesticide solution, enhances pest control, and reduces the required application rate (Mustafa and Hussein, 2020). List of Pesticides and their Surfactant Additives shown in Table 9.1.Henceforth, surfactants as adjuvants have a crucial role in improving the efficiency and sustainability of pesticide applications.

Table 1. List of Pesticides and their Surfactant Additives

Pesticide	Surfactant Additive	Role of Surfactant	Use
Glyphosate (Herbicide)	Polyethoxylated tallow amine (POEA)	Wetting agent and penetrant: Enhances spreading and uptake of the herbicide on plant surfaces.	Used in glyphosatebased herbicide formulations for effective weed control.
Atrazine (Herbicide)	Sodium lignosulfonate	Dispersant: Prevents sedimentation and ensures uniform suspension in liquid formulations.	Applied in corn and sugarcane farming to control broadleaf weeds and grasses.
Imidacloprid (Insecticide)	Tween 80 (Polysorbate 80)	Emulsifier: Stabilizes emulsions of active ingredient for better delivery and efficacy.	Used in crop pest control against aphids, whiteflies, and other insects.
Chlorothalonil (Fungicide)	Dioctyl sodium sulfosuccinate	Wetting agent: Improv	Effective in controlling fungal diseases like blight and mildew in crops such as potatoes and

			tomatoes.
2,4-D (Herbicide)	Alkylphenol ethoxylate	Adjuvant: Enhances spreading, wetting, and penetration of the herbicide on leaves.	Commonly used for broadleaf weed control in grasslands and cereal crops.
Spinosad (Insecticide)	Lecithin	Dispersant and emulsifier: Ensures homogeneity in water-based spray formulations.	Applied for pest control in organic farming and home gardening.
Pyraclostrobin (Fungicide)	Dimethylpolysiloxane	Spreader-sticker: Provides excellent spreading and adhesion on hydrophobic surfaces.	Used in fungicide formulations to prevent fungal infections like rust and scab.
Bifenthrin (Insecticide)	Sorbitan monooleate	Emulsifier: Stabilizes oil-based formulations for effective pest control.	Applied to control soil and foliar insects in fruits, vegetables, and ornamentals.
Metolachlor (Herbicide)	Ethylene glycol alkyl ether	Penetrant: Improves absorption and translocation of herbicide through plant cuticles.	Used in pre-emergent herbicide formulations to control grasses and broadleaf weeds.
Mancozeb (Fungicide)	Glycerol	Humectant: Retains moisture to prolong the effectiveness of the fungicide on treated surfaces.	Applied to protect crops like potatoes, tomatoes, and citrus from fungal diseases.
Lambda-Cyhalothrin (Insecticide)	Cocamidopropyl betaine	Foaming agent: Enhances foam application for better distribution in	Used for insect control in crops, residential settings, and public health

		specific pest control applications.	applications.
Paraquat (Herbicide)	Dioctyl sulfosuccinate	Wetting agent: Improv	Commonly used in desiccation of crops like cotton and sugarcane before harvest.
Tebuconazole (Fungicide)	Propylene glycol	Humectant: Prevents drying of spray solution for extended surface contact.	Used to control fungal diseases like powdery mildew and leaf spots in cereals and vegetables.
Carbaryl (Insecticide)	Benzalkonium chloride	Antimicrobial and emulsifier: Prevents microbial degradation and stabilizes emulsions.	Applied to control pests such as caterpillars, beetles, and aphids in fruits and vegetables.
Abamectin (Insecticide)	Methylated seed oils (MSO)	Penetrant: Enhances absorption and translocation in pest control applications.	Used in managing mites and leafminers in crops like citrus and vegetables.
Fenoxaprop-Pethyl (Herbicide)	Silicone surfactants	Spreader-sticker: Improves uniform distribution and adhesion to plant surfaces.	Commonly used for post-emergent control of grasses in wheat and rice fields.

9.3. Types of surfactants in pesticide formulation

Surfactants, or surface-active agents, are classified based on the charge of their hydrophilic head groups. They are critical in pesticide formulations, influencing various factors such as solubility, stability, and efficacy. An anionic, cationic, nonionic and amphoteric surfactants are often used in various pesticide formulations.

9.3.1. Anionic surfactants

Anionic surfactants, characterized by a negative charge on their hydrophilic head groups, include examples such as alkyl sulfates and sulfonates, with sodium dodecyl sulfate (SDS) being widely used to improve the wetting properties of pesticide sprays (Khalfallah, 2023). They are highly efficient in reducing surface tension, emulsification, and dispersion, making them effective in pesticide formulations (Mulligan, 2005). However, Kaczorek et al. (2018) found that they may exhibit potential phytotoxicity and reduced effectiveness in the presence of hard water ions due to sensitivity to these ions.

9.3.2. Cationic surfactants

Cationic surfactants, characterized by a positively charged hydrophilic head group, are exemplified by quaternary ammonium compounds like cetyltrimethylammonium bromide (CTAB), which is valued for its adhesion-enhancing properties. These surfactants exhibit excellent antimicrobial activity and strong adhesion to negatively charged surfaces, making them effective in certain formulations (Sayed et al., 2023). However, their toxicity to plants and aquatic organisms limits their widespread use in agricultural applications.

9.3.3. Nonionicsurfactants

Nonionic surfactants, such as ethoxylated alcohols and fatty acid esters, are uncharged compounds that achieve solubility through their molecular structure. A notable example is polyethylene glycol esters, known for their superior wetting and spreading properties.They offer advantages like compatibility with diverse pesticides and resistance to hard water ions, making them highly versatile (Green &Beestman, 2007). However, they exhibit reduced foaming capacity and may be less effective in emulsification compared to ionic surfactants.

9.3.4. Amphoteric surfactants

Amphoteric surfactants, such as betaines, can carry either a positive or negative charge depending on the solution's pH, offering versatility in various applications. They are highly stable across a wide pH range and exhibit reduced toxicity compared to cationic surfactants, making them suitable for environmentally friendly formulations (Rosen &Kunjappu, 2012). However, their higher cost and limited availability pose challenges for widespread use. For instance, a cocamidopropyl betaine is commonly employed in formulations requiring mild but effective surfactants. Surfactants offer significant benefits; their environmental implications must be considered. Nonbiodegradable surfactants, especially cationic types, can persist in ecosystems, leading to toxicity concerns (Ying, 2006). Hence, the development of biodegradable surfactants is a priority. The properties of selected surfactants are summarized in Table 9.2.However, the choice of surfactant in pesticide formulations depends on the target pest, environmental conditions, and desired performance. A balanced consideration of advantages and disadvantages, coupled with environmental safety, is essential for effective application. Ongoing advancements in surfactant technology, including biodegradable and nanoemulsion-based formulations, could holds promise for greater efficiency, sustainability, and environmental stewardship of pesticide. The integration of surfactants in pesticide formulations exemplifies the synergy between chemistry and biology in addressing global agricultural challenges.

9.4. Applications of surfactants in pesticide delivery systems

Surfactants are essential in pesticide delivery systems, optimizing the efficacy, stability, and target specificity of active ingredients. By improving solubility, adhesion, and compatibility while minimizing environmental risks, they ensure optimal performance across various formulations, including emulsions, suspensions, and solutions.

9.4.1. Improved solubility and Dispersion

Surfactants act as solubilizing agents by increasing the water solubility of hydrophobic pesticide molecules. Non-ionic surfactants like ethoxylated alcohols are frequently used to dissolve poorly soluble herbicides, ensuring uniform dispersion in water-based formulations (Castro et al., 2013).This enhances the bioavailability of the active ingredient, improving pest control efficacy.

9.4.2. Enhanced adhesion and retention

Adhesion of pesticides to plant surfaces is critical for effective pest control. Surfactants, particularly anionic surfactants such as sodium dodecyl sulfate, improve adhesion by forming a uniform film on hydrophobic plant surfaces (Karamchandani et al., 2022). This reduces pesticide runoff during irrigation or rainfall.

Surfactant	Chemical Formula	Type	Properties	Applications	Reference
Sodium lauryl sulfate (SLS)	$CH_3(CH_2)_{11}OSO_3Na$	Anionic Surfactant	High foaming, good wetting, excellent emulsification, and detergency properties.	Used in wetting agents, emulsifiers, and detergents.	Mulligan (2005)
Alkyl benzene sulfonates	$R-C_6H_4-SO_3Na$ (R = alkyl group)	Anionic Surfactant	High detergency, stable in hard water, excellent emulsification properties.	Used in agricultural formulations, industrial cleaners, and detergents.	Knowles (2008)
Polyethylene glycol (PEG)	$HO-(CH_2CH_2O)n-H$	Nonionic Surfactant	Water-soluble, biocompatible, reduces surface tension, acts as a humectant.	Used in emulsions, dispersions, and stabilizing formulations.	Green & Beestman (2007)
Sorbitan monooleate	C24H44O6	Nonionic Surfactant	Oil-soluble, low HLB, excellent emulsifier for water-in-oil systems.	Used in emulsions, creams, and agricultural sprays.	Green & Beestman (2007)
Lecithin	C42H80NO8P (general structure varies)	Amphoteric Surfactant	Biodegradable, excellent emulsifier, stabilizes	Used in food emulsions, cosmetic formulations, and	Stevens et al. (1993)

			suspensions, and enhances bioavailability.	agrochemicals	
Cocamidopropyl betaine	C19H38N2O3	Amphoteric Surfactant	Biocompatible, mild cleansing, foaming, and conditioning properties.	Used in foaming agents, shampoos, and industrial cleaners.	Knowles (2008)
Tween 80 (Polysorbate 80)	C64H124O26	Nonionic Surfactant	High HLB, water-soluble, excellent emulsifier for oil-in-water systems.	Used in emulsions, dispersions, and as a stabilizer in agrochemicals.	Green & Beestman (2007)
Dioctyl sodium sulfosuccinate	C20H37NaO7S	Anionic Surfactant	Lowers surface tension, excellent wetting, dispersing, and emulsifying properties.	Used in agricultural sprays, food additives, and detergents.	Mulligan (2005)
Dimethylpolysiloxane	$(C_2H_6OSi)n$	Silicone Surfactant	Reduces surface tension, provides hydrophobicity , excellent spreading properties.	Used in spreaderstickers, antifoaming agents, and lubricants.	Stevens et al. (1993)

Trisiloxane surfactants	R-$(CH_3)_2SiOSi(CH_3)_2O$-$(CH_3)_2SiR$	Silicone Surfactant	Superspreading properties, reduces surface tension to near zero.	Used in agrochemical formulations and spreaderstickers.	Stevens et al. (1993)
Benzalkonium chloride	C21H38NCl	Cationic Surfactant	Antimicrobial, strong adsorption to negatively charged surfaces, good foaming properties.	Used in sanitizers, foaming agents, and disinfectants.	Knowles (2008)
Cetyl trimethyl ammonium bromide	C19H42BrN	Cationic Surfactant	High foaming, excellent emulsifying and conditioning properties.	Used in conditioners, foaming agents, and antimicrobial applications.	Mulligan (2005)
Dimethylsiloxane	$(Si(CH_3)_2O)n$	Nonionic Silicone Surfactant	Reduces foam, excellent lubricating and hydrophobic properties.	Used in antifoaming agents and industrial lubricants.	Stevens et al. (1993)
Silicone oils	$(R_2SiO)n$	Nonionic Silicone Surfactant	Provides lubrication, water repellency, and low surface tension properties.	Used in antifoaming agents and spreaderstickers.	Mulligan (2005)

Ethylene glycol alkyl ethers	$HOCH_2CH_2OR$ (R = alkyl group)	Nonionic Surfactant	Soluble in water, excellent penetrant, improves pesticide translocation.	Used as a penetrant in agrochemical formulations.	Green & Beestman (2007)
Methylated seed oils (MSO)	Varies by seed source	Nonionic Surfactant	Enhances pesticide penetration, reduces surface tension, improves wetting properties.	Used in herbicide and fungicide formulations.	Stevens et al. (1993)
Glycerol	C3H8O3	Nonionic Surfactant	Biocompatible , hygroscopic, excellent humectant.	Used to retain moisture in agrochemical and personal care formulations.	Green & Beestman (2007)
Propylene glycol	C3H8O2	Nonionic Surfactant	Soluble in water, hygroscopic, excellent moistureretaining properties.	Used in humectants, emulsions, and as a solvent.	Mulligan (2005)

Table 9.2. Properties of Selected Surfactants

Table 9.3. Role and Type of Surfactants in Pesticide Formulations

Role	**Type of Surfactant**	**Chemical Nature**	**Function in Pesticide Formulation**	**Examples**	**Key Chemistry Context**	**References**
Wetting Agent	Anionic Surfactants	Sulfates, sulfonates, or carboxylates	Reduces surface tension, allowing pesticides to spread uniformly on leaf surfaces.	Sodium lauryl sulfate, Alkyl benzene sulfonates	Lowers surface tension due to hydrophilic and hydrophobic molecular domains.	Mulligan (2005)
Emulsifier	Nonionic Surfactants	Ethoxylated alcohols, fatty acids	Stabilizes emulsions, ensuring that water and oil-based components mix effectively.	Polyethylene glycol (PEG), Sorbitan monooleate	Forms micelles that solubilize oil-based pesticides in water.	Green & Beestman (2007)

Dispersant	Amphoteric Surfactants	Betaine derivatives, amine oxides	Prevents clumping or sedimentation of active ingredients in suspension concentrates.	Lecithin, Cocamidopropyl betaine	Acts as a steric or electrostatic stabilizer, maintaining uniform distribution of active component.	Knowles (2008)
Adjuvant	Nonionic or Anionic Surfactants	Polysorbates, sulfosuccinates	Enhances pesticide performance by improving adhesion, penetration, or retention on target surfaces.	Tween 80, Dioctyl sodium sulfosuccinate	Promotes compatibility and biological efficacy by altering the surface energy of treated areas.	Green & Beestman (2007)
SpreaderSticker	Silicone Surfactants	Polysiloxanes, silicone copolymers	Ensures better spread and adhesion of pesticides on hydrophobic plant surfaces.	Dimethylpolysiloxane, Trisiloxane surfactants	Provides superspreading properties by reducing surface tension to near zero.	Stevens et al. (1993)

Foaming Agent	Cationic Surfactants	Quaternary ammonium compounds	Facilitates foam generation for pesticide application in specific situations (e.g., soil fumigation).	Benzalkonium chloride, Cetyl trimethyl ammonium bromide	Produces foam via cationic headgroups binding with anionic counterparts in solutions.	Knowles (2008)
Antifoaming Agent	Nonionic Silicone Surfactants	Polysiloxane emulsions	Reduces excessive foam during pesticide formulation or application.	Dimethylsiloxane, Silicone oils	Destabilizes foam by disrupting hydrogen bonds and surface film elasticity.	Mulligan (2005)
Penetrant	Nonionic Surfactants	Alkoxylates, glycol ethers	Facilitates the entry of pesticides into plant tissues, improving their effectiveness.	Ethylene glycol alkyl ethers, Methylated seed oils	Enhances pesticide solubility and translocation by increasing cuticle permeability.	Stevens et al. (1993)

Humectant	Nonionic Surfactants	Glycols, sugar alcohol derivatives	Helps in retaining moisture, preventing the pesticide solution from drying out too quickly on plant surfaces.	Glycerol, Propylene glycol	Binds water molecules through hydrogen bonding, maintaining surface moisture for longer periods.	Green & Beestman (2007)

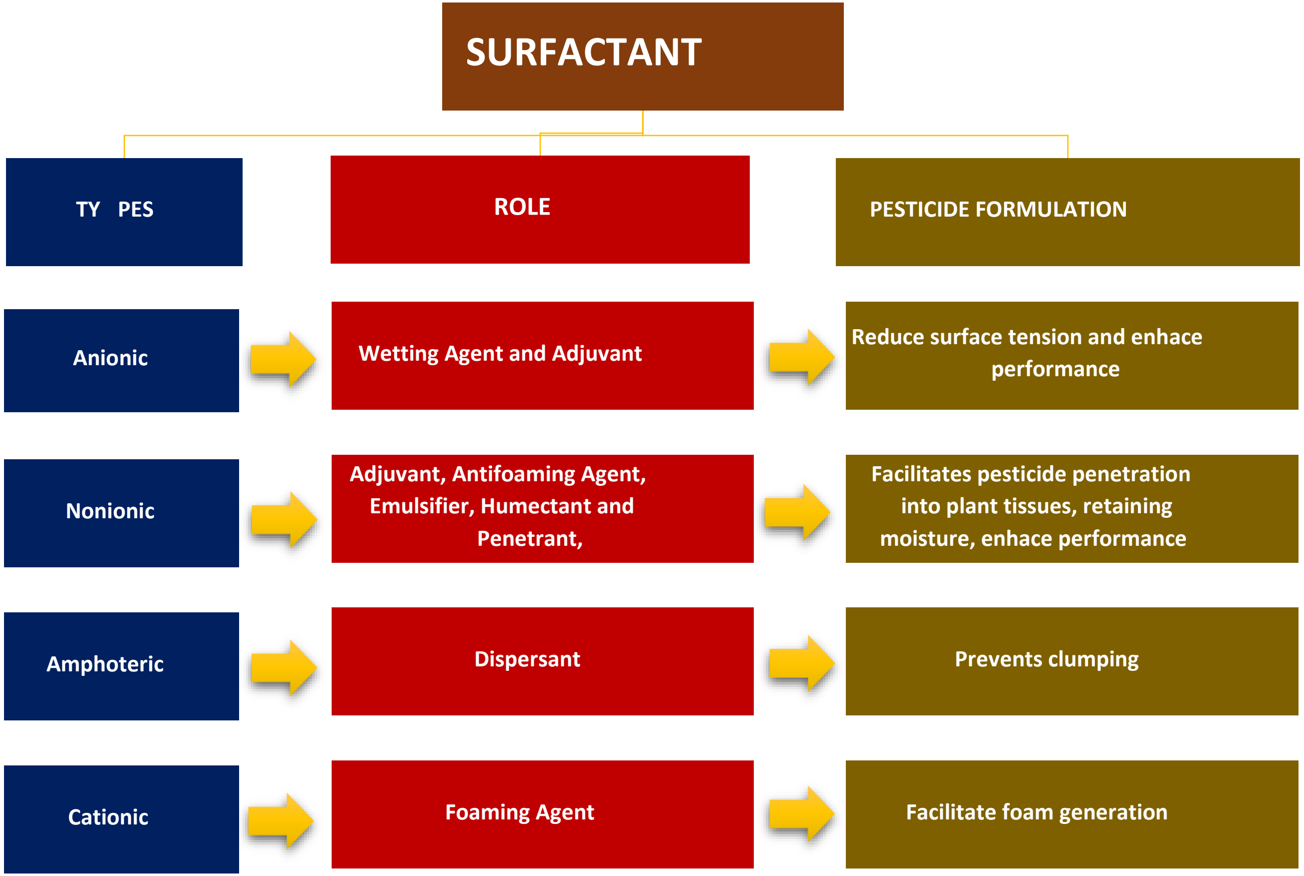

Fig 9.1. Role of Surfactant in pesticide formulation

9.4.3. Reduction of surface tension

Surfactants act as wetting agents, lowering the surface tension of spray solutions. For instance, Rosen &Kunjappu, (2012) mentioned that the alkylphenol ethoxylates in fungicide formulations improve the spreadability of the pesticide on plant surfaces, ensuring maximum coverage and penetration into pest targets.

9.4.4. Controlled release systems

Surfactants are integral to controlled-release pesticide formulations, where they regulate the release rate of active ingredients. de Oliveira et al. (2020) disclosed that the amphiphilic block copolymers, such as Pluronic F68, are used to develop nanocarrier systems for pesticides, providing prolonged pest control and reduced environmental impact.

9.4.5. Compatibility with Multiple Formulations

Surfactants enable compatibility between different pesticide types, such as herbicides and insecticides, in tank-mixed solutions. For example, Vermelho et al. (2024) divulged that a nonionic surfactant Tween 80 stabilizes emulsions in multi-functional pesticide formulations, preventing phase separation during storage and application.

9.4.6. Reduction of Environmental Impact

The inclusion of biodegradable surfactants, such as alkyl polyglucosides, reduces the environmental toxicity of pesticide formulations while maintaining efficiency. Hazra and Purkait (2019) stated that these surfactants are particularly effective in sustainable agricultural practices, minimizing soil and water contamination.

Therefore, the surfactants play critical roles in pesticide formulations by enhancing their efficiency and performance in various way shown in Table 9.3 and Fig 9.1. Wetting agents, often anionic surfactants like sulfates or sulfonates, reduce surface tension to ensure uniform spreading on leaves. Nonionic surfactants, such as ethoxylated alcohols, act as emulsifiers to stabilize oil-water mixtures, while amphoteric surfactants like betaine derivatives serve as dispersants, preventing sedimentation of active ingredients. Adjuvants, which can be anionic or nonionic, improve pesticide adhesion, penetration, or retention. Silicone-based spreader-stickers enhance coverage on hydrophobic surfaces, while cationic surfactants like quaternary ammonium compounds function as foaming agents for specific applications. Nonionic silicone surfactants reduce foam as antifoaming agents, and penetrants like alkoxylates aid pesticide absorption into plant tissues. Humectants, such as glycols, retain moisture, prolonging the pesticide's effectiveness on surfaces. Together, these surfactants optimize pesticide delivery, stability, and action for effective pest and weed control. Glyphosate, a widely used herbicide, relies on non-ionic surfactants like tallow amine ethoxylates to improve penetration into plant cuticles (Baylis, 2000). Similarly, the antifungal pesticide carbendazim is often formulated with anionic surfactants to enhance dispersion and adhesion (Shahid et al., 2023), while Mustafa and Hussein (2020) reported that the insecticide imidacloprid uses surfactants such as alkylbenzene sulfonates to stabilize emulsifiable concentrates, improving pest control effectiveness.

9.5. Environmental and economic impacts of surfactants in pesticides

The integration of surfactants in pesticide formulations has both positive and negative implications for the environment and economy. On the environmental front, surfactants enhance the efficiency of pesticides, reducing the required application dose and thereby minimizing pesticide runoff into soil and water bodies (Hazra and Purkait, 2019). Biodegradable surfactants, such as alkyl polyglucosides, have further decreased the ecological footprint of pesticide use by mitigating soil and aquatic toxicity (Rosen &Kunjappu, 2012). However, non-biodegradable surfactants, including alkylphenol ethoxylates, persist in the environment and pose risks of bioaccumulation and aquatic toxicity (Baylis, 2000). Economically, surfactants improve the cost-efficiency of pesticides by increasing their stability and reducing wastage. However, the production of highperformance surfactants, particularly biodegradable or amphiphilic ones, is cost-intensive, making formulations less accessible to small-scale farmers (Karamchandani et al., 2022). Furthermore, improper application techniques and excessive surfactant use can diminish long-term soil health, indirectly impacting agricultural yields and profitability.

9.6. Future trends and challenges

The future of surfactants in pesticides will focus on sustainability and efficiency. Advances in nanotechnology have led to the development of surfactant-based nanocarriers, which enable controlled pesticide release, reduced doses, and minimized environmental impact (de Oliveira et al., 2020). Biobased surfactants derived from renewable resources, such as rhamnolipids and sophorolipids, are gaining traction due to their biodegradability and lower toxicity profiles (Hazra and Purkait, 2019). However, challenges persist. Developing cost-effective biodegradable surfactants with high performance remains a hurdle. Regulatory frameworks for approving novel surfactants are stringent, delaying their market introduction. Additionally, achieving widespread adoption among farmers requires education on optimal surfactant use to prevent overuse and environmental degradation (Castro et al., 2013). Future research will focus on balancing economic feasibility with environmental sustainability, addressing global agricultural needs.

9.7 Conclusion

Surfactants are essential in pesticide formulations, improving performance, stability, and delivery efficacy in agriculture. These amphiphilic compounds, which have hydrophilic parts and hydrophobic parts, lower surface tension. This makes it easier for pesticides to interact with plant surfaces, pests, and the environment. Their functions encompass wetting agents that promote uniform distribution on plant foliage; emulsifiers that stabilize oil-in-water emulsions for hydrophobic pesticides; dispersants for uniform particle dispersion; and adhesion enhancers that augment retention and minimize wash-off. Glyphosate depends on nonionic surfactants for efficient plant absorption. It is easier to control and has less of an effect on the environment when surfactants are added to advanced formulations like nanoemulsions. They also make the formulations more bioavailable. Biodegradable surfactants, like alkyl polyglucosides, harmonized effectiveness with sustainability while mitigating ecological impacts. These enhancements reduce pesticide application rates, mitigate off-target impacts, and result in cost savings for farmers. New discoveries include surfactants based on nanoemulsions that can go deeper, surfactants that can wet, emulsify, and stick to surfaces, and controlled-release technologies that can keep pests away for longer. Surfactants are essential for effective, environmentally friendly, and sustainable pest management in contemporary agriculture.

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Chapter 10: Application of Surfactants in Anti-Microbial Activity

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Abstract

The application of surfactants in antimicrobial activity has gained significant attention due to their unique physicochemical properties, which enable interactions with microbial membranes. Surfactants, amphiphilic molecules containing both hydrophilic and hydrophobic groups, disrupt the structural integrity of microbial cell membranes, leading to their inactivation. This study explores the mechanisms by which various classes of surfactants, including cationic, anionic, nonionic, and zwitterionic types, exhibit antimicrobial effects against bacteria, fungi, and viruses. Cationic surfactants, such as quaternary ammonium compounds, have demonstrated potent bactericidal activity, primarily by targeting the negatively charged microbial membranes. Nonionic and zwitterionic surfactants, on the other hand, show promising synergistic effects when combined with antibiotics, enhancing their efficacy. Furthermore, the study discusses the environmental implications of surfactant use, emphasizing the need for biodegradable and eco-friendly formulations to minimize ecological impact. By understanding the antimicrobial mechanisms and optimizing surfactant formulations, this research aims to contribute to the advancement of effective and sustainable antimicrobial agents for food safety, environmental applications and healthcare sector.

Keywords: Surfactants, Anti-microbial, Amphiphilic, Physicochemical Properties, Sustainable.

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10.1 Introduction

Surfactants are a broad category of substances that are essential in a wide range of industrial, pharmaceutical, and biomedical uses. These amphiphilic molecules have the unique ability to reduce surface tension, facilitating interactions between different phases and interfaces. Surfactants can be broadly classified into several categories, including anionic, cationic, nonionic, zwitterionic, and biosurfactants. The structures of some surfactants are shown in fig10.1.

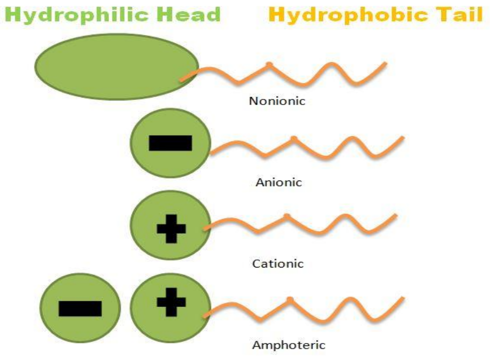

Fig. 10.1. Types of surfactants. Adopted from **(**An Easy Guide to Understanding How Surfactants Work _ IPC, 2022**)**

Cationic surfactants have attracted considerable interest due to their strong antimicrobial properties. These surfactants, usually containing quaternary ammonium groups, have demonstrated broad-spectrum antimicrobial effectiveness against various microorganisms, including bacteria, viruses, and fungi. Lipopeptide surfactants, a subclass of biosurfactants produced by microorganisms such as Bacillus subtilis, have been found to exhibit exceptional antimicrobial activity. These molecules, which combine a peptide backbone with a lipid tail, have been shown to interact with microbial membranes, ultimately leading to cell lysis and death. Lipopeptide surfactants, known for their strong antimicrobial properties, have become promising candidates for developing new antimicrobial agents, providing a potential solution to the increasing issue of antibiotic resistance.

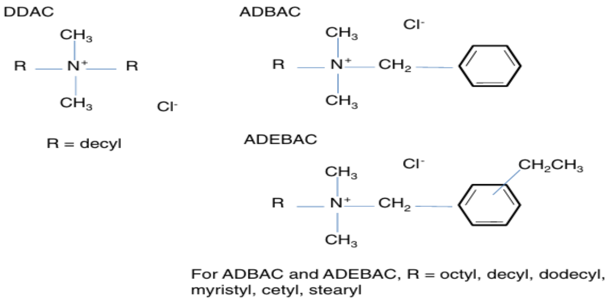

Fig 10.2. Some cationic surfactants like: - alkyldimethylbenzylammonium chloride, alkyldimethylethylbenzylammonium chloride, and didecylammonium chloride **(**N. A. Falk, 2019**).**

The rising prevalence of antimicrobial-resistant microorganisms has become a major global concern, highlighting the call for enhancement of new antimicrobial agents. Surfactants, a class of amphiphilic compounds, have garnered attention for their potential application in antimicrobial therapy. These surface-active agents have been shown to exhibit antimicrobial properties, either alone or in combination with other antimicrobial agents. Recent research has concentrated on the synthesis and analysis of new surfactants with improved antimicrobial properties. For instance, researchers have developed cationic gemini surfactants and amine surfactants based on sulfobetaines. Gemini surfactants, also referred to as dimeric surfactants, are a distinct category of amphiphilic compounds characterized by 2 hydrophobic tails and 2 hydrophilic head groups linked together by a spacer. These molecules demonstrate remarkable surface activity, outperforming traditional surfactants by as much as a thousandfold. Furthermore, the development of CuO-NPs (copper oxide nanoparticles) coated on cotton fibers has been documented, showcasing considerable antimicrobial efficacy against both Gram+ve and Gram-ve bacteria. Research has also explored the antimicrobial properties of natural substances like Melaleuca alternifolia (tea tree) oil in the presence of surfactants. Findings indicate that surfactants can diminish the antimicrobial effectiveness of tea tree oil, emphasizing the importance of understanding surfactant interactions in the formulation of antimicrobial products.

The application of surfactants in antimicrobial therapy is complex, with surfactants capable of both enhancing and inhibiting antimicrobial activity. Understanding the mechanisms underlying these interactions is crucial for the development of effective antimicrobial formulations. This research aims to explore the application of surfactants in antimicrobial activity, with a focus on their potential to enhance or inhibit the activity of various antimicrobial agents. Another class of surfactants are microbial surfactants, which are biodegradable and non-toxic, have gained widespread use across various industries due to their unique properties, including surface activity, emulsification, antimicrobial capabilities, and antiadhesive effects. As a sustainable alternative to traditional chemical surfactants, microbial surfactants are being increasingly adopted in industrial, medical, and environmental conservation applications (P. T. P., 2019). Here are some advantages and disadvantages of a few microbial surfactants given below.

Table 10.1. Advantages and disadvantages of different microbial surfactants as antimicrobial agents

S.No	Surfactants	Advantages	Disdvantages
1	Rhamnolipids	Potential synthesis using industrial waste with a high surfactant concentration.	The producers are classified as conditionally pathogenic microorganisms, with limited antimicrobial activity.
2	Lipopeptides	Exhibit low minimum inhibitory concentrations against a broad spectrum of pathogenic microorganisms.	Produces surfactants in low quantities, utilizes a limited range of substrates for surfactant synthesis (primarily carbohydrates), and its antimicrobial activity is influenced by culture conditions.
3	Sophorolipids	Produced using inexpensive substrates (such as waste oil and byproducts of oil production) and demonstrates high antimicrobial activity even at low surfactant concentrations.	Yields a low product output compared to the substrate used, originates from conditionally pathogenic microorganisms, and its antimicrobial activity is influenced by culture conditions.
4	Complex of amino- and glycolipids of strains IMV B-7241 (Acinetobacter calcoaceticus), IMV B-7405 (Rhodococcus erythropolis) and IMV Ac-5017 (R. Erythropolis)	Synthesized from waste materials (such as waste oil and biodiesel byproducts) with high antimicrobial activity even at low surfactant levels.	Antimicrobial activity is influenced by the culture conditions.

Table 10.1 is adopted from [3]

10.2 What is antimicrobial:

An antimicrobial is a substance that inhibits the growth of microorganisms or kills them, including bacteria, fungi, viruses, and parasites. These agents are vital in preventing and treating infections in healthcare, agriculture, and sanitation. Antimicrobials are categorized into bactericidal (kill bacteria), fungicidal (kill fungi), virucidal (inactivate viruses), and parasiticidal (eliminate parasites). They can be derived from natural sources, such as penicillin from fungi, or synthesized chemically. Antimicrobials work by targeting critical cellular functions of microorganisms, such as disrupting cell walls, inhibiting protein synthesis, or interfering with DNA replication. This specificity makes them effective against harmful pathogens while sparing human cells. In healthcare, antimicrobials treat diseases like tuberculosis, HIV/AIDS, and malaria and are crucial for infection control during surgeries. Beyond medicine, they are widely used in cleaning products, agriculture, and food preservation to ensure hygiene and safety. However, antimicrobial resistance (AMR) has emerged as a global health threat due to the overuse and misuse of these agents. Resistant microorganisms are harder to treat, increasing mortality, costs, and disease spread. To counteract AMR, global strategies emphasize research, antimicrobial stewardship, and public education to ensure sustainable use of these life-saving substances.

10.3 What is Surfactants

A surfactant, short for "surface-active agent," is a chemical compound that reduces the surface tension between two substances, such as a liquid and a solid, or between two immiscible liquids, like oil and water. Surfactants are amphiphilic molecules, meaning they have both a hydrophilic (water-attracting) head and a hydrophobic (water-repelling) tail. This unique structure allows surfactants to interact with both polar and nonpolar substances. Surfactants play a crucial role in various applications by enabling emulsification, wetting, foaming, and detergency. For example, in cleaning products like soaps and detergents, surfactants help break down and remove grease and dirt by surrounding oil particles and dispersing them in water. In industries, surfactants are used in enhanced oil recovery, food production, pharmaceuticals, and cosmetics. They are categorized into four types based on the charge of their hydrophilic head: anionic (negatively charged), cationic (positively charged), nonionic (no charge), and zwitterionic (both positive and negative charges). Each type is suited for specific applications. For example, anionic surfactants are common in household detergents, while cationic surfactants are used as fabric softeners and disinfectants. Surfactants significantly impact industrial processes and everyday products, making them essential in science and technology.

10.4 How surfactants exhibit antimicrobial activity

Surfactants exhibit antimicrobial activity by disrupting microbial cell membranes, altering cell permeability, and interfering with essential cellular processes. Their amphiphilic nature, which combines hydrophilic and hydrophobic properties, plays a key role in this action.

10.4.1 Disruption of Cell Membranes

The hydrophobic tail of the surfactant interacts with the lipid bilayer of microbial cell membranes, while the hydrophilic head interacts with the surrounding water. This destabilizes the membrane structure, causing leakage of intracellular components like ions, proteins, and nucleic acids, ultimately leading to cell lysis.

10.4.2 Alteration of Cell Permeability

Surfactants can increase membrane permeability, allowing harmful substances to enter the cell and essential components to leak out. This disrupts the microbe's metabolic processes and hinders its ability to survive.

10.4.3 Inhibition of Enzymatic Functions

By interacting with membrane-bound enzymes or surface proteins, surfactants can deactivate critical enzymatic functions required for microbial growth and reproduction.

10.4.4. Denaturation of Proteins

Some surfactants can directly interact with microbial proteins, denaturing them and rendering them non-functional. Different types of surfactants have varying antimicrobial efficacy. For example, cationic surfactants like quaternary ammonium compounds are particularly effective due to their strong interaction with negatively charged microbial membranes. This makes surfactants valuable in disinfectants, antiseptics, and cleaning agents.

10.4.5. Different applications of surfactant in anti-microbial activity-a review

The utilization of surfactants as antimicrobial agents has gained significant attention in recent years. Various approaches have been explored to harness the antimicrobial potential of surfactants, including the use of cationic surfactants, lipopeptide surfactants, and biosurfactants. Additionally, researchers have investigated the incorporation of surfactants into nanostructured materials, such as nanoparticles and nanofibers, to enhance their antimicrobial efficacy. Furthermore, the use of surfactant-based formulations, such as emulsions and gels, has also been explored for their potential as antimicrobial agents. These different approaches offer promising avenues for the development of novel surfactant-based antimicrobial therapies which are discussed in this paper.

10.5 Classification of surfactants

10.5.1. Ginger oil-based Surfactants

A ginger essential oil (GEO) film was prepared in one of the experiments. The process involved dissolving fish gelatin in distilled water, adding glycerol to create mixture A. Separately, GEO was mixed with a surfactant (lecithin, Tween-20, or Tween-80) at a 1:1 ratio to form mixture B. Here Tween-20 (Hydrophilic Lipophilic Balance and Lipophilic Balance = 16.7), Tween-80 (Hydrophilic Lipophilic Balance = 15.0) (X. Li & Z. C. Tu et al, 2020). The two mixtures were combined, and the resulting solution (mixture C) was stirred and cast onto a plate to make a film. The film was dried under controlled conditions and analyzed, with a control film prepared without surfactant for comparison. The antimicrobial properties of the film were tested against E. coli (Gram-negative) and S. aureus (Gram-positive) by using a procedure that ensured the use of sterilized reagents and equipment at all stages. The plate serial dilution technique was employed to quantify bacterial populations, expressed in log cfu/ml (cfu= colony forming units). Bacteria were cultured in HLB medium (hydrophilic-hydrophobic balance), with initial concentrations adjusted to 5 log cfu/ml. Film samples (160 mg) were mixed to the medium and incubated with bacteria at 37°Celcius temperature for about 24 hours. A blank sample without film served as a control. Lower log cfu/ml (cfu= colony forming units) values indicated greater antimicrobial activity. All experiments were conducted in triplicate (X. Li & Z. C. Tu et al, 2020).

10.5.2 Gemini Surfactant

Many research on nonwovens for Respiratory Protective Devices (RPDs) has focused on short-term use equipment. However, there's a need for reusable RPDs with biocidal properties for industrial settings where microbial growth is a risk. One study investigates the creation of melt-blown nonwovens containing gemini surfactants, a novel class of biocides with potent antimicrobial properties. GS present a promising solution for developing bioactive nonwovens for respiratory protective devices (RPDs). Also referred to as twin or dimer surfactants, GS are made up of two identical monomers connected by a spacer, with two hydrocarbon chains and two hydrophilic groups. Moreover, GS exhibit significantly higher biocidal activity than their monomeric counterparts. By utilizing GS, such as double quaternary ammonium salts, it is anticipated that the required biocide concentration for nonwoven functionalization can be reduced, enhancing RPD safety. Additionally, the controlled release of these agents from the fiber surface is expected to minimize user exposure to biocides during regular RPD use. The results explained that the modified nonwovens exhibited significant antimicrobial activity against various microorganisms, with higher efficacy against bacteria (87.85-97.46%) than moulds (80.11-94.53%) (K. Majchrzycka & M. Okrasa et al, 2017).

Another study on gemini surfactants examined the biological properties, including cytotoxicity and antimicrobial activity, of a series of bio-compatible, ester-linked cationic based gemini surfactants. The effects of different alkyl chain lengths (12, 14, and 16 C atoms) on antimicrobial activity and cytogenicity were evaluated. The findings revealed that the gemini surfactants exhibited strong antimicrobial activity against various microorganisms, with low toxicity to 3T3-L1 fibroblast cells. However, the antimicrobial effectiveness of the gemini surfactant 16-E2-16 (where 12, 14, and 16 represent the number of carbon atoms in the hydrocarbon chain, and E2 indicates two RCOR groups in the spacer) was lower than that of its single-chain equivalent [6]. The surfactants showed significant inhibitory action against four bacterial strains (S. aureus, B. subtilis, E. coli, and P. aeruginosa) and one fungal strain (C. albicans). The MIC (minimum inhibitory concentration) of the surfactants was determined to be

400μg/ml, suggesting their potential as effective antimicrobial agents. Overall, the gemini surfactants demonstrated excellent surface properties, low critical micelle concentration values, and a promising balance of antimicrobial activity with low toxicity (N. Fatma & M. Panda et al, 2016).

Researchers have developed another novel series of alkylammonium gemini surfactants, specifically 3-oxa-1,5-pentane-bis (N-alkyl-N, N dimethylammonium bromides), which exhibit impressive surface, aggregation, and antimicrobial properties. These surfactants align with the principles of green chemistry, requiring minimal concentrations to achieve desired effects. The study investigated the critical micelle concentrations and antimicrobial activity of these surfactants against various microorganisms, including Aspergillus niger, Escherichia coli, Staphylococcus aureus, Candida albicans, and Penicillium chrysogenum (B. E. Brycki & A. Szulc, 2021).The findings show that these obtained compounds are highly effective microbicides with a wide range of biocidal properties. The most active compounds showed high aggregation activity, and the synthesized compounds also demonstrated a "cut-off effect," where antimicrobial activity depended on chain length. Compound 12-O-12 was found to be the most effective microbiocide, outperforming DTAB (N-dodecyl-N, N, N-trimethylammoniumbromide) by over 30 times. These gemini surfactants showed broad-spectrum biocidal activity, with greater efficacy against Gram-positive bacteria, such as S. aureus, then Gram-negative bacteria, such as Escherichia coli (B. E. Brycki & A. Szulc et al, 2021).

10.5.3 Chemical Surfactant

Two novel surfactants, DHNMMB (4-dodecyl-4-((1-hydroxynaphthalen-2-yl) methyl) morpholin-4-iumbromide) and DHNBMBDMB (4,4-((1,5-dihydroxynaphthalene-2,6-diyl) bis(methylene)) bis (4-dodecylmor pholin-4-ium) bromide), were synthesized through reflux reactions in ethanol [8]. DHNMMB was synthesized by reacting 2-(morpholino methyl) naphthalen-1-ol with 1-bromododecane for 48 hours, yielding a red solid with 98% purity and a melting point of 210-212°C. DHNBMBDMB was synthesized by reacting 2,6-bis (morpholino methyl) naphthalene-1,5-diol with dodecyl bromide for 48 hours, yielding a dark brown solid with 97% purity and a melting point over 300°C.The quaternary salts DHNMMB and DHNBMBDMB exhibited significant antimicrobial activity against Candida albicans, with inhibition zones ranging from 33-37 mm, similar to the control cyclohexamide (35 mm). These findings indicate that the balance between hydrophilic and hydrophobic properties is essential in determining the biocidal effectiveness of these compounds against the tested microbes (A. S. El-Tabei & M. A. Hegazy et al, 2022).

10.5.4 Amine and Nanoparticles based Surfactants

In a separate study, copper oxide nanoparticles (CuO-NPs) were applied to cotton fibers through ultrasound irradiation. The formation of CuO-NPs occurred in following steps: interaction between copper ions and surfactant, creation of stable $Cu(OH)_2$, and its transformation into CuO-NPs through irradiation energy. Surfactants were crucial in modifying the cotton surface and controlling the morphology of copper oxide precursor. Their use enhanced the adhesion of CuO-NPs to the cotton fibers and reduced the nanoparticles leaching during washing. Among the surfactants tested, SDS (sodium dodecyl sulfate) was the most effective at minimizing CuO-NPs leaching, followed by HY ($C_{18}H_{40}NOCl$). CTAB ($C_{19}H_{42}BrN$) and TX ($C_8H_{17}C_6H_4O(CH_2CH_2O)_9.5H$)had minimal impact (I. M. El-Nahhal & A. A. Elmanama, 2018). These findings suggest that anionic surfactants like SDS, promotes the immobilization of CuO-NPs on cotton fibers. The addition of surfactants, particularly SDS and HY, significantly improved the stability of the cotton/CuO-NPs system by enhancing the adherence of CuO-NPs to the cotton fibers and reducing their leaching. However, repeated washing led to a decrease in antibacterial efficiency. The CuO/SDS and CuO/HY systems demonstrated the strongest antibacterial activity, attributed to their smaller crystallite size. The inclusion of surfactants also impacted the overall properties of the coated cotton materials, leading to the formation of smaller CuO-NPs compared to those produced without surfactants (I. M. El-Nahhal & A. A. Elmanama et al, 2018).

A novel method for synthesizing heterocyclic amine surfactants based on sulfobetaines has been developed. The synthesis of N-alkylpiperidine involved a two-step process. Initially, piperidine was reacted with alkyl bromide in diethyl ether at room temperature, yielding liquid piperidine derivatives with carbon chains of varying lengths (10, 12, 14, and 16). In the next step, these derivatives were transformed into N-alkyl-N-(propylpiperidinium-3 sulfate) or N-alkyl-N-(butylpiperidinium-4-sulfate) by reacting them with 1,3-propane or 1,4-butane sultone in ethyl acetate. The resulting products were recrystallized from a methanol/ethyl acetate mixture to obtain the final compounds. The interfacial properties of the prepared surfactants in aqueous solutions were assessed through measurements of its surface tension, and key parameters such as critical micelle concentration (CMC), surface excess concentration (SEC), and standard Gibbs energy ($\Delta G°$) of adsorption were calculated. Additionally, the length of the alkyl chain influenced the biological properties of these surfactants, including their antimicrobial activity, minimum inhibitory concentration (MIC), and growth inhibition zone (GIZ). These compounds demonstrated significant antimicrobial activity (D. Wieczorek & A. Dobrowolski et al, 2017).

In a similar approach, zinc oxide nanoparticles (ZnO NPs) were successfully deposited onto cotton fibers using ultrasound irradiation. Various surfactants (SDS, HY, CTAB, and TX-100) were employed to stabilize and control the size and shape of the ZnO NPs. The utilization of surfactants, particularly SDS, enhanced the durability of the ZnO NPs and minimized their leaching from the cotton fibers. The exceptionally small crystallite size of the ZnO particles, facilitated by the surfactants, was the key factor in reducing leaching. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses provided detailed information on the shape and size of the coated ZnO nanoparticles. Remarkably, the application of SDS and HY (C18H40NOCl, Praepagen

HY, Clariant 40%) surfactants in the synthesis of ZnO NP-coated fabrics resulted in excellent antibacterial and antifungal activities, reducing the presence of various pathogenic bacteria and fungi by over 90% (I. M. El-Nahhal & A. E. R. Manamah et al, 2017).

Researchers examined how different substances and conditions influence the antimicrobial properties of Melaleuca alternifolia oil (tea tree oil). They assessed the oil's effectiveness against bacteria and fungi when exposed to potentially interfering substances like proteins and organic matter. The results showed that certain surfactants, like Tween-20 and skim-milk powder, reduced the oil's antimicrobial activity. However, this effect varied depending on the microorganism and concentration of the substance. The study concluded that the antimicrobial properties of tea tree oil can be influenced by the presence of certain surfactants and organic matter. Surfactants are known to diminish the effectiveness of various antimicrobial agents, including phenols, cresols, and quaternary ammonium compounds. Also reduce the activity of essential oils like tea tree oil.The interference is believed to occur due to the solubilization of antimicrobial molecules within surfactant micelles, which prevents them from interacting with microorganisms. Additionally, some surfactants have been shown to be toxic to microorganisms at high concentrations, highlighting their complex role in antimicrobial activity (K. A. Hammer, C. F. Carson et al, 1999).

In another study four types of biosurfactants were produced and purified SL-1 to SL-4, RL-I to RL-IV, TL-1 to TL-3 and CL-1 and CL-2 respectively. Sophorolipids (SL-1 to SL-4) were obtained by the yeast Torulopsis Bombicola and it is purified by using the technique of silica gel chromatography. Rhamnolipids (RL-I to RL-IV) were prepared by the bacterium Pseudomonas spp. and purified using silica gel chromatography after alkaline hydrolysis. Trehalose lipids (TL-1 to TL-3) were derived from the bacterium Rhodococcus Erythropolis and separated using silica gel chromatography. Cellobiose lipids (CL-1 and CL-2) were obtained from the fungus Ustilago maydis, with CL-2 being produced through alkaline hydrolysis of the mixture of CL-1. Following the initial tests, MICs of the surface-active agents were obtained. Notably, the most hydrophobic Sophorolipid, SL-1, showed the lowest MIC values, effectively inhibiting the growth of B. subtilis, S. epidermidis, and S. faecium at concentrations ranging from 6-15 µg/mL. SL-2 and RL-I/RL-III also exhibited antimicrobial activity against Gram-positive bacteria, though at slightly higher concentrations. Additionally, concentrations between 50 and 1000 µg/mL of SL-2, RL-I, TL-1, and CL-1 were needed to prevent the germination of conidia from the Glomerella Cinguluta which is a type of fungus (S. Lang & Katsiwela Eleftheria et al, 1989).

10.5.5 Quaternary Surfactants

$[R_4N^+]$ $[NO_3^-]$ and $[R_4N^+][OAc^-]$ (Tetraalkylammonium Nitrate and Tetraalkylammonium acetate respectively) surfactants were prepared by following methods respectively. A solution of tetraalkylammonium bromide (R_4NBr) and sodium nitrate ($NaNO_3$) in acetonitrile was prepared and mixed at 70°C for 3 hours. The mixture was then allowed to be cooled, filtered, and then properly washed several times with distilled water to eliminate any remaining halides. Afterward, the acetonitrile solvent was evaporated, leaving behind the desired ionic liquid (IL), which was further dried in a vacuum oven at 40°C for a day maximum, resulting in the formation of Tetraalkylammonium Nitrate ($[R_4N^+][NO_3^-]$). For the formation of Tetraalkylammonium acetate ($[R_4N^+][OAc^-]$) surfactants, a mixture of tetraalkylammonium bromide (R_4NBr) and sodium acetate (NaOAc) was mixed thoroughly in hot water (60°C) and then slowly left for evaporation at 70-80°C, resulting in the precipitation of white solids (S. Chauhan & M. Kaur et al, 2017). The mixture was then extracted along with CH_2Cl_2, causing the expected ionic liquid (IL) to separate into the bottom layer, while the byproduct NaBr remained in the top most layer. The IL was washed with distilled water to eliminate any residual bromide ions and then dried usinga vacuum oven at 40°C temperature for many hours until it was completely dried. The synthesized ionic liquids (ILs) found to increase the antimicrobial properties of surfactants by forming hydrophobic interactions with the bacterial cell walls, thereby increasing the surfactant's resistance to microbial degradation (S. Chauhan & M. Kaur et al, 2017).

10.5.6 Non-ionic Surfactants

A new non-ionic surfactant nano emulsion, 8N8, has shown promising biocidal properties. At a concentration of 1%, 8N8 effectively killed several types of bacteria, including Bacillus cereus and Streptococcus pneumoniae, within 15 minutes. However, it was less effective against certain Gram-negative bacteria. Additionally, 8N8 demonstrated rapid virucidal activity against enveloped viruses, such as Herpes simplex and influenza A, and fungistatic activity against Candida albicans. Given its broad-spectrum antimicrobial activity, low toxicity, and rapid action, 8N8 may be a suitable material for utilised as a topical antimicrobial agent. The 8N8 nano emulsion was prepared by the process involving mixing soybean oil, tributyl phosphate and Triton X-100 to create an oil phase, which was then heated to 82°C for one hour. This oil phase was subsequently combined with de-ionized water using a reciprocating syringe pump, resulting in a nano emulsion with a particle size ranging from 400 to 800 nanometers, as determined by laser light scattering (T. Hamouda, 2001).

In one of the studies, it is investigated that the microbicidal properties of four commercialized surfactants: benzalkonium chloride (BAC), cetylpyridinium chloride (CPC), cetyltrimethylammonium bromide (CTAB), and cocamidopropyl betaine (CAPB). The surfactants' ability to inhibit the growth of various bacteria, including B. subtilis, E. coli, and S. aureus, was evaluated using agar well diffusion assays (D. Wieczorek & D. Gwiazdowska et al, 2020). The results obtained explained the antimicrobial effect of the selected surfactants, along with varying levels of effectiveness over bacteria and fungi. BAC exhibited superior antimicrobial properties compared to CPC, CTAB, and CAPB. This study examined the antibacterial properties of commercial surfactants. The results showed that benzalkonium chloride (BAC), a commonly used disinfectant, exhibited the highest antimicrobial property, particularly against Gram-positive bacteria. The varying antibacterial activity of the surfactants can be attributed to their distinct chemical structures. The length of the alkyl chain in the surfactant molecule was found to impact its antimicrobial activity. Research has shown that many surfactants have an optimal alkyl chain length for maximum effectiveness, typically between 12 and 16 carbon atoms. This explains why BAC, with its mixture of compounds having 8-18 C atoms in the alkyl chain, demonstrated superior antibacterial property. Overall, the surfactants examined in this study demonstrated greater micobicidal property against Gram-positive bacteria compared to Gram-negative bacteria (D. Wieczorek & D. Gwiazdowska et al, 2020).

In another study, investigated the interactions between a custom-designed antimicrobial peptide (AMP), $G(IIKK)_3I\text{-}NH_2$ (G_3), and four conventional surfactants (sodium dodecyl sulfonate (SDS), $C_{16}TAB$ (hexadecyl trimethyl ammonium bromide), $C_{12}EO_{23}$(polyoxyethylene (23) lauryl ether), and $C_{14}DMAO$ (tetradecyldimethylamine oxide)) (K. Liu *et al.*, 2020). The research employed antimicrobial activity assessments, surface tension measurements and circular dichroism (CD) spectroscopy, against Escherichia coli, Staphylococcus aureus, and Candida albicans. Cytotoxicity tests were also conducted on NIH 3T3 and HSF cells (fibroblastic cells). The results demonstrated that the AMP/SDS mixture exhibited enhanced surface activity, while the CD spectroscopy revealed that the AMP's conformation changed significantly in the company of SDS. However, the antimicrobial activity of the AMP decreased when combined with SDS because of strong electrostatic attraction. In contrast, the interrelations between the AMP and $C_{16}TAB$, $C_{12}EO_{23}$, and $C_{14}DMAO$ were fainter resulting in minimal changes to the AMP's secondary structure and antimicrobial activity. Notably, the combination of the AMP with $C_{16}TAB$ enhanced its antimicrobial activity, particularly against C. albicans. However, the mixtures exhibited significant cytotoxicity observed in NIH 3T3 and HSF cells. The study concludes that cationic antimicrobial peptides can be mixed along with all types of nonionic, cationic, and zwitterionic surfactants, but caution is advised when combining AMPs with anionic surfactants, as this may compromise their antimicrobial activity (K. Liu *et al.*, 2020).

A series of Germanium nonionic surfactants were produced by a multi-step process following esterification, condensation, and reaction with germanium dioxide. The resulting surfactants were characterized using various spectroscopic techniques, like their surface properties, including effectiveness, critical micelle concentration (CMC) and compatibility, were evaluated through surface tension measurements (M. F. Zaki & S. M. Tawfik, 2014). The surfactants exhibited high surface activity and spontaneous adsorption and micellization processes. Furthermore, they demonstrated potent antimicrobial activity against a wide range of microbes, including Gram-positive and Gram-negative bacteria, along with many fungi. The surfactants' effectiveness against sulfate-reducing bacteria makes them promising candidates as biocides in various applications. The microcidal properties of 4 newly prepared nonionic surfactants (I, II, III, and IV) were evaluated against various pathogens, including Gram-positive bacteria (B. Pumilus and S. aureus), Gram-negative bacteria (P. Aeruginosa and E. coli), and fungi (C. albicans and A.Niger). The surfactants' effectiveness against sulfate-reducing bacteria called DesulfomonasPigra, was also assessed. The findings showed that the synthesized compounds exhibited antimicrobial activity, with varying levels of effectiveness depending on the length of their hydrophobic chains. The optimum alkyl chain length for maximum inhibition was found to be 12 carbon atoms. This finding aligns with previous research indicating that the optimal antimicrobial activity for various surfactant structures occurs with alkyl chains containing 10-14 carbon atoms (M. F. Zaki & S. M. Tawfik, 2014).

10.5.7 Cationic Surfactants

Some cationic surfactants like Quaternary ammonium salts (QASs) are commonly utilized as disinfectants in hospitals, offering the advantage of being usable as rinse-free solutions. However, their extensive industrial use has resulted in the development of resistant pathogens. To address this issue, researchers investigated the antimicrobial activity of three QASs – cocamidopropyl betaine, dimethylamineoxide, and benzalkonium chloride - both individually and in combination. The study followed standard protocols and tested the QASs against various microorganisms, including bacteria and fungi. The results showed that benzalkonium chloride exhibited the highest antimicrobial activity, while cocamidopropyl betaine had the lowest. Notably, combining the QASs led to increased antimicrobial activity, a positive correlation observedbetween critical micelle concentration (CMC) and anti-microbialactivity (A. Krasowska & A. Biegalska et al, 2012).

A series of saccharide-amide cationic surfactants with varying alkyl chain lengths N-methyl-N-hydroxyethyl group-N[3-(gluconamide)-propyl]-N-alkylammonium bromide C_nMHGPB (n= 10, 12, and 14 C atoms) were produced and investigated for their aggregation and Anti bactericidal and anti-fungal property. The surfactants' adsorption and aggregation behavior were observed using surface tension method and conductivity measurements techniques. The results obtained explained that the critical micelle concentration (CMC) values increased with longer alkyl chains, contrary to expectations. The dynamic surface tension results were influenced highly by the hydrophobic head group comparable to the alkyl chain length. The surfactants exhibited antimicrobial activity against E. coli and S. aureus at concentrations of 50 to100ppm, with the $C_{12}MHGPB$ surfactant demonstrating the best antimicrobial property (L. Zhi & Q. Li et al, 2014).

Poly hexamethylene biguanide (PHMB) is a broad-spectrum antimicrobial agent commonly used in contact lens cleaning solutions. Its effectiveness is attributed to its cationic and hydrophobic properties, which enable it to interact with cell membranes through electrostatic and hydrophobic forces. This study investigates how different ionic and surfactant agents impact the antimicrobial effect of PHMB. Adding the nonionic surfactant Poloxamer 407 (Px407) to a mixture containing the antimicrobial agent PHMB enhanced its effectiveness against certain microorganisms, including S. aureus, C. albicans, and F. Solani. However, the mixing of NaCl reduced the antifungal effect of PHMB when present along with Px407 (R. Yanai & K. Ueda et al, 2011).

In a study on cationic surfactants, researchers found that cationic micelles formed by trimeric, tetrameric, and hexameric surfactants with amide groups can efficiently eliminate Gram-negative *E. coli* bacteria at very low concentrations (1.70−0.93 μM), while causing minimal toxicity to mammalian cells. The antibacterial activity of these surfactants improves with the degree of oligomerization, with the hexameric surfactant proving to be the most effective. Studies explained that the cationic micelles collaborate with the E. coli cell membrane through a two-step process, first they disrupt the outer membrane through electrostatic interactions followed by breakdown of inner membrane through hydrophobic interactions, ultimately resulting in cell death. The capability of these oligomeric surfactants to form micelles at low concentrations allows for efficient interaction with the bacterial cell membrane, making them highly effective as antibacterial agents (C. Zhou *et al.*, 2016).

Researchers have developed a new method to synthesize surfactants based on lactose, producing a series of cationic surfactants, specifically O-β-D-Galactopyranosyl-(1 4)-N-alkyl-(3-sulfopropyl)-D glucosamine hydrochloride, with 12 to14 C atoms present in their alkyl chains. These surfactants exhibit excellent surfaceproperties, low CMC, and good wetting properties. They also produce more foam than commercial surfactants. Furthermore, the surfactants demonstrated antibacterial and fungistatic activity against various microorganisms, including S. aureus, B. subtilis, E. coli, P. aeruginosa, C. albicans, and several species of fungi, such as F.graminearum, F. avenaceum, F. culmorum, F. equiseti, Alternaria alternata, and Botrytis cinerea. The results showed that the new lactose-based surfactants have comparable or even superior antimicrobial activity to the commonly used cationic surfactant cetylpyridinium chloride (K. Michocka & K. Staszak et al, 2019).

10.5.8. Quaternary Ammonium Surfactants

Scientists have studied the co-relation between the microcidal activities and micellar properties of different modified quaternary ammonium surfactants. The study found that a reduction in critical micelle concentration (CMC) resulted in enhanced germicidal activity and protein-binding capacity of quaternary ammonium salts. Compounds with a CMC value ranging from 1×10^{-2} to 1×10^{-4} M exhibited antimicrobial activity, regardless of whether the surfactant was monomeric or polymeric. The antimicrobial activity of these surfactants was tested against three bacterial strains: P. aeruginosa, E.Coli and S. aureus. The results, reported, show that compounds 4-(n-Dodecyl)-N-methylpyridinium Bromide (compound 4)and N-(n-Dodecyl)-4-methylquinolinium Bromide (compound 6) exhibited higher antimicrobial activity than the standard reference compound, benzyldimethyl dodecyl ammoniumbromide. The study also determined the log P parameter, which measures a molecule's lipophilicity, using the fragmental approach of Leo and Hansch and the MacLog P software. The log P value represents the logarithm of the partition coefficient between n-octanol and water. By applying the fragmental method developed by Leo and Hansch and using MacLog P software, the calculated C log P values indicated that compounds 4 and 6 exhibited the highest activity (G. Viscardi & P. Quagliotto et al, 2000).

Chemically synthesized amino acid surfactants (R'=CH_3 and R=$C_{13}H_{27}$i.e MN14)with a specific structure were evaluated for their surface and antimicrobial activity. Increasing the acyl chain length of AAS led to a significant decrease in surface tension and critical micelle concentrations. A strong correlation was found between the CMC of AAS and their potential to hinder the growth of microorganisms such as E. coli, P. aeruginosa, A.niger, and S. cerevisiae. The effectiveness of these microorganisms to AAS varied, with S. aureus being the most reactive and Pseudomonas aeruginosa being the least sensitive. Notably, AAS (MN14) exhibited 2-8 times higher antimicrobial activity against Gram-negative bacteria, Gram-positive bacteria, and fungi compared to methyl p-hydroxybenzoate. The mechanism of AAS action on microorganisms may involve bifunctional binding to the cell membrane and/or surface adsorption (J. Xa & Y. Xa et al, 1995).

One more quaternary ammonium Gemini surfactants were prepared and found to act as ionic liquids due to inter-molecular Hydrogen bonding involvingOH^-functional groups in their spacers. These compounds were categorized using ^1H NMR, ^{13}C NMR,mass spectrometry and IR spectroscopy. Their surface properties were examined through surface tension measurements, yielding key parameters such as surface excess concentration, critical micelle concentration (CMC), surface area per molecule (A_{cmc}), efficiency in surface tension reduction (pC_{20}), effectiveness of surface tension reduction (G_{cmc}) and the std. free energy of micellization (ΔG°_{ads}) and (ΔG°_{mic}). The findings showed that these Gemini surfactants had considerably lower CMC values and were more efficient at reducing surface tension of wateras compared to conventional single-chain surfactants. Foamability and foam stability decreased with increasing spacer chain length, while surfactants with medium-length alkyl chains (C12 or C14) exhibited optimal foamability and stability. Additionally, few of the Gemini surfactants demonstrated microcidaleffect against the Gram-negative bacterium E. coli (H. Li & C. Yu et al, 2012).

Lipopeptides, a class of microbial surfactants produced by Bacillus species, such as B. subtilis, have garnered significant scientific and therapeutic interest. These compounds show a wide range of biological properties, including antimicrobial, antiviral, antitumor, immune modulatory, and enzyme inhibitory effects. This study investigated the antimicrobial activity of biosurfactants produced by B. subtilis R14 against multidrug-resistant bacteria. The findingsdemonstrated that the biosurfactants reduced the surface tension of culture medium and exhibited broad-spectrum antimicrobial activity against 29 bacterial strains, including E. faecalis, S. aureus, P. aeruginosa, and

E. coli, with Enterococcus faecalis being the most sensitive. These findings demonstrate the potential of lipopeptides as effective antimicrobial agents against multidrug-resistant microorganisms (P. André *et al.*, 2007).

10.6. Conclusion

In conclusion, the present study demonstrates the potential of surfactants as effective antimicrobial agents against a wide range of microorganisms. The results show that certain surfactants, particularly cationic and lipopeptide surfactants, exhibit broad-spectrum antimicrobial activity, making surfactants apromising agent for the development of novel antimicrobial agents. The study highlights the importance of surfactant structure and properties in determining their antimicrobial activity. The results indicate that the hydrophobic and hydrophilic regions of the surfactant molecule are key in interacting with microbial membranes and compromising their integrity. The application of surfactants as antimicrobial agents offers several advantages, including their ability to target a wide range of microorganisms, their potential to reduce the development of antibiotic resistance, and their relatively low toxicity to human cells. In conclusion, this study adds to the expanding research on the antimicrobial properties of surfactants and emphasizes their potential as a new class of antimicrobial agents. Additional research is required to fully understand the capabilities of surfactants as antimicrobial agents and to develop innovative surfactant-based antimicrobial treatments.

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Chapter 11: Application of Surfactants in Soil Chemistry

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Abstract

Surfactants are molecules that lower interfacial tension and enhance the solubility of pollutants in water. These characteristics make them valuable for a wide range of domestic and industrial uses, including soil remediation and pesticide formulation, among others. However, the toxicity of surfactants has raised global concerns, prompting the introduction of various regulations. Despite this, questions regarding their biodegradability and environmental impact remain. Ongoing research is investigating the effectiveness of synthetic surfactants, biosurfactants, and other types of surfactants in the context of soil reclamation. Numerous studies have demonstrated the potential of surfactants to improve the remediation of contaminated soils. By enhancing the solubility and mobility of hydrophobic pollutants, surfactants aid in their removal from the soil. The success of surfactant-based remediation methods, however, depends on several factors, such as the nature of the contaminant, soil characteristics, and the concentration and type of surfactant used. While surfactant-enhanced soil remediation offers a promising and sustainable solution for addressing soil contamination, the ideal conditions for their use vary depending on specific site conditions and the pollutants involved. Additional research is needed to refine and optimize surfactant use in soil remediation. This chapter focuses on various types of soil pollutants worldwide and explores how surfactants can be used to remove them.

Keywords: Soil remediation; surfactant-enhanced soil remediation; biosurfactant; Application of Surfactants

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11.1 Introduction

The rapid acceleration of industrialization and urbanization has drawn attention away from ecosystem health and mortality, which are both greatly impacted by increased environmental pollution, on a global scale. Endocrine-dismembering substances and essence poisoning are examples of the implicit health risks associated with defiled soil that contains heavy essence and patient organic adulterants. Over the course of the most recent few decades, there have been other notable factors contributing to soil impurity, including the mining of minerals, heavy input in husbandry exercises, fortified force and military medication, and the development of residue caused by mortal exercises, (Balachandran 2012). Associated details and the oil painting industry are major sources of pollution to the soil. The decline of adulterants in the air, water, and soil continues to have a significant impact on global health initiatives. It is thought that environmental pollution is the main cause of health hazards, and in a similar vein, clearings advance research into the underlying causes of patient fatalities.

It is common knowledge that surfactants are used in soil washing to extract essence. Poisonous essence can be eliminated from soil by irrigating it with clean water combined with colorful chelating agents, chemical complements detergents and surfactant. However, the length of treatment and poor vacuum caused by interactions with soil patches remain the main limitations. Surfactants increase the benefits of these styles and decrease the amount of time required. Ex situ or in situ treatments can be used in soil cleaning with surfactants. Ex situ treatment comprises the following steps: the soil is dug up, moved to a predetermined location, and then treated with a biosurfactant. By directly applying a face-active material to the soil, in situ treatment reduces interfacial pressure and complexes with essence ions of various charges, facilitating the movement of the ions. Micelles use electrostatic contact, while charged surfactants use an ion exchange process. Essence can be reclaimed and permanently removed from the terrain with minimum time investment (C. N. Mulligan, 2009). 11 distinct types of surfactants have been investigated for their potential to remediate heavily contaminated soil that contains elements like Cd, Ni, Cu, As, Zn, and Pb from manufacturing processes. Surfactants are also utilized in the creation of novel, logical procedures for the identification and quantification of Re, Ru, Th, and lead (Roy et al. 1999). These days, biosurfactants have emerged as a viable replacement for synthetic surfactants due to their low toxicity, cost-effectiveness, and biodegradable nature. Biosurfactants are produced from natural renewable resources such as bacteria and leaves. Microorganisms add oxygen or polar particles to the carbon-hydrogen bonds of molecules that resemble hydrocarbons in order to produce biosurfactants through a biochemical process. The hydrophobic groups are typically made up of water-repelling (or hydrophobic) peptides and/or hydroxylated, saturated, and/or unsaturated adipose acids. The nonionic di- or polysaccharide mixes, anionic or cationic amino acids, and peptide-derived products make up the hydrophilic groups. Inappropriate management results in the release of these contaminants into the environment without proper treatments (Iglesias et.al.2012 & Nguyen et.al., 2008).

11.2 How do surfactants work?

As the micelle forms, the surfactant heads position themselves, so they're exposed to water, while the tails are grouped together in the center of the structure defended from water. The hydrophobic tails are attracted to soils and compass them, while the hydrophilic heads pull the girdled soils off the face and into the cleaning result. Also, the micelles reform with the tails suspending the soil in the center of the structure. Surfactants can enhance desorption of adulterants from soil and promote bioremediation of organics by adding bioavailability of adulterants. The jilting of heavy substance and radionuclides from soils involves the mechanisms of dissolution, surfactant- associated complexation, and ionic exchange.

11.3 Types of Soil Contaminants and Their Harmful Effects

The usage of fertilizers and pesticides are examples of direct inputs (point source pollution) that can pollute agricultural soils, whereas air deposition and flooding are examples of indirect inputs (diffuse pollution). Additionally, contaminated soils are a secondary source of pollutants that are released into the surrounding air, surface waters, groundwater, and eventually the seas. Concerning environmental issues have resulted from the overuse of fertilizers in some areas and nations, including the saturation of soil nutrients and fertilizer loss through runoff to surface water and leaching to groundwater, which pollutes drinking water and eutrophies freshwater lakes, rivers, and oceans. There are multiple reasons for this excessive use:

- A lack of current and precise fertilizer recommendations for many crops, especially tree crops;
- A low price in comparison to the perceived absence of drawbacks to excessive use, as measured by decreasing yields;
- a lack of knowledge and instruction on how to use the product.

11.4 Importance of surfactant in Soil Remediation

Surfactant-enhanced technology has numerous benefits over traditional soil remediation methods. Its ability to effectively remove a variety of pollutants from the soil is one of its main advantages. Surfactants, also known as face-active agents, have special rates that enable them to dissolve and degrade a wide range of pollutants, such as heavy essence, fungicides, and hydrocarbons. Because of its rigidity, surfactant-enhanced soil remediation can be used in a range of soil impurity conditions. The capacity of surfactants to increase the mobility and vacuity of adulterants in the soil is another important benefit. Surfactants enhance the desorption and solubility of adulterants, making them simpler to eliminate or decompose by lowering the interfacial pressure between the adulterant and soil patches (Richard 2006).

By greatly speeding up the remediation process, this method lowers the total cost and effort needed to clean up the contaminated soil. Technology for improving soil remediation with surfactants is also very compatible with other remediation techniques. To increase their effectiveness, it can be used with methods like soil washing, soil vapor extraction, and bioremediation. By facilitating the release of pollutants from the soil matrix, the surfactants increase their suitability for extraction or degradation by other remediation techniques. Soil remediation can be approached more thoroughly and successfully thanks to this synergy. Compared to several other approaches, this one is comparatively non-invasive and eco-friendly. It lessens the requirement for transportation or soil excavation, which lessens site disturbance and related expenses. By significantly accelerating the cleanup procedure.

This approach reduces the overall cost and labor needed to clean up the weakened soil by significantly accelerating the remediation process. Surfactant-grounded technology for enhancing soil remittal is also veritably compatible with other remediation styles. It can be combined with ways like soil washing, soil vapor birth, and bioremediation to boost their efficacity. The surfactants ameliorate the pollutants' adequacy for birth or declination by other remediation styles by promoting their release from the soil matrix (Befkadu, & Quanyuan 2018).This community allows for a more comprehensive and effective approach to soil remediation. This system is relatively non-invasive and environmentally benign in comparison to a number of other styles. It reduces the need for soil excavation or transportation, which lowers point disturbance and associated costs. The surfactants used in the process are generally biodegradable and pose no threat to mortal health or ecosystems when used meetly (Mao 2015 & Pandey 2020

11.5 Surfactants in Soil Remediation

In order to give an overview of how the properties of surfactants affect the remediation process and the interactions between soil contaminants and eluents that contain surfactants, the factors that should be taken into account for a surfactant-enhanced soil washing as well as the mechanism for removing various types of contaminants from soils are compiled and discussed. As a result, the developments over the last 15 years regarding the use of surfactants—including ionic, nonionic, bio, and mixed surfactants—for the rehabilitation of polluted soils and sites are examined and addressed. In addition to surfactant-enhanced soil washing, the article's coverage encompasses surfactant-enhanced phytoremediation and bioremediation.

Soil pollution is an international issue and a major barrier to sustainable development. It disturbs the delicate balance of the ecosystem and increases economic loss and harm to human health. The main causes of soil pollution are improper or negligent disposal methods, such as stockpiles, mining tailings, improper industrial discharge, and trash disposal. The most prevalent contaminants in soil are heavy metals, radionuclides, and toxic organics (Zhou 2019). Elevated levels of heavy metals in soil have been recorded in many developed countries and regions. Metals and their metalloids, including lead, cadmium, mercury, and chromium, can pose a threat to human health and the environment through food chains or direct contact with contaminated soil or water (Nguyen 2008). Organic contaminants include things like polychlorinated biphenyls (PCBs), petroleum products, and volatile chlorinated solvents.

11.6 Elimination of Agrochemicals from Soils

Although agrochemicals have many benefits for agriculture and the economy, over use of them can have negative environmental effects. A common feature of soils with dryness and persistent vegetation is soil-water repellency. Because it prevents infiltration, which leads to surface runoff and soil erosion, this has a significant impact on soil–water hydrology. In both dry and humid regions, loam, clay, and peat soils have also been reported to be impacted by this phenomenon, in addition to sandy soils. Additionally, plants may suffer from decreased water availability as a result of soil water repellency due to uneven water retention and flow as well as dry soil volume between the paths of preferential channels.

According to recent studies, water repellent soil, which in turn creates preferred flow in the field, is the result of constant watering with treated wastewater, a typical substitution in Israel and other Mediterranean nations due to the scarcity of freshwater. The use of treated wastewater for irrigation as a means of preserving freshwater is anticipated to rise in light of the growing effects of climate change, particularly in areas that are not typically considered desert. Though much research has been done on preferential flow in water-rejecting soils, little has been done to comprehend how this flow pattern influences the distribution of nutrients and salt in the root zone. Additionally, the soil profile's salinity, nitrate and phosphate, concentrations as well as their corresponding regional distributions will be shown. (Ogunmokun & Wallach, 2020) investigated the effectiveness of two nonionic surfactants in treating hydrophobic sandy soils in both the lab and the field. Their research showed how the application of surfactants to the orchards' water-resistant soils affected the spatial distribution of soil moisture and the associated agrochemicals(Zhou 2022 & Saxena 2023).

11.7 Elimination of heavy metals from Soils

Humans, animals, plants, aquatic life, and bacteria can all suffer negative, long-lasting effects from heavy metals in the water supply. Metal contamination reduces the sustainability of soil quality by impeding the biodegradation of organic contaminants, which affects microorganisms' physiological and ecological aspects. Through a range of methods, such as soil-washing, extraction, desorption, and phytoremediation, researchers have investigated the use of surfactants in the removal of heavy metals. Additionally, surfactants have demonstrated their ability in the ultrafiltration process. By pretreating the membrane with surfactants or biosurfactants to eliminate metal ions, its capacity can be increased.The use of biosurfactants in heavy metal cleanup is a new and eco-friendly technique, claim (Kosaric 2001). They provided a thorough analysis that shows how bacterial biosurfactants can be a great substitute method for soil heavy metal purification. Using bacterial biosurfactants is thought to offer a novel way to remove metal contamination from the soil, Banat 1993.

The production of a biosurfactant and its application in removing heavy metals from surfactants were investigated (Abdurrahim et.al. 2012). When cultured in distilled water with 2.5% molasses, 2.5% frying oil, and 4% corn steep liquor, the yeast Candida tropicalis created the biosurfactant. The production of the biosurfactant with a surface tension of 30 mN/m increased to 27 g/L in a 50 L bioreactor. Surface tension and engine oil emulsification tests showed that the biosurfactant remained stable in the presence of NaCl as well as a range of pH levels and temperatures. GC-MS and NMR were used to infer the biosurfactant's structural composition (Rath et.al.2012).

The biosurfactant was found to be a negatively charged molecule that could lower the surface tension of water from 70 to 30 mN/m at 0.5% of the CMC without negatively affecting plant or brine shrimp germination. As low as 30% to as high as 80% of Cu and Zn were removed from contaminated sand using crude and extracted biosurfactants, according to the studies. Furthermore, the biosurfactant's capacity was further validated in packed columns, where the Cu and Zn removal rates ranged from 45 to 65%. On the other hand, in static conditions, no lead was eliminated (Fan et.al.2023).

Heavy metals were able to desorb as a result of biosurfactants competing with them for adsorption sites on the soil particles. The soil particles' negative ZETA potential may increase as a result of the biosurfactant adsorption, further mobilizing the heavy metals via electrostatic connections. Complex micelles were created as a result of the attraction between heavy metal ions and organic molecules. Additionally, these micelles exhibited a significant degree of resistance to heavy metal ions that would typically reintegration into the soil.

Utilizing anionic surfactants to remove heavy metals from soil was comparable to utilizing biosurfactants. The soil particles were coated by the anionic surfactants, which then interacted with the metals to dissolve them in a solution. However, by altering the soil's surface characteristics, cationic surfactants eliminated heavy metals from the ecosystem. The heavy metals could be moved into the washing solution by trading cationic surfactants with heavy metal ions. Secondary contamination resulted from the soil's subsequent absorption of cationic surfactants. Additionally, there were heavy metal ions in the washing solution that were easily absorbed by the soil, resulting in a low washing efficiency (Xuhui et.al.2019).

11.8 Conclusion

Innovative techniques for remediating contaminated environments, both through ex situ and in situ methods, are incorporating surfactants. These surfactants are beneficial because they enable oil-based pollutants, which are typically insoluble in water, to mix with water, facilitating the effectiveness of water-based cleaning agents. This advancement helps mitigate issues like trailing and rebound, ultimately enhancing remediation outcomes. Traditional remediation methods often come with drawbacks such as high costs, compliance challenges, limited versatility, and potential environmental impacts. These limitations can hinder their application across various sectors aimed at cleaning up contaminated sites. However, many surfactants have demonstrated effectiveness in treating soil and wastewater contaminated with pharmaceuticals, heavy metals, personal care products, and dyes. The adoption of surfactant-based remediation technologies can address these concerns while adhering to stringent environmental regulations. Biosurfactants, known for their eco-friendliness, have shown potential in this arena, although their high production costs pose challenges for widespread implementation. Nevertheless, these innovative remediation solutions can fulfill the requirements for integrity and stability, paving the way for a more sustainable environment for future generations.

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Chapter 12: Application of Surfactant in Bioremediation

Swati Chandrawanshi

Abstract

Various pollutants such as heavy metals, total petroleum hydrocarbons (TPHs), polynuclear aromatic hydrocarbons (PAHs), nonaqueous phase liquids (NAPL) and hydrophobic organic compounds (HOCs) toxicity has emerged as a major ecological issue that poses a major risk to public health and impacts ecosystems through bioaccumulation. Thus, areas contaminated by these pollutants have been decontaminated and restored using a variety of traditional techniques. However, because to their high energy requirements, post-waste disposal issues, secondary pollutant formation and high operating costs, these traditional methods are not environmentally safe for pollutants treatment. Because of its capacity for biodegradation, economic viability and environmental friendliness, surfactant-based bioremediation of pollutants is therefore a viable and sustainable strategy. Surface-active substances are known as surfactants. These compounds can reduce the growth medium's surface tension and interfacial tension because they have both hydrophobic and hydrophilic groups. Surfactant, types of surfactant, surfactant selection, surfactant enhanced bioremediation (SEB) mechanism, surfactant-microorganism interactions in SEB and bioremediation of pollutants as discussed in this chapter.

Keywords: Surfactant, pollutants, toxicity and bioremediation.

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12.1. Introduction

Numerous dangerous substances, such as heavy metals, organic pollutants, plastics, solvents, nuclear hazards and medical wastes, are found in the soil in sufficient quantities to contaminate the soil environment. Numerous hydrophobic organic dangerous substances have been found in the environment, posing major risks to mammals such as mutagenic, carcinogenic and teratogenic consequences. A vast range of organic xenobiotic compounds that are nearly insoluble in the aquatic environment that can wind up in water, sediment or biota make up organic pollutants. The soil ecosystem is seriously endangered by organic pollutants, particularly those found in petrol, plastics, paints, pesticides, polycyclic aromatic hydrocarbons (PAHs), adhesives, polychlorinated biphenyls, benzene, ethylbenzene, toluene, and many other substances. Therefore, cleaning up contaminated soil is essential to restoring our environment to its natural state. Numerous methods that focus on the transformation and detoxication of contaminants have been developed to preserve the quality of soil (Sar et al., 2023; Mohanty et al., 2013). Polluted environments have traditionally been decontaminated and recovered using a variety of physicochemical techniques, including solvent extraction, incineration, adsorption, chemical precipitation, nanomaterial-based removal, reverse osmosis, ion exchange and membrane filtration. But from an environmental and financial perspective, these methods are frequently inappropriate for environmental pollutants remediation due to their limited applicability, high energy and operational costs and production of toxic secondary pollutants and waste sludge. In order to facilitate cleaner, greener and more sustainable environmental pollutants remediation, innovative, economical and ecologically friendly biotechnological techniques have been investigated. Bioremediation is a sustainable, eco-friendly and natural method that is highly recommended for treating environmental toxicants without producing any harmful side effects or secondary pollutants (Mishra et al., 2021; Bhatt et al., 2020; Huang et al., 2021; Zhang et al., 2021). Despite their structural complexity, microbial activity has the ability to fully mineralize environmental pollutants. Therefore, the main cause of environmental pollutants resistance is that the majority of microbes cannot reach these substances. In this situation, surfactants can be introduced to change the characteristics of solution interfaces, giving the microbe access to hydrocarbons. This process is known as "Surfactant enhanced bioremediation" (SEB) or "Surfactant aided bioremediation”. The nature of surfactants is amphiphilic. They promote the mass transfer of hydrocarbons from the oil phase into the aqueous phase by reducing the surface tension of water and the interfacial tension at the oil-water interface. When a surfactant is added to contaminated soil, the interfacial tension is decreased, which increases the mass transfer of the pollutants. Numerous studies have demonstrated that different surfactants can improve desorption, solubilisation and biodegradation of organic molecules and the removal of environmental pollutants from soil (**Mohanty et al., 2013;** Paria 2008; Mulligan et al. 2001).

In this chapter, we present a general and rigorous review on this topic. The several obstacles that must be taken into account for the successful implementation of SEB are highlighted in this chapter. The use of chemical surfactants for SEB is the main area of interest.

12.2. Pollutants and possible route of pollutants

A number of pollutant agents are primarily absorbed by soils and their contamination raises the risk to ecological systems globally. Numerous inorganic and organic contaminants and compounds can exist in soil in a wide range of identities, compositions and quantities. These are the main substances that pollute soils such as agrochemicals, polycyclic aromatic hydrocarbons (PAHs), persistent organic pollutants (POPs), toxic heavy metals, radioisotopes and emerging pollutants etc. The quality and enrichment of the soil are altered by the overuse of synthetic fertilizers, which leads to soil pollution. The continuous use of agrochemicals in agriculture causes a significant amount of residues and degradation products to accumulate in the soil environment, which may cause serious risks to soil and food chain pollution (Figure 1). Agrochemicals come in a variety of forms, including insecticides (like chlordimeform, diazinon, dimethoate, aldrin, chlordane, DDT, tau-uvalinate, thymol, etc.), acaricides (like fenpyroximate, menthol, formic acid, tau-uvalinate, thymol, etc.), herbicides (like acetanilides, barban, alachlor, chlorbromuron, 2,4-D, 2,4,5-T, etc.), and bactericides (like copper hydrochloride, copper oxychloride, copper sulphate, various rice blast nets, dithane, polytrin and ridomil). Polycyclic aromatic hydrocarbons (PAHs) have poisonous, mutagenic and carcinogenic properties. Anthracene, naphthalene and phenanthrene are examples of low molecular weight (LMW) PAHs, whereas chrysene, pyrene, benzo(a)pyrene and other compounds with four or more rings are classified as high molecular weight (HMW) PAHs. Their physicochemical and toxicological characteristics vary according to their molecular weight. POPs are organic molecules that have a higher affinity for the soil matrix, which explains why they bioaccumulate over an extended period of time. Similarly heavy metal inputs into the environment include the usage of commercial fertilizers, sewage sludge, waste disposal and treatment, the atmospheric deposition of heavy metals from industrial areas and other processes brought on by the degradation of different materials. The most polluting metals are hazardous metals found in soils, such as As, Cd, Cr, Cu, Hg, Pb and Zn. These metal’s basic characteristics include non-degradability, persistence, bioaccumulation and biological magnification in a food chain. However, the majority of the public's concerns over radiation from radio nuclides have been brought on by the worldwide effects of atmospheric nuclear weapons development and nuclear facility operations. These two activities have discharged a significant amount of man-made radio nuclides into the environment and contaminated large areas of land with radio nuclides (Sar et al., 2023, Li et al., 2019, Dragovic et al., 2022).

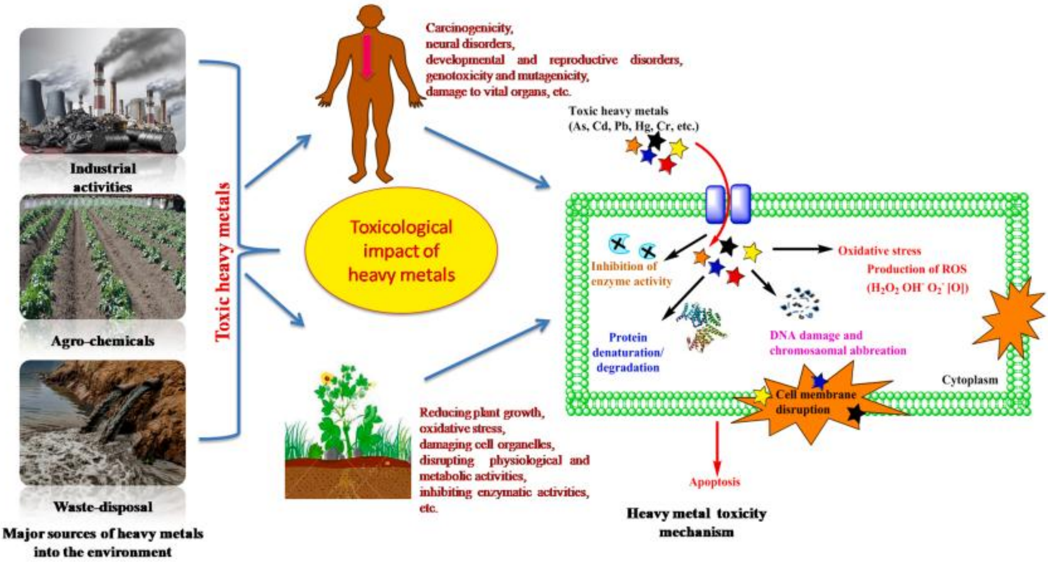

Figure 12.1: Source of pollutants into the environment and mechanism of their toxicity (Mishra et al., 2021)

12.3. Surfactant and biosurfactant

Amphipathic compounds known as surfactants have both hydrophilic and hydrophobic groups. They preferentially partition at fluid-phase interfaces with varying degrees of hydrogen bonding and polarity, such as those between water and oil or air and water. The hydrophilic groups can be nonionic, positively or negatively charged, or amphoteric and the hydrophobic group is a hydrocarbon. Because of their dual nature, surfactants lower interfacial energy by adsorbing at surfaces. Surfactants are classified as anionic, cationic, nonionic, or zwitter ionic (cationic and anionic groups), according their head group. Firstly surfactant present in the form of monomer (Cameotra & Makkar, 2010). These monomers will gather at systemic interfaces, such as soil-water, oil-water and air-water. The monomers group together to form micelles as the concentration of aqueous surfactant rises and the interfacial spaces are filled. The critical micelle concentration (CMC) is the concentration at which micelles initially start to form. Surfactants can solubilize more of a hydrophobic chemical in nature than they could in water alone at concentrations higher than the CMC (*Ron and Rosenberg, 2002, Desai and Banat, 1997*). Biosurfactants are the microbial compounds, which produced by the microorganisms with high surface activity. Because of their many advantages over their chemical counterparts, including being biodegradable and less toxic, effective at extreme temperatures or pH values, and able to be made from a variety of low-cost waste substrates, biosurfactants-a term derived from biological surface-active agents are a molecule of the future (*Hamme at al., 2006, Cameotra and Bollag, 2003*).

12.4. Characteristic and properties of the surfactants

Critical micelle concentration (CMC), hydrophilic-lipophilic balance (HLB), chemical structure, charge and characteristics from their source are some of the characteristics of the surfactants. Various factors affect the CMC such as temperature, ionic strength, surfactant composition, structure and the type and quantities of organic compounds present in the solutions. Surface tension, conductivity and turbidity are just a few of the physicochemical characteristics that significantly change at the CMC of surfactant solutions. Micelles have the ability to dissolve hydrophobic pollutants within their hydrophobic core, increasing the pollutant's apparent solubility in water. The HLB number is also an important factor of the surfactants, showing their physical properties and is specific for every surfactant. The relationship between the hydrophilic and hydrophobic components of the surfactant molecule determines this value. When HLB value is low, which indicate lipophilicity and high HLB value is shows good water solubility (Hamme et al., 2006, Fuget *et al*., 2005, Prak and Pritchard, 2002, Tiehm, 1994).

12.5. Mechanism of surfactant enhanced bioremediation (SEB)

Surfactants are implemented in enhanced bioremediation to aid in the degradation of contaminants in soil and water by microorganisms. Surfactants increase the contact between contaminants and microorganisms by modifying the characteristics of the solution interface (Ling et al., 2023). The mechanisms of SEB of polluted sites are categorized into mobilization, solubilization, emulsification and soil roll-up method.

Mobilization: By lowering the surface tension between contaminants and water, surfactants promote the passage of pollutants through porous medium. At the water-pollutants contact with each other, surfactant forms an adsorption layer as part of the mobilization effect mechanism. This lowers the capillary resistance in the porous media by lowering the interfacial tension between the water and non-aqueous phase liquids (NAPL) phases. As a result, the stable dense nonaqueous phase liquids (DNAPLs) are released and move with the liquid water flow. The effectiveness of surfactant on NAPL mobilisation is determined by its capacity to lower the oil-water interfacial tension. The mobilization effect is affected differently by different kinds of surfactants. The water solubility of NAPLs can be greatly increased by combining several surfactants, which will make the mobilization mechanism easier to occur. Low interfacial tension can support in improving mobilization, while high surfactant concentration can accelerate the reduction of interfacial tension. Despite the nature of the surfactant, the nature of the porous medium, the pore water flow rate, and the environmental salinity may all affect the mobilization mechanism **(**Wu et al., 2024, Mishra et al., 2021**).**

Solubilization: Surfactants form micelles that entrap hydrocarbon chains, which increase the solubility of the contaminants in water. The surfactant can improve the solubilization (occurs above the CMC) of hydrophobic organic contaminants in the micelles when the concentration is higher than the CMC, which significantly improves the partition of contaminants in the aqueous phase. NAPLs are distributed into the hydrophobic core of the micelles by the micellization process of surfactants, which contributes to the solubilization behaviour. By creating nanoscale agglomerates that enclose the pollutants, this makes insoluble or only slightly soluble NAPLs more soluble in the aqueous phase, facilitating their migration from the porous media to the aqueous phase. Micellar solubilisation is the primary way that surfactants exhibit their solubilising effect **(**Wu et al., 2024, Mishra et al., 2021**)**.

Emulsification Surfactants assist spread pollutants by stabilizing them in water and forming tiny droplets of the contaminants. Surfactants cooperate an important role in the treatment of NAPL-contaminated soil and their emulsification is one of the key mechanisms for enhanced remediation. Surfactants provide an emulsifying effect by adsorbing at the "oil–water interface" to create stable nanoscale oil or water droplets. This promotes the dispersion of NAPLs into micro-droplets, increases the efficiency of mass transfer and improves the mobility and recovery rate of NAPLs. Microemulsions and emulsions are the two types of emulsification products. Micellar solubilisation creates microemulsions, which are transparent or semi-transparent structures that are thermodynamically stable. On the other hand, emulsions are thermodynamically unstable systems, formed by the emulsification process that disperses the NAPL phase within an immiscible liquid phase. Surface-active molecules quickly migrate to the interfacial region during the dynamic process of emulsification, destroying the emulsified droplets in the process. The type of NAPLs, their ratio to water and the system's water content all have an impact on the emulsion stability in addition to the surfactant solution's characteristics **(**Wu et al., 2024, Mao et al., 2014, Mishra et al., 2021**).**

Soil roll-up: Surfactant monomers before the CMC are able for the soil roll-up mechanism (occurs below the CMC). Surfactant monomers accumulate at the soil-pollutants and soil-water interfaces and change the wettability of the system by increasing the contact angle between the soil and the hydrophobic pollutants. Surfactant molecules adsorbed on the surface of the pollutants cause the repulsion between the head groups of the surfactant molecules and the soil particles, thereby further promoting the separation of the pollutants from the soil particles (Mao et al., 2014).

12.6. Factors of SEB

SEB is affected by various factors such as surfactant selection, surfactant microorganism interaction in SEB, biodegradability of surfactant, its impact on SEB and toxicity of surfactants. These factors play an important role in controlling the process and consequent successful performance of SEB in polluted sites.

12.6.1. Surfactant selection

The selection of the suitable surfactant is important for bioremediation of a particular type of pollutant in any situation. The results of SEB may vary depending on the surfactant's structure, hydrophile-lipophile balance (HLB) number, dosage and mode of action (emulsification versus micellar solubilisation). Surfactants are mostly divided into four classes according to the charge on the hydrophilic head group, such as, cationic, anionic, nonionic and zwitter ionic. In cationic surfactant the head group like the quaternary ammonium group possesses positive charge. In anionic surfactants carboxylic group or sulphonate group hold a net negative charge. In nonionic surfactants, the hydrophilic head groups generally consist of sucrose, polyoxyethylene, or polypeptide, which have no ions. Zwitterionic surfactants are those which have both cationic and anionic groups, which mostly consist of one or more hydrophilic head or hydrophobic tail groups (Paria, 2008, Mohanty et al., 2013). On the other hand synthetic surfactants, biosurfactants produced by microorganisms, which utilized for bioremediation of pollutants. Biosurfactants are mostly anionic or nonionic. Chemically, the hydrophilic head group of biosurfactants may contain a carbohydrate, peptide, amino acid, phosphate, carboxylic acid, or alcohol while the hydrophobic tail contain fatty acids, hydroxy fatty acids, or α-alkyl-β-hydroxy fatty acids. Biosurfactants like trehalose lipids obtained by *Mycobacterium* sps. and *Rhodococcus erythropolis*, rhamnolipids obtained by *Pseudomonas* sps., Sophorolipids produced by *Candida apicola*; lipopolysaccharides obtained by *Acinetobacter calcoaceticus* (RAG1), and phospholipids obtained by *Thiobacillus thiooxidans.* Various biosurfactants are used for the remediation of total petroleum hydrocarbons (TPHs) like rhamnolipids and surfactin have been found to remove TPH at higher rates (Lai et al., 2009).

12.6.2. Surfactant microorganism interaction in SEB

It is essential to carry out investigations to unravel the relationship between surfactants and microorganisms, as it varies in each instance. The interplay between surfactants a nd microorganisms may influence the way substrates are assimilated. In this section, the direct uptake of hydrocarbons is preferential by increase in cell surface hydrophobicity of the microorganism. The influence of surfactant-microorganism interaction is also manifested through changes in zeta potential which reflects the cell surface charge (Mohanty and Mukherji, 2013). Van Hamme and Ward described that *Rhodococcus* sp. firstly participed to crude oil degradation in the absence of surfactants by direct uptake mechanism and uptake after solubilization, respectively. While, in presence of the surfactant, Igepal CO-630, the *Pseudomonas* sp. played a important role in the degradation of aromatics in crude oil as Igepal CO-630 stuck the attachment of *Rhodococcus* sp. to the oil water interface. The surfactant changes the hydrophobicity/surface charge characteristics of the microorganism and its uptake mechanism, surfactant nature and absorption capacity. These changes have a strong influence of pollutant remediation and the achievement of SEB (Van Hamme and Ward 2001).

12.6.3. Biodegradability of surfactant and its impact on SEB

The surfactant itself increases pollution when it is added to a contaminated location. Therefore, from the perspective of environmental sustainability, it might be preferable to use biodegradable surfactants for SEB rather than ones that are resistant and persistent. However, a major factor influencing the selection of surfactants must be their solubilisation ability and impact on the biodegradation of hydrocarbons. The biodegradation of surfactants has effects that are beneficial as well as negative. Surfactants can be categorized according to their toxicity and biodegradability as follows: hardly degradable, but not preventing the breakdown of other carbon sources; posing a toxicity to the microorganism and preventing its growth; and readily degradable (either preferentially or nonpreferentially). Environmental parameters, microorganism's capacity for degradation and surfactant characteristics are some of the significant factors of degradability. The three key features of surfactants are their source (chemically synthesized or formed by microbes), structural complexity (simple chain or with polymeric structures) and charge (cationic, anionic, or nonionic) (Zeng et al., 2007). The capacity of the microbes to catabolically absorb the surfactant as a source of carbon and energy leads to the biodegradation of surfactants. The hydrocarbon contained in the micellar core may be released when the micelle's structural stability is compromised. According to Lee et al. 2013, soil bacteria that break down PAHs use the Tween family of surfactants as their main growth substrate. The hydrophobic chain of fatty acids was selectively broken down, causing preferential surfactant breakdown and increasing the surfactant's hydrophilia (Lee et al., 2013). Wyrwas et al. observed in their Triton X-100 research that microbial consortia preferentially used Triton X-100 in aerobic circumstances, which inhibited diesel biodegradation (Wyrwas et al. 2011). Removal of surfactants from the contaminated area and an improvement in hydrocarbon uptake are two benefits of surfactant degradability. Degradable surfactants can occasionally act as a major substrate during the cometabolic breakdown of the pollutant. Culture growth on the surfactant may accelerate the rate of hydrocarbon biodegradation in additional situations where microbial cultures are able to break down both the hydrocarbons and the surfactant (Lee et al., 1995).

12.7. Consequences of SEB

By accumulating petroleum hydrocarbon degradation intermediates and surfactant partial biotransformation products, the introduction of surfactants into oil-contaminated soil and aquatic ecosystems could lead to pollution. Both land and aquatic plants and animals may be at risk from this. To successfully apply SEB, these ecotoxicological concerns must be taken into account. Oil does not completely degradation. There may be an accumulation of intermediates because some of the components in oil are only partially converted. As surfactants increase bioavailability, certain substances that are not naturally broken down by microbes may undergo partial transformation. Often more poisonous than the parent molecule, these incomplete transformation products have a tendency to accumulate. The intermediates tend to lower the system's pH because they are frequently acidic in nature. This may lead to the loss of feasibility of microorganisms due to adverse environmental conditions.

Furthermore, as the application of surfactants enhances micellar solubilization, it promotes desorption and transport of the sparingly soluble components in oil that typically remain sequestered through sorption (Mohanty and Mukherji, 2013).

12.8. Conclusions

Due to the significant harm that soil contamination causes to both humans and the ecology, it is a global concern. Because of its special ability to improve desorption of contaminants from soils, surfactant plays an essential role to the recovery of polluted soils. The basic principles of using surfactants to clean up contaminated soil are outlined in this chapter, along with a review and discussion of surfactant-enhanced bioremediation. By making pollutants more bioavailable, surfactants improve the partitioning of pollutants in the aqueous phase and may facilitate the bioremediation of organics. The ion exchange method and surfactant-associated complexation can be used to eliminate radionuclides and heavy metals from soils. Surfactants based on macrocyclic compounds show promise for cleaning up radionuclide-contaminated soil due to their high selectivity. Numerous factors determine whether SEB is successful or unsuccessful, such as the surfactant's choice and dosage to be applied at the contaminated site, the environment's hydrocarbon-degrading microorganisms and how they react to oil and hydrocarbons, how the hydrocarbon degraders interact with the surfactants and surfactant biodegradability and toxicity considerations. The use of surfactants ought to be reasonably priced. Thus, it is quite difficult to apply SEB successfully and it depends on all of the previously mentioned factors such as surfactant selection, surfactant microorganism interaction in SEB and biodegradability of surfactant and its impact on SEB.

12.9. References

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