



POLYMER–SURFACTANT INTERACTIONS: FROM FUNDAMENTAL CONCEPTS TO EMERGING APPLICATIONS

¹Dr. Riddhi Joshi Dave, ²Dr. Tejas P. Joshi

¹Assistant Professor, ²Professor,

¹Dr. D. Y. Patil Arts, Commerce and Science College, Pimpri, Pune, Maharashtra, India, ²Department of Chemistry, Maharaja Krishnakumarsinhji Bhavnagar University, Bhavnagar, Gujarat, India

Abstract: Surfactant–polymer interactions play a significant role in numerous industrial, pharmaceutical, and environmental applications due to their ability to modify solution properties such as viscosity, solubilization, surface tension, and stability. When surfactants and polymers coexist in an aqueous medium, their association leads to the formation of complexes driven by hydrophobic, electrostatic, and hydrogen-bonding interactions. These interactions strongly influence micellization behavior, critical micelle concentration (CMC), and aggregation number of surfactants, while also altering the conformational and rheological properties of polymers. Such systems are extensively employed in detergency, enhanced oil recovery, cosmetics, drug delivery, food processing, and wastewater treatment. Understanding these interactions is essential for tailoring formulations with desired physicochemical properties and functional performance. Experimental techniques such as surface tension measurement, viscometry, spectroscopy, light scattering, and calorimetry are often employed to study the nature and strength of these interactions. This paper highlights the fundamental aspects of surfactant–polymer interaction, their thermodynamic implications, and the practical significance of such systems in modern applications.

Keywords – Surfactant, cmc, surface tension, Polymer

Introduction

Surfactants, or **SURFACE ACTIVE agents**, are amphiphilic organic compounds composed of two distinct structural regions: a hydrophilic (water-loving, polar) “head” group and a hydrophobic (water-repelling, nonpolar) “tail,” typically a long hydrocarbon chain. This dual structural feature enables surfactants to localize at interfaces, rendering them soluble in solid–liquid, liquid–liquid, and gas–liquid systems. The term *amphiphilic* originates from the Greek words *amphi* (“both”) and *philos* (“attraction”). The concept of surfactancy was first described by Winsor about 60 years ago, while McBain pioneered the idea of self-aggregation of amphiphiles in polar solvents. Depending on their solubility, surfactants are classified as hydrophilic (water-soluble) or hydrophobic (water-insoluble). The hydrophilic region contributes polarity, while the hydrophobic region is nonpolar, creating a balance that governs interfacial activity. A schematic representation of a surfactant molecule is shown in figure 1 [1–4].

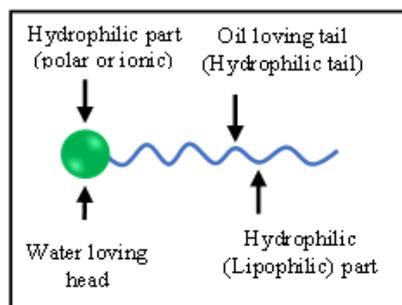


Fig. 1 Schematic illustration of a surfactant molecule.

A **surfactant** is a chemical compound that significantly reduces the surface tension of water, even at very low concentrations. When mixed with water, surfactants produce a characteristic foamy effect due to their ability to lower interfacial tension. These compounds readily adsorb at various interfaces, resulting in a remarkable decrease in water’s surface tension.

Structurally, surfactants are **amphiphilic molecules**, composed of two distinct parts:

- a **polar (hydrophilic) group** containing heteroatoms such as S, N, O, or P, often present in functional groups like alcohols, acids, esters, ethers, thiols, sulfates, sulfonates, amines, and amides;

- a **non-polar (hydrophobic) group**, usually a long hydrocarbon chain.

Surfactants are generally **low in toxicity, economically viable, and can be synthesized from renewable raw materials**, making them highly valuable for commercial and industrial applications.

1.2 Classification of Surfactants:

Surfactants are commonly classified according to the nature of their hydrophilic group. The hydrophobic (or lipophilic) portion of a surfactant typically consists of one or more hydrocarbon chains containing 8 to 20 carbon atoms. These chains may be saturated or unsaturated, straight or branched, and may also incorporate aromatic rings, heteroatoms, esters, amides, or other functional groups.

Surfactants with straight-chain alkyl groups generally display higher viscosity and better biodegradability but lower solubility compared to those with branched or cyclic hydrophobic groups. The solubility in water increases with the presence of multiple hydrophilic groups, which also shifts the optimal hydrocarbon chain length. Incorporation of ethoxyl groups further enhances aqueous solubility. Based on the nature of their hydrophilic head group, surfactants are broadly divided into several categories: anionic, cationic, nonionic, zwitterionic, and amphoteric surfactants. Types of surfactants are depicted in figure 2.

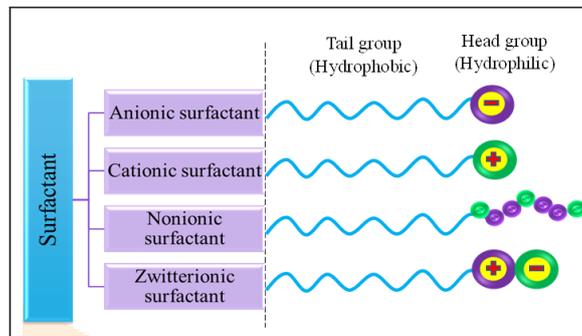


Fig. 2 Schematic diagram of classification of surfactants

The types and general structure of surfactants are shown in Table 1, and common hydrophilic groups found in commercially available surfactants are shown in Table 2.

Table 1: Types of surfactants

Type	Class	General Structure
Anionic	Sulphate	$R - SO_3^- M^+$
	Sulphonate	$R - OSO_3^- M^+$
	Carboxylate	$R - COO^- M^+$
	Phosphate	$R - OPO_3^- M^+$
Cationic	Ammonium	$R_x H_y N^+ X^-$ ($x = 1 - 3, y = 4 - x$)
	Quaternary ammonium	$R_4 N^+ X^-$
Nonionic	Polyoxyethylene	$R - OCH_2CH_2(OCH_2CH_2)_n OH$
	Polyols	Sorbitan, ethylene glycol, glycerol, etc
	Polypeptide	$R - NH - CHR - CO - NH - CHR' - CO - \dots - CO_2H$
Zwitterionic	Amine oxide	$R^+ R_3 O^-$
	Betaines	$RN^+(CH_3)_2 CH_2 COO^-$
	Sulfobetaine	$RN^+(CH_3)_2 CH_2 CH_2 SO_3^-$

Table 2: Common hydrophilic groups found in commercially available surfactants

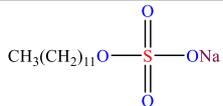
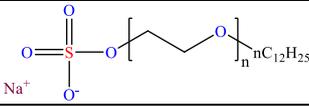
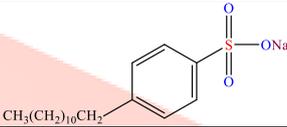
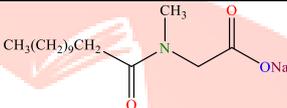
Group	General structure	n = No. of carbons
Natural fatty acids	$CH_3(CH_2)_n$	n = 12-18
Petroleum paraffins	$CH_3(CH_2)_nCH_3$	n = 8-20
Olefins	$CH_3(CH_2)_nCH=CH_2$	n = 7-17
Alkylbenzenes	$H_3C_n(H_2C)_nH_2C - \text{C}_6\text{H}_5$	n = 6-10, linear or branched
Alkylaromatics	$H_3C - (CH_2)_n - \text{C}_6\text{H}_4 - R$	n = 1-2 for water-soluble, n = 8 or 9 for oil-soluble surfactant
Alkylphenol	$H_2C_n(H_2C)_nH_3C - \text{C}_6\text{H}_4 - OH$	n = 6-10, linear or branched
Polyoxypropylene	$H_3C - \overset{H}{\underset{X}{C}} - \overset{H_2}{C} - O - (CHCH_2)_n$	n = degree of oligomerisation, X = oligomerisation initiator

Fluorocarbons	$CF_3(CF_2)_nCOOH$	$n = 4-8$, linear or branched, or H-terminated
---------------	--------------------	---

1.2.1 Anionic Surfactants

Anionic surfactants are the most widely used class of surfactants that dissociate into negatively charged particles when dissolved in water, with their hydrophilic group carrying a negative charge. These surfactants typically feature a hydrophobic C12-16 linear paraffin chain connected to an ionizable hydrophilic group, following the general formula $CH_3-(CH_2)_n-X$, where X represents the negatively charged group such as sulfate, sulfonate, phosphate, or carboxylate. Their popularity stems from their ease of manufacturing, low cost, and excellent solubilizing properties, making them ideal for detergents, dishwashing solutions, and shampoos where they excel at dislodging dirt and preventing its redeposition on fabrics [5-7]. The choice of counterion significantly affects their solubility characteristics: sodium and potassium ions enhance water solubility, calcium and magnesium boost oil solubility, while amine or alkanol amine salts provide balanced water and oil solubility, allowing formulators to tailor the surfactant properties for specific applications. Some examples of anionic surfactants are shown in table 3.

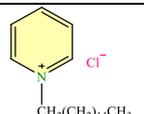
Table 3. Examples of some anionic surfactants

Sr. No.	Name of anionic surfactant	Abbreviation	Molecular weight (g/mol)	Structure
1.	Sodium dodecyl sulfate or sodium lauryl sulfate	SDS or SLS	288.38	
2.	Sodium lauryl ether sulfate	SLES	288.38	
3.	Sodium dodecyl benzene sulfonate	SDBS	348.48	
4.	Sodium N-lauroylsarcosinate	SNLS	293.38	

1.2.2 Cationic Surfactants

Cationic surfactants are characterized by their positively charged hydrophilic head group, which may be permanently charged or pH-dependent, with the majority being quaternary ammonium compounds (QACs). These surfactants are naturally attracted to negatively-charged surfaces commonly found on most materials, allowing them to bind to these sites and impart a smooth, luxurious feel to fabrics, making them particularly valuable as fabric softeners. However, environmental toxicity has become an increasingly significant concern, as quaternary ammonium surfactants demonstrate high potential for aquatic toxicity and environmental persistence. The quaternary ammonium head groups cannot be produced using only plant-derived compositions since they require some carbon content sourced from petrochemicals, limiting their sustainability. The bacteriostatic properties of specific cationic surfactants were first recognized by Domagk in 1935, who discovered their antimicrobial activity and published his findings on their disinfectant properties. Examples of cationic surfactants include long-chain alkyl trimethylammonium halides [8,9] benzalkonium halides (which are widely used as disinfectants and preservatives but have been identified as highly toxic to aquatic organisms with EC_{50} values below 1 mg/L), benzethonium halides, and long-chain alkyipyridinium halides. These versatile compounds find extensive applications as anticaking agents, anticorrosion additives, antistatic agents, fabric softeners, bactericides, hair conditioners, dispersants, and flotation collectors, though their environmental impact requires careful consideration in formulation and disposal practices [8-11]. Some examples of cationic surfactant is shown in table 4.

Table 4. Examples of some cationic surfactant

Sr. No.	Name of cationic surfactant	Abbreviation	Molecular weight (g/mol)	Structure
1.	Dodecyl pyridinium chloride	DPC	283.88	
2.	Cetyl pyridinium chloride	CPC	339.99	

3.	Dodecyl trimethylammonium bromide	DTAB	308.34	
4.	Tetradecyl trimethylammonium bromide	TTAB	336.40	
5.	Cetyl trimethylammonium bromide	CTAB	364.46	

1.2.3 Nonionic Surfactant

Nonionic surfactants are characterized by their lack of electric charge on the hydrophilic head group, making them milder than ionic surfactants and ranking as the second most common type of surfactant. The polar group in these surfactants consists of either polyether units (primarily polyoxyethylene chains) or polyhydroxyl groups, with polyether-based surfactants predominating in the market. The polyether chains are formed through the polymerization of ethylene oxide (EO), creating polyethylene glycol chains that provide hydrophilic properties through ethylene oxide polycondensation. Examples of polyhydroxyl-based (polyol-based) surfactants include sucrose esters, sorbitan esters, polyglycerol esters, and alkyl glucosides, each offering unique properties for specific applications. Sorbitan esters are particularly valuable in the food industry due to their edible nature, being manufactured through the dehydration of sorbitol which forms their characteristic five-membered ring structure[10]. These food-grade emulsifiers are widely used in baked goods, sauces, spreads, frozen desserts, and whipped toppings to maintain emulsion stability, improve texture, and extend shelf life. Alkyl glucosides represent a newer generation of biodegradable, plant-derived surfactants produced from renewable resources like glucose and fatty alcohols, offering excellent wetting, foaming, and detergency properties while being compatible with sensitive skin formulations. The versatility of nonionic surfactants extends across multiple industries including personal care (where they provide mildness and stability), pharmaceuticals (for drug delivery systems), agriculture (as spray adjuvants), and industrial applications (in paints, polishes, and cleaning formulations), with their performance being easily tailored through molecular structure modifications.

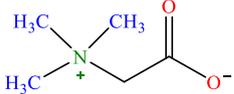
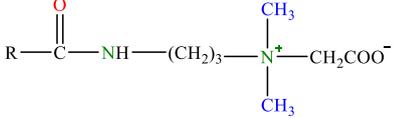
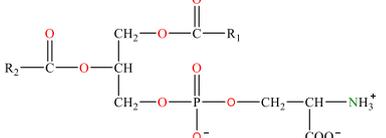
Table 3. Example of some nonionic surfactants

Sr. No.	Name of nonionic surfactants	Abbreviation	Molecular weight (g/mol)	Structure
1.	Polyethylene (20) monolaurate	Tween 20 or Polysorbate 20	1226.00	
2.	Polyethylene (20) monopalmitate	Tween 40 or Polysorbate 40	1283.63	
3.	Polyethylene (20) monostearate	Tween 60 or Polysorbate 60	1311.70	
4.	Polyethylene (20) monooleate	Tween 80 or Polysorbate 80	1310.00	

1.2.4 Zwitterionic Surfactant

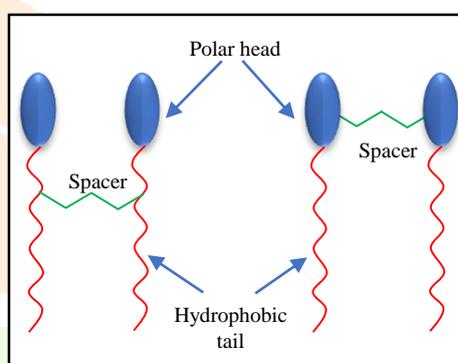
Zwitterionic or amphoteric surfactants have both cationic and anionic centres attached to the same molecule depending upon pH of the solution. The cationic component is composed of quaternary ammonium cations or primary, secondary, or tertiary amines. In solutions with a pH less than 7 (acidic medium), the molecule develops a (+ve) charge and behaves as a cationic surfactant, whereas, in solutions with a pH greater than 7 (basic medium), the molecule behaves as an anionic surfactant [11,12]. These types of surfactants are used in shampoos and cosmetics. Examples of this type of surfactants are quaternary amine group and carboxyl group containing surfactants are alkyl betaine, alkyl imidazoline, quaternary amine group and sulfonic group containing surfactant are alkyl sulfobetaine, phospholipids surfactant are phosphatidyl serine, phosphatidyl choline, phosphatidyl ethanolamine and carbohydrate-based surfactants are alkyl polyglucoside and alkyl glucamide.

Table 4. Examples of some zwitterionic surfactant

Sr. No.	Name of zwitterionic surfactants	Abbreviation	Molecular weight (g/mol)	Structure
1.	Betaine or <u>N,N,N-trimethylglycine</u>	TMG	117.15	
2.	Cocamidopropyl betaine	CAPB	342.52	
3.	Phosphatidylserine	PtdSer	385.30	

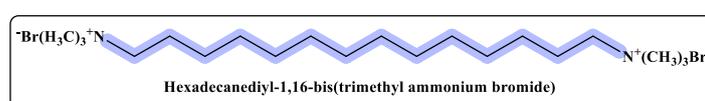
1.2.5 Gemini Surfactants

Gemini Surfactants are composed of two hydrophilic or hydrophobic chains linked together by a spacer [13,14]. Depending on the charge on the head group, they can be Anionic Gemini, Cationic Gemini, Non-ionic Gemini, Zwitterionic Gemini, or Herero Gemini.

**Fig. 3** Schematic diagram of gemini surfactant

1.2.6 Bolaform Surfactants

Bolaform surfactants, originally termed "bolaform electrolytes" when first described in relation to electrolytes, are unique organic compounds characterized by two charged groups connected by a single linear polymethylene chain. The term "bolaform" derives from the weapon "bola," consisting of a long cord with heavy metal balls at each end, reflecting the structural similarity of these molecules [15,16]. When the polymethylene chain reaches sufficient length, these bolaform electrolytes transform into bolaform amphiphiles or surfactants, also known as bolaamphiphiles, bolaphiles, or alpha-omega-type surfactants. Due to their additional polar group compared to conventional single-headed surfactants, bolaform surfactants exhibit significantly enhanced hydrophilicity, resulting in higher water solubility and increased critical aggregation concentrations (CAC) typically ranging from 10^{-4} to 10^{-6} M, which is substantially higher than conventional phospholipids (10^{-8} M). This structural arrangement leads to unique self-assembly behaviors, including the formation of monolayer membranes rather than the bilayer structures typical of conventional surfactants. The dual hydrophilic head groups can be identical (symmetric) or different (asymmetric), and may be ionic or non-ionic in nature. These molecules demonstrate remarkable versatility in forming various aggregate morphologies including spheres, cylinders, disks, vesicles, and even helical structures that can self-assemble into monolayer microtubular arrangements. Natural bolaform surfactants are found in archaeobacterial membranes as tetraether lipids, which enable these organisms to survive under extreme conditions such as high temperatures, acidic environments, and high salt concentrations due to their exceptional membrane stability and reduced permeability. An example of a bolaform surfactant is Hexadecanediyl-1,16-bis(trimethyl ammonium bromide) $\text{Br}(\text{CH}_3)_3\text{N}^+(\text{CH}_2)_{16}\text{N}^+(\text{CH}_3)_3\text{Br}^-$, which is shown in Figure 1A.8.

**Fig. 4** Example of Bolaform surfactant

1.3 Properties of Surfactants

Some properties, such as critical micelle concentration (CMC), cloud point (CP), krafft point (KP), hydrophilic-lipophilic balance (HLB), etc., are very significant depending on the molecular structure and characteristics of surfactants. It is highly intriguing in both circumstances when the krafft point (KP) and cloud point (CP) depend on temperature due to the surfactant's solubility. Surfactant solubility is temperature-dependent.

1.3.1 Micellization

The existence of micelle was originally created by McBain and then by G.S. Hartley [17]. Amphiphilic molecules, which have both polar or charged groups and non-polar areas, aggregate to form "micelles" in aqueous solutions. Some substances exhibit colloidal behaviour at higher concentrations due to the formation of aggregates, whereas at low concentrations they behave as normal strong electrolytes. The resulting aggregated particles are referred to as "micelles." A small number of surfactants—typically 50–150—make up the micelles.

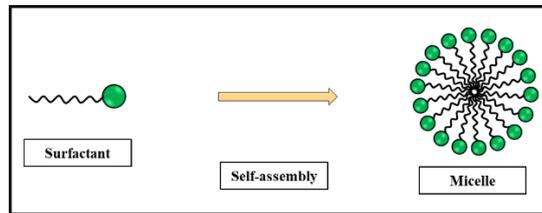


Fig. 5 Schematic representation of micelle

Surfactants self-assemble into micelles, tiny spheres with hydrophilic heads pointing out and hydrophobic tails pointing in, when added to water. Critical micelle concentration (CMC) is the concentration at which micelle production first manifests itself. The CMC values rise as the number of surfactant head groups rises. We can find CMC with the help of different techniques such as specific conductivity, surface tension, turbidity, solubilization, magnetic resonance, etc. A schematic representation of the determination of cmc is shown in the below figure. In which a graph of different properties verses concentration is plotted. Where the dotted line shows cmc at a particular concentration.

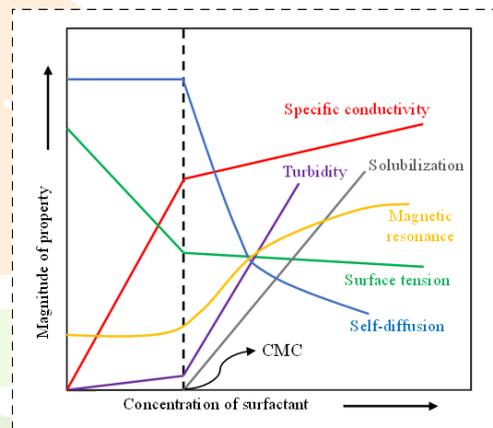


Fig. 6 Schematic representation of determination of CMC using different techniques

Micelles are aggregates of surfactant monomers that are non-covalently bound and labile. They can take on the form of a disc, spherical, or cylinder. The presence of the surfactant and the parameters of the solution, such as temperature, pH, surfactant concentration, ionic strength, etc., affect the size and morphology of the micelles [15].

1.3.2 Critical micelle concentration (CMC)

Critical Micelle Concentration (CMC) exhibits complex temperature dependence, typically displaying a U-shaped curve with a minimum around 25-50°C for most surfactants. At low temperatures, increasing temperature weakens hydrogen bonding between ethylene oxide chains and water molecules in nonionic surfactants, making them more hydrophobic and decreasing CMC. However, at higher temperatures, the alkyl chains become more soluble in water, causing CMC to increase again [18]. This dual effect creates the characteristic minimum in CMC versus temperature plots, with ionic surfactants showing particularly sharp increases above 120.

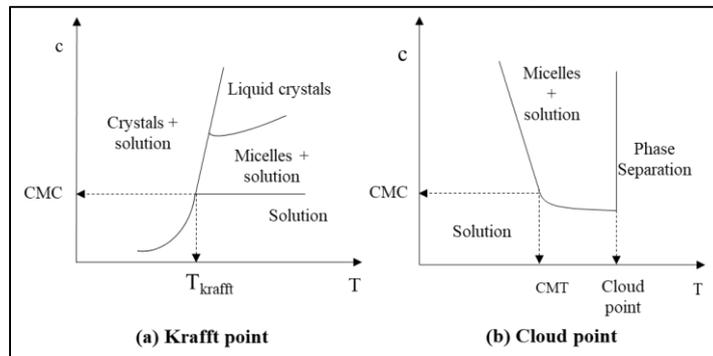
1.3.3 Krafft Point (KP)

The Krafft point (KP) is a property that varies with temperature. The KP of a surfactant is the temperature at which the solubility of the surfactant equals its CMC. In other terms, micelles can only form above a specific temperature, known as the Krafft temperature (T_k) [19]. Below the Krafft point, surfactants remain in crystalline form and cannot solubilize effectively, making them functionally useless. Structural factors significantly influence KP: longer hydrocarbon chains increase KP due to enhanced van der Waals forces, while branching, double bonds, or polar atoms in the chain decrease KP. Counterions also affect KP, with highly hydrated counterions generally lowering the Krafft point and increasing solubility.

1.3.4 Cloud Point (CP)

Cloud point (CP) is an important property of nonionic surfactants. When a nonionic aqueous solution is heated, it separates into two phases and becomes cloudy. This temperature is referred to as the cloud point (CP). The solution mixture becomes cloudy at this point. The CP increases with increasing ethylene oxide (EO) content in a nonionic solution. For laundry and cleaning applications ideal cleaning generally occurs at a temperature above the CP [20]. The schematic illustration of krafft point and cloud point is shown in below figure respectively.

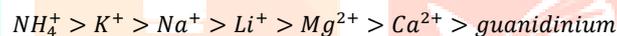
Fig. 7 Schematic diagram of (a) Krafft point and (b) Cloud point



The CP lowers as the nonpolar hydrocarbon tail and the polar PEO hydrophilic group grow. The CP of surfactants with long polyoxyethylene chains may surpass 100 °C. The effect of different salts on nonionic surfactant CP increasing/decreasing is frequently discussed in terms of ‘salting in’ and ‘salting out’. Salting in or salting out electrolytes can exist. ‘Salting in’ electrolytes aids in the solubilization of organic compounds that are insufficiently solvent in water, and the effect can be significant. The Hofmeister series, named after a renowned publication from the late 1800s in which ions were categorized in order of their propensity to salt out proteins, determines the order in which salts appear on this scale [21]. The Hofmeister series for anion is:



For cation it is:



1.3.5 Hydrophilic-lipophilic balance (HLB) value:

The hydrophilic-lipophilic (or hydrophobic) balance, abbreviated as HLB value, indicates the relative ratio of polar and nonpolar groups in the surfactant [22]. Griffin attempted to group surfactant molecules according on the strength and size of their hydrophilic and lipophilic (hydrophobic) bits. The equilibrium of these two restriction groups is known as the ‘hydrophilic-lipophilic balance’, abbreviated as HLB value. A surfactant with a major lipophilic (hydrophobic) character has a low HLB value (9), a surfactant with a predominant hydrophilic character has a high HLB value (> 11), and a surfactant with a moderately hydrophilic and moderately lipophilic character has an HLB value in the range of 9–11.

Table 5. HLB value: relative ratio of polar and nonpolar groups in surfactant

HLB value	Applications
1-3.5	Antifoaming agents
3.5-8	Water-in-Oil Emulsions
7-9	Wetting and spreading agents
8-16	Oil-in-Water Emulsifiers
13-16	Detergents
16-40	Solubilizing agents

1.3.6 Micellar Structure

The molecular geometry of a surfactant—principally the relative sizes of its hydrophilic head and hydrophobic tail—dictates the type of aggregates it forms in solution; above the critical micelle concentration (CMC), small head-to-tail ratios favor tight, spherical micelles, whereas larger head groups or longer tails yield cylindrical or rod-like micelles, and extreme concentrations can drive lamellar phases in which parallel bilayer sheets trap water between surfactant layers. In nonpolar solvents or at very low water content, reverse micelles form with the hydrophilic heads inward, while at moderate concentrations surfactants with roughly equal head and tail volumes can assemble into vesicles—closed bilayer spheres that encapsulate aqueous cores. The chemical nature of the head group (ionic vs. nonionic), tail length, and degree of unsaturation all influence the CMC, curvature, and eventual micelle shape, enabling tailored self-assembly ranging from lamellar sheets to cylindrical, discoidal, and complex rod-like micellar structures.

Spherical micelle in which molecules arranged themselves into tiny clusters called spherical micelles.

Reverse micelle

In a nonpolar media, reverse micelles are generated. Surfactant orientations in reverse micelles differ from those in micelles generated in polar solvents. The hydrocarbon moieties are kept solubilized in the nonpolar solvent while the head groups are directed inward. So, with the aid of surfactants, a nonpolar solvent can be dispersed in a polar solvent and vice versa. Surfactant molecules are arranged so that the polar portion is on the inside, where it may dissolve water, while the nonpolar portion is exposed to organic solvent.

Vesicle micelle

The aggregate is known as vesical when a micelle that starts out as a disc and develops a curved form before becoming a sphere with the solvent inside of it. Spherical, cylindrical, or rod-like micelles, lamellar sheet micelles, reverse micelles, etc. all reduced the water content.

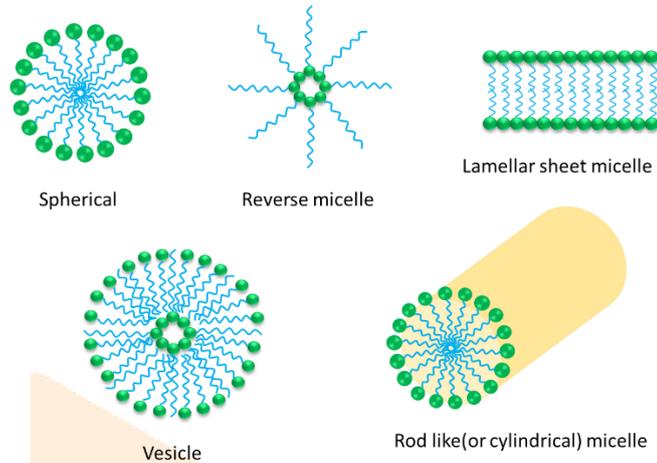


Fig. 8. Schematic illustration of different types of micellar structure

1.4 Application of surfactants

Surfactants serve a multitude of functions across diverse industries by reducing water's surface tension to enhance interaction with oils, soils, and particulates: as cleaning agents in detergents and household cleaners; dispersants in paints, inks, and herbicides; emulsifiers and solubilizers in cosmetics, food products, and pharmaceuticals; and foaming or antifoaming additives in firefighting foams, pipeline construction fluids, and lubricants. Beyond household and industrial cleaning, they act as fabric softeners in laundry, antistatic agents in textiles, and conditioning agents in personal care products such as shampoos, shower gels, hair conditioners, and toothpaste. In agriculture they improve pesticide formulations, in enhanced oil recovery they facilitate hydrocarbon displacement, and in the petroleum industry they stabilize drilling fluids. Even biological systems rely on surfactants: pulmonary surfactants synthesized in the lungs reduce alveolar surface tension to keep airways open and enable efficient gas exchange, while in shaving foams they help razors glide smoothly over skin, minimizing irritation [23-25].

2.1 Overview of Polymers

Polymers—Macromolecules Derived from Repeating Units—are large molecular-mass substances composed of many repeating monomeric units (from Greek poly “many” and mer “unit”) that assemble through covalent bonds and can adopt linear, branched, or crosslinked architectures. Their adsorption at surfaces is governed by noncovalent interactions such as hydrogen bonding, dipolar attractions, hydrophobic contacts, and electrostatic (Coulombic) forces, while copolymers incorporate more than one monomer type, enabling tailored properties. Based on the ionic character of their monomeric groups, polymers may be anionic, cationic, or nonionic, and they naturally divide into biological macromolecules (e.g., proteins, polysaccharides) and synthetic nonbiological macromolecules (e.g., plastics, adhesives). Synthetic polymers predominate in everyday applications—from fibres and elastomers to plastics—because they are cost-effective and durable, and they are further modified to meet specific human needs; for instance, in microelectronics they serve as photoresists, dielectric materials, and plasma-resistant barrier coatings [26].

2.2 Polymeric Micelles

Polymeric surfactants are specialized macromolecules in which hydrophilic and hydrophobic segments are covalently linked along one or more polymer chains, combining the interfacial activity of conventional surfactants with the unique rheological, steric-stabilization, and film-forming properties of polymers. Structurally, they fall into two main categories: Polysoaps: polymers whose repeating units each contain both polar (e.g., carboxylate, sulfate, quaternary ammonium) and nonpolar (e.g., long alkyl) moieties, rendering every monomer inherently amphiphilic. These can homogeneously coat interfaces and form micelle-like aggregates at sufficiently high concentration. Macro-surfactants (block or graft copolymers): copolymers comprising discrete hydrophilic blocks (e.g., poly(ethylene oxide), poly(acrylic acid)) and hydrophobic blocks or side chains (e.g., polystyrene, poly(alkyl methacrylate)). By varying block lengths, architectures, and compositions, critical parameters such as the critical micelle concentration (CMC), aggregate morphology, and solution viscosity can be finely tuned.

Unlike small-molecule surfactants, polymeric surfactants exhibit low CMC values, pronounced steric stabilization, and enhanced resistance to changes in pH, ionic strength, and temperature. Their high molecular weight also enables them to form thick, viscoelastic interfacial films that improve foam stability, emulsion shelf life, and the dispersion of particles in paints or drilling fluids. Although some natural polymeric surfactants exist (e.g., certain glycoproteins or polysaccharide derivatives), their structural heterogeneity and challenging isolation processes have limited their use, making synthetic polymeric surfactants—produced via controlled radical polymerization, anionic polymerization, or ring-opening polymerization—the dominant class in both research and industrial applications.

Application areas span enhanced oil recovery (where they reduce interfacial tension and stabilize microemulsions under harsh reservoir conditions), coatings and adhesives (for improved wetting and film integrity), pharmaceuticals (as solubilizing agents and controlled-release stabilizers), personal care products (for mild cleansing, thickening, and conditioning), and colloidal formulations (where steric stabilization prevents aggregation of nanoparticles or pigments). By tailoring monomer selection, copolymer architecture, and molecular weight, polymeric surfactants offer a versatile platform for designing advanced formulations that meet stringent performance and stability requirements across diverse industries [27-29].

2.3 Block Copolymers

Block copolymers (BCs) are macromolecules in which two or more chemically distinct polymer segments are covalently linked in a single chain, yielding unique amphiphilic behavior analogous to small-molecule surfactants. Depending on the number and arrangement of blocks, BCs are classified as diblock (A–B), linear triblock (A–B–A or A–B–C), or multi-block polymers, and can further adopt nonlinear architectures such as star-block or grafted structures. The relative lengths and chemistries of the hydrophilic and hydrophobic blocks dictate their self-assembly in solution, enabling micelle formation, surface adsorption, and stabilization of emulsions or suspensions. This tunable self-assembly gives BCs exceptional utility in drug delivery—where they can solubilize both hydrophilic and hydrophobic drugs and target release—as well as in nanofabrication and porous material synthesis, where block-length control drives the formation of nanoscale spheres, cylinders, lamellae, or gyroid structures. Commercial examples, such as ICI’s “Hypermers,” illustrate how precisely engineered BCs combine surfactant-like interfacial activity with polymeric stability to meet diverse industrial and biomedical challenges [30-31].

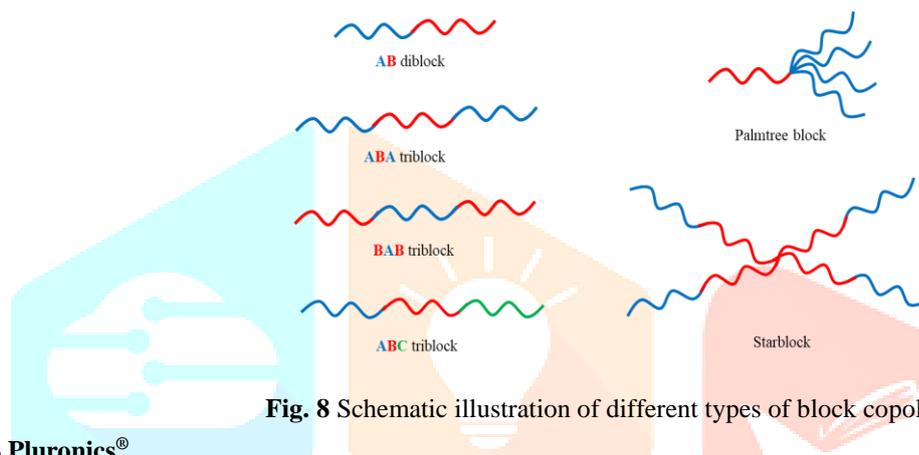


Fig. 8 Schematic illustration of different types of block copolymers.

2.4 Pluronic®

Water-soluble block copolymers are a specialized class of polymeric surfactants that incorporate both aquaphilic (water-loving) and aquaphobic (water-repelling) segments within the same macromolecule, enabling them to self-assemble into micelles and other aggregates much like conventional surfactants. A prominent example is the nonionic EO–PO copolymers—poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO)—commercially marketed by BASF under the Pluronic® (or Poloxamer) trade name. These linear triblock copolymers span molecular weights from 2,000 to 20,000 g/mol with PEO contents of 10–80 wt %, allowing fine-tuning of their hydrophilic–lipophilic balance and micellar properties. Upon heating, the solubility of the PPO middle block decreases sharply, leading to micelle formation above a defined critical micelle temperature (CMT), which governs applications ranging from drug delivery and protein stabilization to temperature-responsive coatings and detergents [32,33].

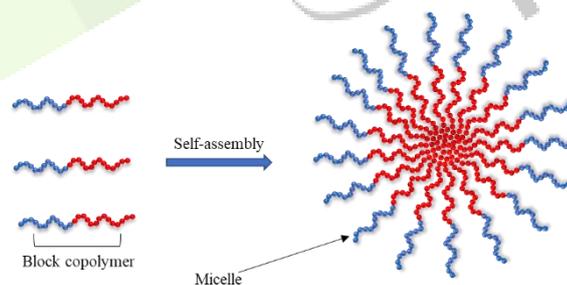


Fig. 9 Schematic illustration of self-assembly of BCs.

2.5 Application of Polymers

Water-soluble polymeric surfactants find broad application across industries due to their combined amphiphilic architecture, which imparts both interfacial activity and polymeric stability: in personal care, they stabilize emulsions, thicken lotions, and enhance foam structures; in pharmaceuticals, they solubilize poorly water-soluble drugs and control release profiles; in agrochemicals, they improve the dispersion and adhesion of pesticides and herbicides; in paints and coatings, they act as dispersants and film-control agents to prevent pigment flocculation; in oil and gas, they serve as drilling fluid additives and facilitate enhanced oil recovery by reducing interfacial tension and stabilizing microemulsions; and in water treatment, they aid in flocculation and contaminant removal. Beyond these, they are employed in emulsion polymerizations, nanotechnology, biotechnology, cosmetics, food processing, and electronics, underscoring their versatility wherever the precise management of interfaces, stabilization of colloids, or tailored rheological properties are required [34,35].

REFERENCES

- [1] Joshi, T. A Short History of Preamble of Surfactants Int. J. Appl. Chem, 2017, 13, 283–292.
- [2] Sohrabi, B. “Amphiphiles.” Self-Assembly of Materials and Supramolecular Structures . IntechOpen. <https://doi.org/10.5772/intechopen.107880>.
- [3] Ghosh, S.; Ray, A.; Pramanik, N. Self-assembly of surfactants: An overview on general aspects of amphiphiles. Biophysical Chemistry, 2020, 265, 106429. <https://doi.org/10.1016/j.bpc.2020.106429>.
- [4] Pinazo Gassol, A.; Pons Pons, R.; Pérez, L.; Infante, M. R. Amino acids as raw material for biocompatible surfactants, 2011. <https://doi.org/10.1021/ie1014348>.
- [5] Van Os, N. M.; Haak, J. R.; Rupert, L. A. M. Physico-chemical properties of selected anionic, cationic and nonionic surfactants. Elsevier, 2012.
- [6] Kronberg, B.; Holmberg, K.; Lindman, B. Surface Chemistry of Surfactants and Polymers; Wiley 2014. <https://doi.org/10.1002/9781118695968>.
- [7] Dave, N.; Joshi, T. A Concise Review on Surfactants and Its Significance. Int. J. Appl. Chem, 2017, 663..
- [8] Joshi, R. H., Dave, N. N., & Joshi, T. P. Physicochemical Properties of Cetrimonium Bromide in Electrolytes and Nonelectrolyte Environments. Current Physical Chemistry, 2024, 14(1), 32-46.
- [9] Gonçalves, R. A.; Holmberg, K.; Lindman, B. Cationic surfactants: A review. J. Mol. Liq., 2023, 121335. <https://doi.org/10.1016/j.molliq.2023.121335>.
- [10] Joshi, R., Oza, A., Kukadiya, K., Pandya, M., & Joshi, T. Physicochemical and molecular docking studies of tween 20 in the presence of NaX salts and hydrotropes in aqueous media. Journal of Dispersion Science and Technology, 2024, 1-10.
- [10] Bhatti, U. and Hanif. M. 2010. Validity of Capital Assets Pricing Model.Evidence from KSE-Pakistan.European Journal of Economics, Finance and Administrative Science, 3 (20).
- [11] Uphues, G. Chemistry of Amphoteric Surfactants. Lipid/Fett, 1998, 100 (11), 490–497. [https://doi.org/10.1002/\(SICI\)1521-4133\(199811\)100:11%3C490::AID-LIPI490%3E3.0.CO;2-2](https://doi.org/10.1002/(SICI)1521-4133(199811)100:11%3C490::AID-LIPI490%3E3.0.CO;2-2).
- [12] Lomax, E. G. Amphoteric Surfactants, CRC Press 1996, 59.
- [13] Sekhon, B. S. Gemini (Dimeric) Surfactants. Resonance, 2004, 9 (3), 42–49. <https://doi.org/10.1007/BF02834987>.
- [14] Kanoje, B., Joshi, R., Joshi, T., Parikh, J., & Kuperkar, K. Surface activity and antimicrobial performance of synthesized gemini surfactant and silver nanoparticles loaded gemini surfactants integrated with microscopy and scattering investigation. Emergent Materials, 2020, 3(2), 213-222.
- [15] Lombardo, D.; Kiselev, M. A.; Magazù, S.; Calandra, P. Amphiphiles Self-Assembly: Basic Concepts and Future Perspectives of Supramolecular Approaches. Adv. Condens. Matter Phys, 2015, 1–22. <https://doi.org/10.1155/2015/151683>.
- [16] Landsmann, S., Luka, M., & Polarz, S. Bolaform surfactants with polyoxometalate head groups and their assembly into ultra-small monolayer membrane vesicles. Nature Communications, 2012, 3(1), 1299.
- [17] Vincent, B. McBain and the Centenary of the Micelle. Adv Colloid Interface Sci, 2014, 203, 51–54. <https://doi.org/10.1016/j.cis.2013.11.012>.
- [18] Anderson, J. L.; Pino, V.; Hagberg, E. C.; Sheares, V. V.; Armstrong, D. W. Surfactant solvation effects and micelle formation in ionic liquids. Chemical Communications, 2003, (19), 2444-2445. <https://doi.org/10.1039/B307516H>.
- [19] Manojlovic, J. Z. The Krafft Temperature of Surfactant Solutions. Thermal Science, 2012, 16 (suppl. 2), 631–640. <https://doi.org/10.2298/TSCI120427197M>.
- [20] Tanford, C. Micelle shape and size. J. Phys. Chem, 1972, 76(21), 3020-3024. <https://doi.org/10.1021/j100665a018>.

- [21] Clint, J. H., & Clint, J. H. Micelle formation. *Surfactant aggregation*, 1992, 82-129. <https://doi.org/10.1007/978-94-011-2272-6>.
- [22] McGowan, J. C. A New Approach for the Calculation of HLB Values of Surfactants. *Tenside Surfactants Detergents*, 1990, 27 (4), 229–230. <https://doi.org/10.1515/tsd-1990-270407>.
- [23] Tai; Louis Ho Tan; Veronique Nardello-Rataj. *Application of Personal Care Detergent Formulations*; CRC Press Taylor & Francis Group, New York 2009.
- [24] Aslam, R.; Mobin, M.; Aslam, J.; Aslam, A.; Zehra, S.; Masroor, S. Application of Surfactants as Anticorrosive Materials: A Comprehensive Review. *Adv Colloid Interface Sci* 2021, 295, 102481. <https://doi.org/10.1016/j.cis.2021.102481>.
- [25] Holmberg, K. Natural Surfactants. *Curr Opin Colloid Interface Sci* 2001, 6 (2), 148–159. [https://doi.org/10.1016/S1359-0294\(01\)00074-7](https://doi.org/10.1016/S1359-0294(01)00074-7).
- [26] Holmberg, K. Natural Surfactants. *Curr Opin Colloid Interface Sci* 2001, 6 (2), 148–159. [https://doi.org/10.1016/S1359-0294\(01\)00074-7](https://doi.org/10.1016/S1359-0294(01)00074-7).
- [27] Raffa, P.; Wever, D. A. Z.; Picchioni, F.; Broekhuis, A. A. Polymeric Surfactants: Synthesis, Properties, and Links to Applications. *Chem Rev*, 2015, 115 (16), 8504–8563. <https://doi.org/10.1021/cr500129h>.
- [28] Garnier, S.; Laschewsky, A.; Storsberg, J. Polymeric Surfactants: Novel Agents with Exceptional Properties. *Tenside Surfactants Detergents*, 2006, 43 (2), 88–102. <https://doi.org/10.3139/113.100290>.
- [29] LASCHEWSKY, André. Polymeric Surfactants. *Tenside, surfactants, detergents*, 2003, 40 (5), 246–249.
- [30] Kim, H.-C.; Park, S.-M.; Hinsberg, W. D. Block Copolymer Based Nanostructures: Materials, Processes, and Applications to Electronics. *Chem Rev* 2010, 110 (1), 146–177. <https://doi.org/10.1021/cr900159v>.
- [31] Joshi, T. P. Cloud Point Phenomena of Mixed Block Copolymers. *J Dispers Sci Technol*, 2016, 37 (6), 816–819. <https://doi.org/10.1080/01932691.2015.1065417>.
- [32] Patel, D.; Patel, D.; Ray, D.; Kuperkar, K.; Aswal, V. K.; Bahadur, P. Single and Mixed Pluronics® Micelles with Solubilized Hydrophobic Additives: Underscoring the Aqueous Solution Demeanor and Micellar Transition. *J Mol Liq*, 2021, 343, 117625. <https://doi.org/10.1016/j.molliq.2021.117625>.
- [33] Patel, D.; Ray, D.; Kuperkar, K.; Aswal, V. K.; Bahadur, P. Parabens Induced Spherical Micelle to Polymersome Transition in Thermo-Responsive Amphiphilic Linear and Star-Shaped EO-PO Block Copolymers. *J Mol Liq*, 2020, 316, 113897. <https://doi.org/10.1016/j.molliq.2020.113897>.
- [34] Raffa, P.; Broekhuis, A. A.; Picchioni, F. Polymeric Surfactants for Enhanced Oil Recovery: A Review. *J Pet Sci Eng*, 2016, 145, 723–733. <https://doi.org/10.1016/j.petrol.2016.07.007>.
- [35] Kwak, J. C. T. *Polymer-Surfactant Systems* CRC Press, 2020.