

Surfactant micelle, their Impact on Reaction system and Applications

Dr. Basant Kumar* and Rajkumar Bind

* Assistant Professor Department of Chemistry, MLK PG College Balrampur, UP, India, 271201

*Corresponding Author Email: hellobasant@gmail.com

Abstract

Surfactant micelles are nano-sized particles that are formed by the aggregation of a number of monomer units containing a hydrophilic polar head and a hydrophobic nonpolar tail. When such amphiphilic molecules are present at a particular minimum concentration, called the critical micelle concentration (CMC), they aggregate and form micelles. Recently, micelles with metal nanoparticles have been used in many fields due to their excellent biocompatibility, pharmacokinetics, targetability, longevity, and adhesion to biosurfaces. In this paper, there is a discussion on several aspects related to micelles, including CMC, general features, properties, size, shape, and different types of mechanisms of polymer micelles. The classification of polymeric micelles is based on intermolecular forces and charges on their hydrophilic heads. We also focused on their application in different fields, such as the treatment of cancer, oral drug delivery, cutaneous drug delivery, smart drug delivery, and many more.

Keywords: Micelle, Surfactant micelle, Critical micelle concentration (CMC) and Applications of micelles.

Date of Submission: 11-06-2024

Date of acceptance: 23-06-2024

I. Introduction

Micelles are dynamic aggregates that have both hydrophilic and hydrophobic regions in their structures and have a number of applications in the fields of polymer science, biochemistry, pharmaceutical chemistry, biological science, organic chemistry, and many more because they are useful in catalysis, drug delivery, studying reaction mechanisms, synthesis of a number of compounds, purification processes, emulsification, membrane formation, many enzymatic functions, applications as nanoparticles, and many more. Micelles are nanoparticles of self-assembled surfactant molecules, and when the temperature of the medium is normal and the electrolytic concentration in the aqueous medium is fixed, the molecules of the electrolytes aggregate themselves into a particular structure, which is called a micelle, which is formed by the aggregates of about 20 to 200 monomer units generally and have a hydrophobic core at the center and a hydrophilic surface in their exterior portions.

When surfactant molecules dissolve in an aqueous medium, among them, about 20 to 200 monomer units at the interface of air and water start aligning above a particular concentration range, called critical micelle concentration, in spherical dimensions generally, leading to the formation of micelles. The micelles may have different shapes, and their dimensions range from approximately 10 to 100 nanometers. Surfactant molecules are soluble in both the organic and water phases because they have both polar and non-polar portions in their structures, and the portion of surfactant molecules that is soluble in the organic phase is termed the hydrophobic tail, while the other portion that is soluble in the aqueous phase is termed the hydrophilic head.

The properties of micelles can be enhanced by the application of additives in the surfactant, which increases the utility of micelles in various fields. [1-5]

Today's polymeric micelles are widely used in the treatment of a variety of cancers in different body parts, and they play a role in drug delivery at the infected sites. [6,7,8]. Different micellar systems may also be applied for the detection of various cations, including alkali metals, alkaline earth metals, and certain transition metals, in many environmental and biological systems. [9]. Recent reports are available that indicate the use of polymeric micellar systems as biosensors for different biological analyses. [10-16]

II. Types of micelles

In order to study the properties and characteristic parameters of micelles, it is necessary to classify them, and on the basis of intermolecular forces, surfactant micelles are classified into the following three classes:

2.1 Conventional Polymeric Micelles

When the core and shell interact hydrophobically in an aqueous medium, conventional polymeric micelles are formed.

e.g., poly (ethylene oxide)-b-poly (propylene oxide)-b-poly (ethylene oxide).[17]

2.2 Polyion Complex Micelles

When two oppositely charged moieties electrostatically interact, polyion-complex micelles are formed. They are formed due to the combined interactions of hydrophobic and electrostatic effects. Examples of this category of micelles are polyethyleneimine, polyamidoamide, and poly(2-(N,N-dimethylamino)ethyl methacrylate).

2.3 Non-Covalently Connected Polymeric Micelles

When the core and corona are non-conventionally connected at the homopolymer chain and by hydrogen bonding, non-conventionally polymeric micelles form.

Examples of this category of micelles are sulfonated polystyrene/PVP, poly(styrenemethacrylic acid)/poly(vinyl pyrrolidone), hydroxyl-containing polystyrene (PSOH)/P4VP, CPB/poly(vinyl alcohol), and PCL/poly(acrylic acid). [18-21]

III. Classification on the basis of charge

According to the charge on their hydrophilic heads, surfactants are classified into the following four types:

Anionic surfactant micelles

Cationic surfactant micelles

Non-ionic surfactant micelles.

Zwitter ionic (amphoteric) surfactant micelles.

3.1 Anionic surfactant micelles

When the polar head of the surfactant monomer carries a negative charge in solution, they are called anionic surfactant micelles. These types of micelles are very effective and widely used in preparing shampoo. They have excellent cleaning properties and are effective at oily cleaning and oil/clay suspension. Alkyl sulfates and alkyl ethoxylate sulfates are mostly used as monomers. A non-polar straight chain (tail) is formed by a saturated or unsaturated C12–C18 aliphatic carbon chain, which may be branched or linear.

Anionic surfactants are divided into five subgroups. Alkyl metal soaps are sodium potassium or ammonium salts of long-chain fatty acids like stearic, oleic, and ricinoleic acid. They produce oil or water emulsions that are stable above pH 10 and very sensitive to acid. Divalent and trivalent surfactants are types of water or oil emulsions that are less alkaline and less sensitive to acid.

Alkyl sulfate surfactants are the esters of fatty alcohols and sulfuric acid. Sodium Lauryl Sulfate is a widely used surfactant; it is an oil or water emulsifying agent.

Alkyl phosphates Anionic surfactants are similar to alkyl sulfates, which are mostly used in oil and water emulsions.

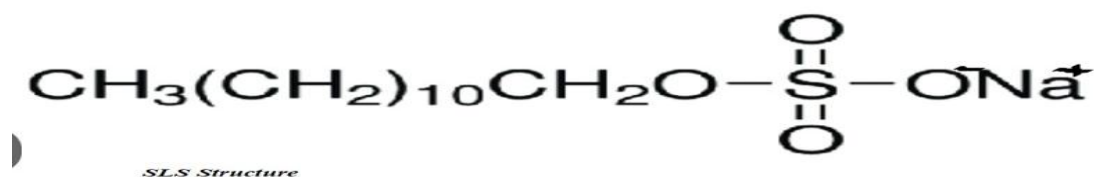


Fig 1 Structure of Anionic Micelle

3.2 Cationic Surfactant Micelles:

In cationic surfactant micelles, the head of the surfactant carries a positive charge on it. Generally, quaternary ammonium salts belong to this category of surfactant micelles. They are used in skin cleaning, wound care, and burns as they have the properties to kill bacteria and have preservative properties. Benzalkonium chlorides, Cetyl Pyridinium chloride, tetradecyl trimethyl ammonium bromide with dodecyl, and hexadecyl compounds are examples of this category of surfactant micelles.

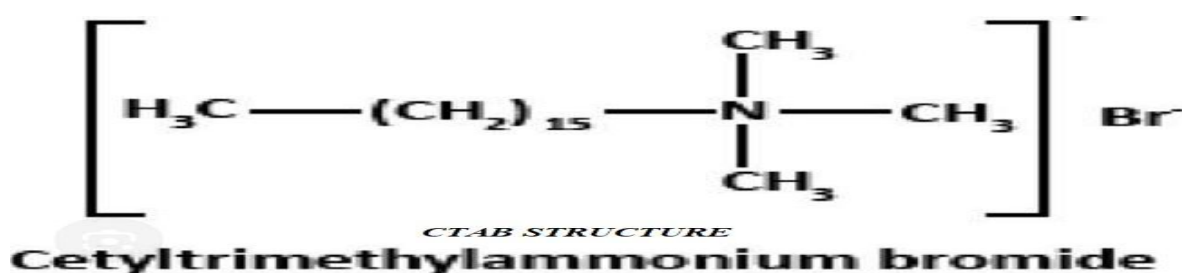


Fig 2 Structure of Cationic Micelle

3.3 Non-Ionic Surfactant Micelles

Surfactant micelles' having no electrical charge in their structure belongs to this category of micelles. Poly-ol esters and Poly-oxy-ethylene esters belong to this category of surfactant micelles.

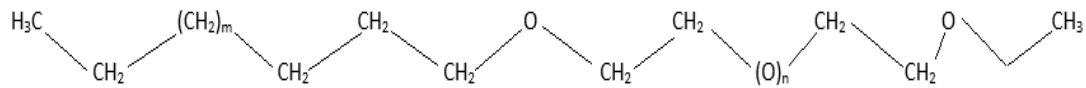


Fig 3 Structure of Non-Ionic Surfactant Micelle

3.4 Zwitter Ionic (Amphoteretic) surfactant micelles

Based on the acidity or pH of the water, this type of surfactant micelles have anionic, cationic, or non-ionic properties in the medium. The surfactant, which carries two charged groups of different signs, belongs to this category. They are generally used in hand-washing liquids and shampoos. Carboxylate, sulfate, and sulphonates belong to this category of micelles.

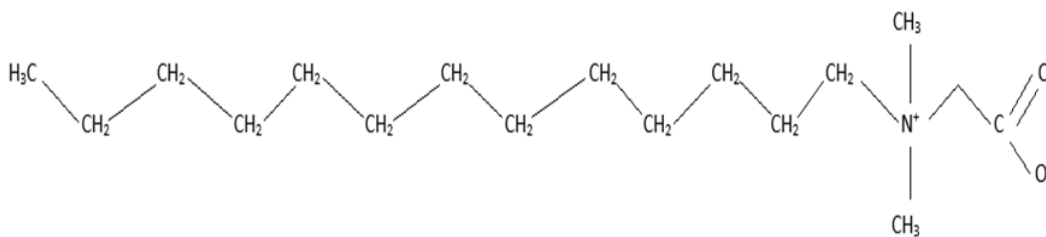


Fig 4 Structure of Amphoteric Micelle

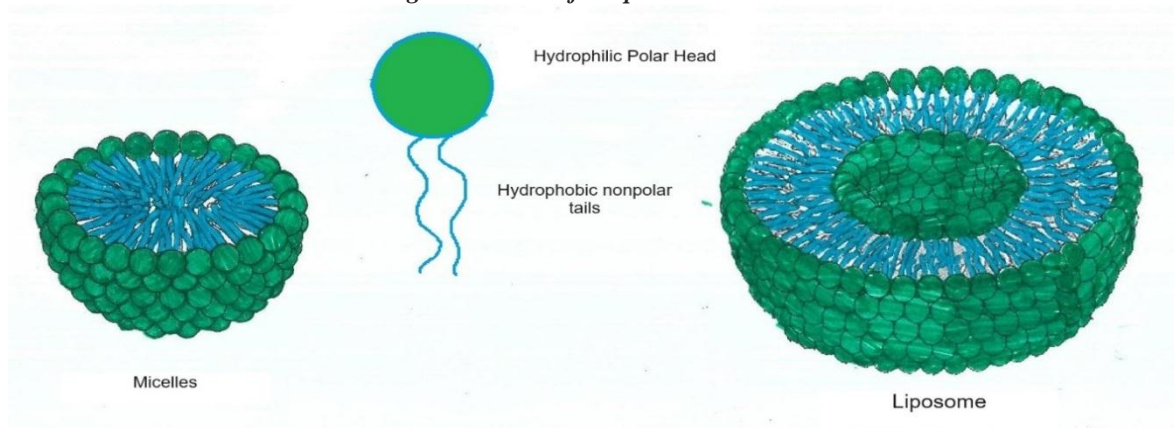


Fig 5 Surfactant and Micelle structure

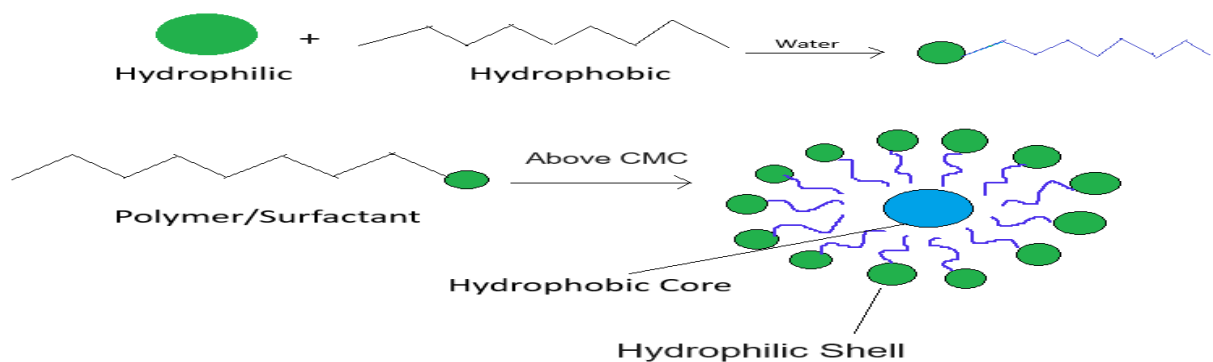


Fig 6 Micelle Formation

IV. Impact and important applications of Surfactant and Micelles

- The impact of surfactant micelles on a number of chemical reactions has been investigated by many researchers belonging to the basic science fields of biology, physics, and chemistry. The reaction rates are generally altered by surfactant and micelles; among them, certain reaction rates are enhanced while certain reactions are retarded.
- Micellar systems are also utilized for photocatalysis; in these reactions, the micelles control the reactivity and selectivity of the reaction system.
- There are a number of reactions in which they are catalyzed in micellar medium; the micellar catalysis also controls the reactivity of catalysts.
- The activation parameters of reactions, such as energy of activation, enthalpy of reaction, and entropy of reactions, are also altered when the reactions are carried out in micellar mediums, and the values of these parameters decrease significantly.
- Certain synthetic reactions involve multistep synthesis; by applying micellar medium, multistep synthesis becomes more feasible as this medium facilitates the reaction. That increases the reaction yield, decreases solvent quantity, and also decreases the extreme reaction conditions requirements.
- Micelle formation is a necessary condition for the adsorption of fat-soluble vitamins in the human body.
- Targeted drug delivery in the infected part of our body is facilitated by the application of micellar medium.
- Micellar medium provides important information related to the kinetics and mechanisms of many reaction systems.

V. Conclusion

The interest in reaction systems occurring in micellar medium has grown as it provides an environment-friendly platform for a number of reactions. The multistep synthesis, catalysis, photocatalysis, adsorption, low requirement of solvents, and less extreme reaction conditions make the micellar medium valuable as it leads to environmentally friendly green chemistry. Different types of organic reactions are carried out in an aqueous medium by the application of different types of micelles. Enzymes and biocatalysis activities are also affected by the application of micelles.

References

- [1]. T.P. Niraula et al. Influence of solvent permittivity and divalent salt on micellization behavior of sodium dodecyl sulfate: conductivity measurements and simulation study *J. Mol. Liq.* (2022)
- [2]. D. Ray et al. Sodium carboxymethylcellulose-induced aggregation of 1-decyl-3-methylimidazolium chloride in aqueous solutions *Carbohydr. Polym.* (2015)
- [3]. B. Das et al. Influence of carboxymethylcellulose on the aggregation behavior of aqueous 1-hexadecyl-3-methylimidazolium chloride solutions *Carbohydr. Polym.* (2014)
- [4]. C.S. Buettner et al. Surface-active ionic liquids: A review *J. Mol. Liq.* (2022)
- [5]. L.M. Gonçalves et al. Effects of micelles and vesicles on the oximolysis of p-nitrophenyl diphenyl phosphate: a model system for surfactant-based skin-defensive formulations against organophosphates *J. Pharm. Sci.* (2009)
- [6]. Yu, G.; Ning, Q.; Mo, Z.; Tang, S. Intelligent polymeric micelles for multidrug co-delivery and cancer therapy. *Artif. Cells Nanomed. Biotechnol.* 2019, 47, 1476–1487.
- [7]. Kotta, S.; Aldawsari, H.M.; Badr-Eldin, S.M.; Nair, A.B.; Yt, K. Progress in Polymeric Micelles for Drug Delivery Applications. *Pharmaceutics* 2022, 14, 1636.
- [8]. Ghosh, B.; Biswas, S. Polymeric micelles in cancer therapy: State of the art. *J. Control. Release* 2021, 332, 127–147.
- [9]. Han, J.; Cai, Y.; Wang, Y.; Dai, X.; Wang, L.; Li, C.; An, B.; Ni, L. Mixed polymeric micelles as a multifunctional visual thermosensor for the rapid analysis of mixed metal ions with Al³⁺ and Fe³⁺. *New J. Chem.* 2018, 42, 12853–12864.
- [10]. Velusamy, K.; Periyasamy, S.; Kumar, P.S.; Rangasamy, G.; Pauline, J.M.N.; Ramaraju, P.; Mohanasundaram, S.; Vo, D.-V.N. Biosensor for heavy metals detection in wastewater: A review. *Food Chem. Toxicol.* 2022, 168, 113307.
- [11]. Xia, N.; Liu, G.; Zhang, S.; Shang, Z.; Yang, Y.; Li, Y.; Liu, L. Oxidase-mimicking peptide-copper complexes and their applications in sandwich affinity biosensors. *Anal. Chim. Acta* 2022, 1214, 339965.
- [12]. Rahmawati, I.; Einaga, Y.; Ivandini, T.A.; Fiorani, A. Enzymatic Biosensors with Electrochemiluminescence Transduction. *ChemElectroChem* 2022, 9, e202200175.
- [13]. Zhu, Z.; Song, H.; Wang, Y.; Zhang, Y.-H.P. Protein engineering for electrochemical biosensors. *Curr. Opin. Biotechnol.* 2022, 76, 102751.
- [14]. Hosseini, S.S.; Jebelli, A.; Vandghanooni, S.; Jahanban-Esfahlan, A.; Baradaran, B.; Amini, M.; Bidar, N.; de la Guardia, M.; Mokhtarzadeh, A.; Eskandani, M. Perspectives and trends in advanced DNA biosensors for the recognition of single nucleotide polymorphisms. *Chem. Eng. J.* 2022, 441, 135988.
- [15]. Huang, Q.-D.; Lv, C.-H.; Yuan, X.-L.; He, M.; Lai, J.-P.; Sun, H. A novel fluorescent optical fiber sensor for highly selective detection of antibiotic ciprofloxacin based on replaceable molecularly imprinted nanoparticles composite hydrogel detector. *Sens. Actuators B Chem.* 2021, 328, 129000.
- [16]. Kamyabi, M.A.; Moharramzadeh, M. A promising electrochemiluminescence herbicide sensor based on ternary nanocomposite and boron nitride quantum dots for trace analysis of tribenuron-methyl in environmental samples. *Microchem. J.* 2021, 168, 106518.
- [17]. Mourya, V.; Inamdar, N.; Nawale, R.; Kulthe, S., 2011. Polymeric micelles: general considerations and their applications. *Ind. J. Pharm. Educ. Res.* 45, 128-138.
- [18]. Yuan, X.-F., Zhao, H., Jiang, M., An, Y., 2000. The self-assembly of polymer blends in selective solvents. *Acta Chim. Sin.* 58, 118.

- [19]. Yuan, X., Jiang, M., Zhao, H., Wang, M., Zhao, Y., Wu, C., 2001. Noncovalently connected polymeric micelles in aqueous medium. *Langmuir* 17, 61226126.
- [20]. Zhang, Y., Jiang, M., Zhao, J., Zhou, J., Chen, D., 2004. Hollow spheres from shell cross-linked, noncovalently connected micelles of carboxyl-terminated polybutadiene and poly(vinyl alcohol) in water. *Macromolecules* 37,1537-1543.
- [21]. Zhang, Y., Jiang, M., Zhao, J., Wang, Z., Dou, H., Chen, D., 2005. pH-responsive coreshell particles and hollow spheres attained by macromolecular self-assembly. *Langmuir* 21, 15311538.