

RECENT ADVANCES AND APPLICATIONS OF SURFACTANTS: A REVIEW

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Abstract

Since surfactants have distinct structures made up of two different molecular sections and a wide range of selection, they are frequently employed in various industrial items including detergents, medications, and anti-corrosive treatments. Additionally, surfactants have made a substantial contribution to a wide range of scientific areas, particularly nanotechnology. For instance, the stabilization of hydrophobic nanoparticles in water through the amphiphilic character of surfactants has opened up a wide range of scalable solution-processed nanomaterial-based applications. Another essential ingredient in the creation of precisely regulated nanoparticles is surfactant. The development of colorimetric sensors, which are highly desirable for a wide range of interdisciplinary applications due to their affordability, practicality, high stability, and selectivity, has been made possible via surfactant-assisted metallic nanoparticle synthesis. Because surfactants directly alter the characteristics of nanoparticles, they are essential for optimizing sensor sensitivity and selectivity during nanoparticle manufacturing. In addition, a brand-new class of magnetic surfactants has been developed for use in medication delivery systems. We give an outline of the principles of surfactants and how they are used in the advancement of nanotechnology in this brief review.

Keywords: [Surfactant; stabilizer; nanoparticle; nano- sensors; magneto surfactants]

1. Introduction

Surfactants are organic compounds consisting of two polarity-differentiating chemical groups: a tail group that is drawn to nonpolar phases and a head group that has an attraction for polar phases [1-7]. Surfactants are commonly employed to lower the surface and interfacial tension between two or more phases because of their distinctive structural makeup [8-11]. Micelles with dimensions ranging from nanometers to microns can also arise as a result of their propensity to construct self-assembled structures in solution [12, 13].

Surfactants are useful in a wide range of industrial products because of their amphiphilic nature. These products include pharmaceutical formulations [35-37], drug delivery [38-40], detergents [21-23], de-emulsifiers [24, 25], wetting agents [26, 27], oil recovery enhancers [28-31], pour-point depressants [32-34], and medicines [14-16]. Surfactants offer enormous potential to get above the present constraints in nanotechnology in addition to industrial uses [41-46]. Amphiphilic surfactants, for instance, have been documented to function as stabilizers in the process of creating stable dispersions of hydrophobic inorganic nanomaterials, including graphene [50], carbon nanotubes [47-49], transition metal dichalcogenides [51], and black phosphorus [52].

In order to further improve the dispersion stability and

adjust the surface/interface tensions across solid/liquid interfaces, surfactants may be a crucial ingredient in the synthesis of nanoparticles with precisely regulated geometries. One approach is to use localized surface plasmon resonance phenomena on a nanoparticle array, where the nanoparticle size and shape, degree of aggregation, and refractive index affect the sensitivity of the sensors [53, 54]. Furthermore, advanced sensing systems have been developed for enhancing both the identification and transduction processes by using many novel nanoparticles rather than conventional organic dye-based sensing assays, where the former offer advantages in sensitivity, selectivity, stability, reusability, and practical applicability [55-61]. For colorimetric applications, the unique physical and chemical properties (size, shape, large active surface area, and higher activity) of nanoparticles afford tremendous catalytic activities that differ from those of their bulk counterparts due to size-induced quantum confinement effects in the former [62, 64-67].

In this brief review, we give a general introduction to surfactants for the synthesis of nanoparticles and go through the intricate connections between the surfactant's molecular structure and the ensuing particle structure distributions for maximizing ultrasensitive detection in sensing application devices. We also talk about a novel class of surfactants with

magnetic properties that can be used as catalysts, for protein separation, drug delivery, and DNA extraction.

2. Surfactant structure dependent synthesis process of nanoparticles

Because they prevent the synthesised nanoparticles from aggregating and increase stability in colloidal systems, surfactants' amphiphilic properties are crucial to the synthesis of nanoparticles [43, 68-73]. The synthesis of surfactant-assisted nanoparticles has garnered significant interest in the creation of nanoscale sensors that can identify biomaterials, biomarkers, and hazardous compounds [74-76, 77-79]. In order to detect even minute amounts of material, nanoscale sensors must attain high sensitivity and selectivity for a particular analyte. The exact size distribution and other structural characteristics of the nanoparticles have a significant impact on their sensitivity and selectivity.

As a result, altering the surfactant's molecular structure to adjust the size can offer a fresh approach to optimizing the sensitivity increase. Recently, a method was disclosed [71, 72] that involved modifying the surfactant's tail length to regulate the size, growth, and colloidal stability of nanoparticles. The durability of zirconium oxide nanoparticles, ZrO₂, was studied by Ordóñez et al. in relation to nonionic surfactants (polyvinyl pyrrolidone, PVP), cationic surfactants (cetyltrimethylammonium bromide, CTAB), and anionic surfactants (sodium dodecylbenzene sulfonate, SDBS). The results showed that the synthesized ZrO₂ had better stability and less agglomeration with the surfactant [71]. With zeta potentials of 50.38 ± 2.13 and 42.22 ± 3.27 mV, respectively, both SDBS and CTAB surfactants provided the ZrO₂ suspension with greater stability than that produced by PVP, which had a zeta potential of 19.99 ± 2.9 mV. Grzódka et al. noted a similar pattern, stating that the stability of alginate acid/ZrO₂ nanofluid was enhanced by several cationic surfactants, including silicone surfactants, CTAB, and fluorocarbon (S-106-A) surfactants [80].

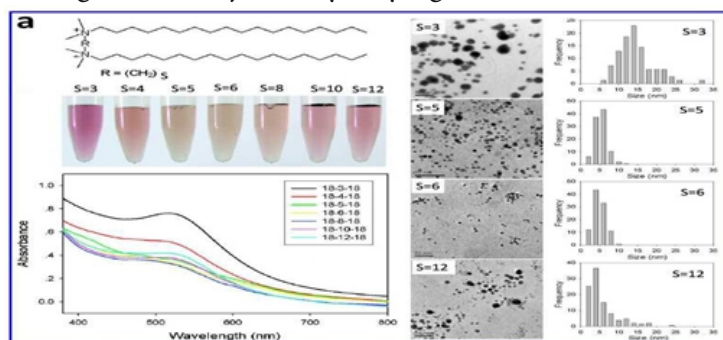
According to Shaban et al. [81], the length of the

hydrocarbon tail of a series of cationic surfactants was found to affect the colloidal stability of the as-prepared AgNPs. With a zeta potential of 52 ± 10.7 mV, the longer-tail surfactant C16Dim produced more stable AgNPs than the shorter-tail surfactant C10Dim, which produced less stable AgNPs with a zeta potential of 34.1 ± 10.4 mV. According to Aiad et al., the stability of AgNPs is dependent on two series of antipyrine cationic surfactants' amphiphilic alkyl chains [82]. The zeta potential increased to +31, +34, and +40 mV for the series APB8, APB12, and APB16, respectively, by using a series of surfactants (APC8, APC12, and APC16; 8, 12, and 16 refer to the number of carbon atoms in the alkyl chain), indicating an increase in the stability of the nanoparticles with the surfactants [82]. Qian Liu et al. reported on the impact of spacer length on the stability of AuNPs in a produced Gemini cationic surfactant with structures [83]. The synthesised AuNPs' enhanced zeta potential confirmed that the stability of the AuNPs increased as the spacer length increased. The zeta potential reached its maximum when $s = 8$ carbon atoms. Pišárík Martin et al. [84], who looked at the relationship between the stability of as-synthesised AgNPs and the surfactant structure, reported similar findings. AgNPs with a larger zeta potential were formed as a result of lengthening the hydrophobic carbon substituents linked to the ammonium head, indicating their increased stability [84]. According to Morsi et al., yttrium oxide nanoparticle stability was increased by employing CTAB and SDS as the corresponding cationic and anionic surfactants. The zeta potentials for the Y₂O₃/CTAB and Y₂O₃/SDS systems, respectively, were examined and showed stable nanofluid systems of 37.3 mV and 61.7 mV. As per earlier findings, Peng et al. demonstrated that SDBS enhanced the stability of C60 nanoparticles, with the C60-SDBS complex exhibiting a zeta potential of 49.5 mV [72]. It is determined from earlier findings that the surfactant has a significant

impact on the produced nanoparticles' stability. As demonstrated by the Gemini surfactant, which increased the stability of the generated nanofluid system, the hydrophobic tail of the surfactant and the spacer also had an impact on stability. The size distribution of the as-synthesised nanoparticles is generally controlled by altering the chain length of surfactants and the hydrophobic spacers that sit between the hydrophilic heads. This can help increase the sensitivity of nanoscale sensors. The stability of the nanomaterials is mostly regulated by the adsorption of surfactant molecules onto their surface, which also greatly regulates particle size. The surfactant can easily form micelles and exhibits good adsorption on the surface of the nanoparticles. The growth of the nanoparticles can be regulated by the surfactant present during their nucleation. The rate of migration onto the surfaces of nanoparticles in nanomaterials rises with the hydrophobicity of the surfactant, creating a more protective coating that helps to maintain the dispersion of the nanoparticles in solution with less agglomeration. Larger particle sizes are therefore obtained.

Figure 1. Gemini surfactant (18-s-18)-formed Au nanoparticles with varying spacer lengths are characterized. Adapted from Reference [83].

Pisár?ik Martin et al. [84], who looked at the relationship between the surfactant structure and particle size of as-synthesised AgNPs, observed findings similar to these. Smaller AgNPs were produced by lengthening the hydrophobic carbon substituents connected to the ammonium head. According to Feng Xu et al., the size of the AgNPs was adjusted by varying the surfactant.



tail's length. It was demonstrated that the size of the AgNPs decreased as the number of carbon atoms attached to the hydrophilic head increased; the sizes were 5.6 ± 1.9 , 5 ± 1.8 , 3.9 ± 1.4 , and 4 ± 1.4 nm, respectively. A new series of Gemini surfactants, C_n-C₄-C_n.2Br, where n = 12, 14, 16, and 18 carbon atoms, were prepared [85].

AgNP size control based on the amphipathic alkyl chain of two series of antipyrine cationic surfactants was described by Aiad et al. [82]. The size of the AgNPs dropped from 25 to 15 nm as the length of the hydrophobic tail increased by using the APC8, APC12, and APC16 series, where 8, 12, and 16 denote the number of carbon atoms in the alkyl chain [82]. ZnS nanoparticles have also been shown to exhibit surfactant-dependent size modification; particle diameters of 55.5 ± 0.5 , 13.4 ± 0.5 , and 11.6 ± 0.5 nm were obtained with various surfactants, DTAB, TTAB, and CTAB, respectively, where the hydrophobicity of the surfactant tail caused the formation of smaller nanoparticles [86].

Changes to the head groups of surfactants can impact the size, degree of aggregation, and hydrophobicity/hydrophilicity of nanoparticles. According to Mehta et al., altering the hydrophilic head group of ZnS nanoparticles can regulate both their size and dispersion stability [87]. Cetyltrimethylammonium chloride (CTAC) and cetyltrimethylpyridinium chloride (CPyC), two cationic surfactants with distinct hydrophilic properties, were investigated; of these, CPyC, the large head surfactant, exhibited a greater affinity and produced smaller ZnS nanoparticles with greater colloidal stability than CTAC [87].

Based on the methodology, it was demonstrated that ZnS could be synthesized in smaller sizes using CPyC because it has a more hydrophobic pyridine ring than CTAC's trimethyl groups. As a result, CPyC's hydrophobicity is significantly higher than CTAB's, which may be a determining factor in the size of ZnS nanoparticles.

Apart from regulating their size, nanoparticle forms can also be manipulated by manipulating the facet growth process, which is based on the included surfactant's molecular structure. Surfactants function as a shape-directing agent in this situation [88-91].

According to Gao et al., the hydrophobic tail length of a surfactant has a substantial impact on the morphology of gold nanorods; specifically, the aspect ratio of produced gold nanorods increases as the alkyl chain lengthens from 10 to 16 carbon atoms [89]. Due to stronger hydrophobic tail interactions, a longer hydrocarbon chain results in a compacted bilayer and reduces the possibility of newly generated gold atoms penetrating laterally. As a result, both ends of the nanorod are preferred for further growth, which leads to the formation of higher aspect ratio gold nanorods [91, 92]. Additionally, surfactants regulate the nucleation and growth of nanoparticles during seed-mediated growth, producing gold and silver nanoparticles in a variety of forms, including rods, spheres, cubes, and octahedra [93-96].

A new approach to customizing the desired attributes of nanoparticles may be to modify the geometry of as-synthesised nanoparticles based on the surfactant molecular structures, where the size distribution and the colloidal stability are significantly associated to the alkyl chain length. Dadwal and Joy et al. used myristic, palmitic, and stearic acid as long-chain alkyl surfactants to report the colloidal stability of Fe₃O₄ nanoparticles in toluene solvent. It was shown that, when a magnetic field was applied, the magnetite nanofluid's thermal conductivity was affected by varying chain lengths. As the surfactant chain lengthened, the thermal conductivity reduced [97].

Aiad et al. reported a similar outcome in another work [82], showing that the surfactant tail length altered the AgNPs' antibacterial activity in addition to their size. It was demonstrated in a different material prepared by Negm et al. [98] that cationic polymeric surfactants with varying alkyl chain lengths (eight and twelve carbon

atoms) affected the antibacterial activity but not the size of copper nanoparticles. Furthermore, smaller silver nanoparticles with strong microbiological activity against sulfate-reducing bacteria were obtained by increasing the amount of ethylene oxide units in a cationic quaternary polymer that was created [99]. Zhou et al. looked at how SDS and TiO₂ nanoparticles worked together to increase the viscosity of water-based nanofluids at various temperatures.

According to Zhou's findings [100], adding SDS and TiO₂ combined in water resulted in a suspension with a lower viscosity than adding them separately. The effects of CTAB, SDS, and TX-100, three surfactants, on the toxicity of AgNPs toward the crop *Fagopyrum esculentum* L were studied by Kumari et al. [101]. When compared to the control group that did not include AgNPs, the phytotoxic effect of the AgNPs generated without any surfactant caused 77.4% cell death. Cell death was significantly reduced (by 37%) when AgNPs containing surfactants (TX-100, CTAB, and SDS) were applied to the plant crop *Fagopyrum esculentum*. As seen in Figure 2, this study offers encouraging information on the important function surfactants play in improving plant stress tolerance to AgNP and guaranteeing food safety [101].

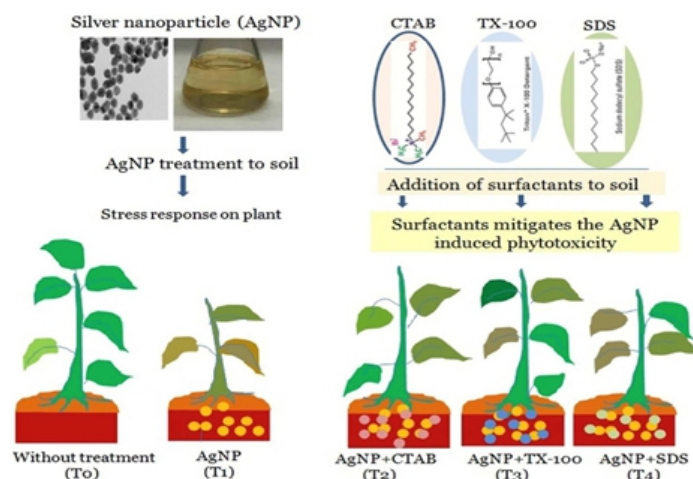


Figure 2. Diagrams illustrating how the application of various surfactants alters the phytotoxic effect of AgNPs on the crop *Fagopyrum esculentum*. Adapted from Reference [101].

Conclusion

We covered the most recent developments in surfactants and their adaptable, structure-dependent characteristics for optimal uses in nanotechnology in this brief overview. Surfactants are essential for regulating the size distributions of the as-synthesised nanoparticles and enhancing dispersion stability during the nanoparticle synthesis process in solution. More specifically, smaller, less aggregated, and more stable nanoparticles are formed as the tail length of the surfactant utilized in nanoparticle formation rises. This advancement has the potential to greatly advance size-tunable nanoparticle-based colorimetric sensor applications.

To offer concrete proof of this association and molecular fingerprints, much research is still needed to define the relationship between surfactant structure and nanoparticle geometry. In addition, a brand-new class of surfactants known as magneto surfactants has been presented. It is possible to successfully manufacture a novel series of surfactants with distinct magnetic characteristics by combining magnetic components and ordinary surfactants. Magneto surfactants' great sensitivity and selectivity to target a specific position have led to their continued use in the medication delivery industry. Despite extensive research on this emerging class of surfactants, given the short time since surfactants were first discovered, it is still necessary to clarify the underlying mechanisms, offer technical solutions, gain a deeper understanding of their toxicity, and open the door to large-scale production for commercial applications.

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