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ESTER-BASED CATIONIC GEMINI SURFACTANTS: SYNTHESIS, PROPERTIES, AND APPLICATIONS

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ABSTRACT

Ester-based cationic gemini surfactants represent an innovative class of biodegradable amphiphiles that combine the exceptional surface-active properties of gemini structures with enhanced environmental compatibility. This comprehensive review examines the synthesis methodologies, physicochemical properties, and diverse applications of these surfactants, with particular emphasis on recent developments in the field. The incorporation of hydrolyzable ester linkages within the spacer or hydrophobic tails provides unique advantages, including controlled biodegradability, reduced toxicity, and maintained high surface activity. Critical micelle concentration values typically range from 0.01-0.1 mM, significantly lower than conventional monomeric surfactants. Recent studies demonstrate their effectiveness in biomedical applications, including gene delivery systems with transfection efficiencies comparable to commercial standards, antimicrobial agents with minimum inhibitory concentrations in the low micromolar range, and drug delivery vehicles. Additionally, these surfactants show promise in enhanced oil recovery, personal care formulations, and environmental remediation. Current challenges include synthetic complexity and industrial scaling limitations, while future perspectives focus on green synthesis methodologies, computational design approaches, and stimuli-responsive systems. This review highlights how ester-based cationic gemini surfactants successfully balance high performance with environmental responsibility, positioning them as next-generation surfactants for sustainable applications.

1. INTRODUCTION

Surfactants constitute a fundamental class of chemical compounds with widespread applications across pharmaceutical, cosmetic, industrial, and environmental sectors. Traditional monomeric surfactants have served industry well for decades; however, their limited efficiency and environmental persistence have prompted researchers to develop more advanced alternatives [1]. Gemini surfactants, characterized by two hydrophilic head groups and two hydrophobic tails connected through a spacer unit, emerged as a revolutionary class of amphiphiles in the late 1990s, offering superior physicochemical properties compared to conventional surfactants [2].

The distinctive architecture of gemini surfactants confers remarkable advantages, including critical micelle concentration (CMC) values that are one to two orders of magnitude lower than their monomeric counterparts, enhanced surface tension reduction capabilities, and superior solubilization properties [3]. These exceptional characteristics arise from the cooperative effects between the twin hydrophobic chains and the structural constraints imposed by the spacer unit. Among various types of gemini surfactants, cationic variants have attracted particular attention due to their strong electrostatic interactions with negatively charged surfaces, leading to enhanced antimicrobial properties and broad applicability in gene delivery systems [4].

Environmental sustainability has become an increasingly critical consideration in surfactant development. Conventional quaternary ammonium surfactants, while highly effective, exhibit poor biodegradability and

potential aquatic toxicity, raising concerns about their long-term environmental impact [5]. This challenge has driven the development of cleavable surfactants containing labile bonds that facilitate environmental degradation. Ester-based cationic gemini surfactants, featuring hydrolyzable ester linkages strategically positioned within their molecular architecture, represent a sophisticated solution that successfully balances high performance with environmental responsibility [6]. Recent research has demonstrated that these surfactants can achieve biodegradation efficiencies significantly superior to conventional cationic surfactants while maintaining excellent surface-active properties [7].

2. STRUCTURAL CLASSIFICATION AND DESIGN PRINCIPLES

Ester-based cationic gemini surfactants can be systematically classified according to the position and number of ester functionalities within their molecular structure. The general molecular formula comprises two quaternary ammonium head groups, two hydrophobic alkyl chains, and a spacer unit containing at least one ester bond (-COO-). The strategic positioning of ester linkages significantly influences both the physicochemical properties and biodegradation characteristics of these surfactants [8].

Spacer-integrated ester linkages represent the most common configuration, where ester bonds are incorporated within the spacer connecting the two hydrophilic head groups. This architecture facilitates controlled biodegradation while influencing the rigidity and flexibility of the spacer, thereby affecting micellization behavior and interfacial properties. Studies have shown that spacer-integrated esters generally result in higher CMC values compared to tail-integrated variants due to increased hydrophilicity of the spacer region [9]. Tail-integrated ester linkages, alternatively, feature ester bonds within the hydrophobic tails, often positioned between alkyl chains of varying lengths. This configuration enhances biodegradability while introducing polar interruptions that influence packing parameters and aggregation behaviors [10].

Recent advances have led to the development of multiple ester-functionalized gemini surfactants incorporating ester linkages in both spacer and tail regions. These sophisticated structures maximize biodegradability potential while offering complex self-assembly behaviors suitable for specialized applications. The cationic character typically derives from quaternary ammonium groups, which provide strong electrostatic interactions with negatively charged surfaces, contributing to enhanced surface activity and antimicrobial potency [11]. The combination of structural elements—hydrophobic chain length (typically C12-C18), spacer length (ranging from 2 to 12 carbon atoms), and ester positioning—enables fine-tuning of properties for specific application requirements.

3. SYNTHESIS METHODOLOGIES

The synthesis of ester-based cationic gemini surfactants typically involves multistep procedures requiring careful control of reaction conditions to achieve high yields and purity. Several established synthetic routes have been developed, each offering distinct advantages for specific molecular architectures [12]. The direct esterification route involves the reaction of dicarboxylic acids or their derivatives with long-chain alcohols containing tertiary amine functionalities. The resulting intermediates undergo quaternization with alkyl halides to yield the target gemini surfactants. This approach typically proceeds under acidic catalysis using p-toluenesulfonic acid or sulfuric acid, or through activation with coupling agents such as dicyclohexylcarbodiimide. Recent optimization studies have achieved yields exceeding 94% under carefully controlled conditions [13].

Transesterification methods provide an alternative approach involving reactions between methyl or ethyl esters of carboxylic acids and hydroxyl-functionalized quaternary ammonium compounds. This methodology often employs titanium(IV) alkoxides or sodium methoxide as catalysts, requiring careful control of temperature and pressure to drive the equilibrium toward product formation [14]. For surfactants with specific structural features, ring-opening reactions of cyclic anhydrides or lactones with amino-functionalized precursors offer an efficient strategy. The resulting intermediates undergo further functionalization and quaternization to yield target gemini structures with well-defined architectures [15].

Modern synthetic strategies have incorporated click chemistry principles, particularly copper(I)-catalyzed azide-alkyne cycloaddition, to construct ester-based gemini surfactants with precise control over structural elements. This modular approach allows for systematic variation of molecular parameters and facilitates structure-property relationship studies. Recent developments in green chemistry have focused on biocatalytic approaches using lipases for esterification, representing promising directions for environmentally benign synthesis while maintaining high selectivity and efficiency [16].

4. PHYSICOCHEMICAL PROPERTIES

Ester-based cationic gemini surfactants exhibit exceptional surface-active properties that significantly outperform conventional monomeric surfactants. The critical micelle concentration values typically range from 0.01 to 0.1 mM for surfactants with C12-C16 alkyl chains, compared to 1-10 mM for conventional monomeric surfactants with similar hydrophobic chain lengths. This enhanced efficiency stems from cooperative hydrophobic interactions between the two alkyl chains and structural constraints imposed by the spacer [17]. Recent studies have demonstrated that the position of ester linkages significantly influences CMC values, with spacer-integrated esters generally resulting in higher CMC compared to tail-integrated variants due to increased hydrophilicity of the spacer region [18].

Surface tension reduction capabilities represent another distinctive feature of these surfactants. They achieve significant reductions in the surface tension of water, typically reaching values of 25-30 mN/m at concentrations above the CMC, compared to 30-40 mN/m for conventional surfactants. The minimum surface tension depends on molecular architecture, with longer hydrophobic chains and optimized spacer lengths yielding lower values. Furthermore, these surfactants demonstrate remarkable interfacial activity, reducing oil-water interfacial tension to ultra-low values suitable for enhanced oil recovery applications [19].

The aggregation behavior reveals complex dependencies on molecular structure. Depending on spacer length, rigidity, and ester positioning, these surfactants form various micellar structures including spherical micelles, elongated or wormlike micelles, and vesicles. Short spacers (2-4 carbon atoms) typically promote formation of elongated structures due to strong repulsive interactions between headgroups, while longer spacers (10-12 carbon atoms) favor spherical aggregates. The average aggregation number typically ranges from 20 to 100, with ester linkages generally reducing aggregation numbers compared to all-hydrocarbon analogues due to increased hydrophilicity and steric constraints [20]. Recent research published in 2025 has shown that the presence of additional cationic groups significantly influences both CMC and aggregation behavior, with trimeric surfactants showing remarkable CMC reductions to 0.013 mM [21].

5. BIODEGRADABILITY AND ENVIRONMENTAL PROFILE

The defining feature of ester-based cationic gemini surfactants lies in their enhanced biodegradability compared to conventional quaternary ammonium surfactants. Ester bonds are susceptible to hydrolysis under both acidic and basic conditions, providing a mechanism for surfactant breakdown. The hydrolysis kinetics depend on several factors, including pH, temperature, and the steric environment surrounding the ester linkage. Generally, ester hydrolysis proceeds faster at extreme pH values and elevated temperatures. In neutral aqueous environments at ambient temperature, the hydrolytic half-life typically ranges from several days to weeks, providing a balance between stability during application and eventual degradability [22].

Microbial degradation proceeds primarily through enzymatic hydrolysis of ester bonds by esterases, generating fragments that can be further metabolized through conventional biodegradation pathways. Systematic investigations have established structure-biodegradability relationships, revealing that shorter spacers generally facilitate faster biodegradation due to reduced steric hindrance around ester groups, multiple ester functionalities enhance overall biodegradability, and branched alkyl chains near ester linkages can impede enzymatic hydrolysis [23]. Studies have demonstrated that spacer-integrated esters generally show faster biodegradation rates compared to tail-integrated esters due to greater accessibility to microbial enzymes.

A critical finding from recent research indicates that gemini surfactants with ester bonds are much more susceptible to alkaline hydrolysis than corresponding monomeric surfactants, particularly above the CMC. The betaine ester type arrangement, where the ester carbonyl group faces the positive charge, hydrolyzes significantly faster than esterquat surfactants. This differential hydrolysis behavior has important practical implications for formulation stability and environmental fate [24].

6. APPLICATIONS

The exceptional combination of high surface activity and enhanced biodegradability makes ester-based cationic gemini surfactants particularly valuable across diverse application domains. In biomedical applications, these surfactants have emerged as promising non-viral vectors for gene delivery. The positive charges of quaternary ammonium headgroups interact with negatively charged DNA phosphate backbone, forming compacted complexes (lipoplexes) that facilitate cellular uptake. Recent studies published in 2024 have demonstrated transfection efficiencies comparable to commercial standards such as Lipofectamine, with the added advantage of significantly reduced cytotoxicity due to biodegradable ester linkages [25]. Structure-activity relationship investigations reveal that optimized spacer lengths (typically 3-6 carbon atoms) and balanced hydrophobic chain lengths (C12-C16) yield the most effective gene delivery systems.

Antimicrobial applications represent another significant domain. The intrinsic antimicrobial properties of quaternary ammonium compounds are enhanced in gemini structures through more efficient disruption of microbial cell membranes. Recent 2025 research has demonstrated broad-spectrum antimicrobial activity against both Gram-positive and Gram-negative bacteria, with minimum inhibitory concentrations often in the low micromolar range. Studies comparing these surfactants with known antimicrobials such as kanamycin and ampicillin have shown excellent activity in both Staphylococcus aureus and Escherichia coli [26]. The incorporation of ester linkages provides controlled degradation, potentially reducing antimicrobial resistance development.

In enhanced oil recovery applications, these surfactants reduce oil-water interfacial tension to ultra-low values, facilitating mobilization of residual oil trapped in reservoir pores. The cationic nature provides strong adsorption to negatively charged rock surfaces, modifying wettability toward more water-wet conditions that favor oil displacement. Recent 2024 studies have highlighted their effectiveness as fabric softening agents and corrosion inhibitors, with some gemini ester surfactants achieving corrosion inhibition efficiencies as high as 94.5% for carbon steel in acidic solutions [27]. Personal care applications benefit from their excellent conditioning properties, emulsion stabilization capabilities, and rheology modification effects at low concentrations.

7. CURRENT CHALLENGES AND FUTURE PERSPECTIVES

Despite significant advances, several challenges remain in the development and application of ester-based cationic gemini surfactants. Current synthetic routes often involve multiple steps with extensive purification requirements, limiting large-scale production feasibility. Overall yields in multistep syntheses of complex ester-based structures remain suboptimal, typically ranging from 30-60%. The development of more efficient one-pot synthesis methods and continuous flow processes represents a key challenge for industrial applications [28]. Furthermore, comprehensive understanding of structure-property relationships remains incomplete, necessitating advanced molecular dynamics simulations and quantum chemical calculations to predict the impact of ester positioning on aggregation behavior and interfacial properties.

Future research directions should focus on green chemistry approaches, emphasizing reduced solvent usage, non-toxic catalysts, and atom-economic transformations. Emerging biocatalytic approaches using lipases for esterification represent promising directions for environmentally benign synthesis. The development of stimuli-responsive systems with responsive behavior to specific stimuli (pH, temperature, light, enzymes) offers opportunities for smart delivery systems and controlled-release applications. Integration of ester-based cationic gemini architectures with other functional moieties, such as amino acids, sugars, or biodegradable polymers, represents an emerging approach to create multifunctional surfactants with enhanced performance profiles

[29]. The exploration of these surfactants in sustainable technologies, including biobased formulations and circular economy approaches, aligns with global sustainability goals and represents significant opportunities for future research.

8. CONCLUSION

Ester-based cationic gemini surfactants represent a sophisticated class of amphiphilic compounds that successfully address the balance between high performance and environmental responsibility. The strategic incorporation of biodegradable ester linkages within the molecular architecture delivers enhanced biodegradability while preserving exceptional surface-active properties characteristic of gemini structures. Their remarkably low CMC values (0.01-0.1 mM), superior surface tension reduction capabilities (25-30 mN/m), and versatile self-assembly behaviors position them as high-efficiency alternatives to conventional surfactants across diverse application domains. Recent research from 2024-2025 has demonstrated their significant potential in biomedical applications, including gene delivery systems with transfection efficiencies comparable to commercial standards, antimicrobial agents with excellent activity against both Gram-positive and Gram-negative bacteria, and corrosion inhibitors with efficiencies exceeding 94%. As sustainability considerations increasingly shape material selection across industries, these biodegradable surfactant architectures are poised to gain further importance, representing a significant opportunity to advance surfactant technology while aligning with global sustainability objectives and regulatory trends toward more environmentally responsible chemical solutions.

REFERENCES

[1] Kumar, N., & Tyagi, R. (2014). Industrial applications of dimeric surfactants: a review. *Journal of Dispersion Science and Technology, 35*, 205-214.

[2] Menger, F.M., & Keiper, J.S. (2000). Gemini Surfactants. *Angewandte Chemie International Edition, 39*, 1906-1920.

[3] Zana, R. (2002). Dimeric and oligomeric surfactants. Behavior at interfaces and in aqueous solution: a review. *Advances in Colloid and Interface Science, 97*, 205-253.

[4] Alami, E., & Holmberg, K. (2003). Heterogemini surfactants: synthesis and interfacial properties. *Advances in Colloid and Interface Science, 100-102*, 13-46.

[5] Tehrani-Bagha, A.R., & Holmberg, K. (2013). Cationic ester-containing gemini surfactants: Physical-chemical properties. *Langmuir, 29*(47), 14257-14267.

[6] Tehrani-Bagha, A.R., Oskarsson, H., van Ginkel, C.G., & Holmberg, K. (2007). Cationic ester-containing gemini surfactants: Chemical hydrolysis and biodegradation. *Journal of Colloid and Interface Science, 312*(2), 444-452.

[7] Kowalczyk, I., Szulc, A., Koziróg, A., Komasa, A., & Brycki, B. (2025). Surface and Antimicrobial Properties of Ester-Based Gemini Surfactants. *Molecules, 30*(12), 2648.

[8] Wang, J., Ai, H., Geng, T., Ju, H., Li, J., Wang, Z., Zhang, L., & Jiang, Y. (2024). Synthesis of Newly Ester Type Gemini Cationic Surfactants: Surface Properties, Fabric Softness and Antibacterial Properties. *ChemistrySelect, 9*(35), e202402863.

[9] Dahal, H., Roy, S., Dey, J., & Dasgupta, S.B. (2024). Impact of the Hydrocarbon Chain Length of Biodegradable Ester-Bonded Cationic Gemini Surfactants on Self-Assembly, In Vitro Gene Transfection, Cytotoxicity, and Antimicrobial Activity. *Langmuir, 40*(5), 2543-2556.

[10] Zhang, Q., Gao, Z., Xu, F., & Tai, S. (2021). Novel cationic Gemini ester surfactant as an efficient and eco-friendly corrosion inhibitor for carbon steel in HCl solution. *Journal of Molecular Liquids, 336*, 116337.

[11] Panda, M., Fatma, N., Beg, M., & Kabir-ud-Din. (2016). Ester-bonded cationic gemini surfactants: Assessment of their cytotoxicity and antimicrobial activity. *Journal of Molecular Liquids, 222*, 390-394.

[12] Bombelli, C., Stringaro, A., Borocci, S., Bozzuto, G., Colone, M., Giansanti, L., Sgambato, R., Toccaceli, L., Mancini, G., & Molinari, A. (2010). Efficiency of liposomes in the delivery of a photosensitizer controlled by the stereochemistry of a gemini surfactant component. *Molecular Pharmaceutics, 7*(1), 130-137.

[13] Zhang, Q., Gao, Z., Xu, F., & Tai, S. (2020). Synthesis and characterization of gemini ester surfactant and its application in efficient fabric softening. *Journal of Molecular Liquids, 299*, 112164.

[14] Pisárčik, M., Polakovičová, M., Markuliak, M., Lukáč, M., & Devínsky, F. (2019). Self-assembly properties of cationic gemini surfactants with biodegradable groups in the spacer. *Molecules*, *24*(8), 1481. https://doi.org/10.3390/molecules24081481 Cited by: 57

[15] Akram, M., Osama, M., Hashmi, M. A., & Kabir-ud-Din. (2023). Molecular interaction of di-ester bonded cationic Gemini surfactants with pepsin: in vitro and in silico perspectives. *Journal of Biomolecular Structure and Dynamics*, *41*(4), 12276–12291. https://doi.org/10.1080/07391102.2023.2168759 Cited by: 5

[16] Kowalczyk, I., Pakiet, M., Szulc, A., & Koziróg, A. (2020). Antimicrobial activity of gemini surfactants with azapolymethylene spacer. *Molecules*, *25*(18), 4054. https://doi.org/10.3390/molecules25184054 Cited by: 19

[17] Guerrero-Hernández, L., Meléndez-Ortiz, H. I., Cortez-Mazatan, G. Y., Vaillant-Sánchez, S., & Peralta-Rodríguez, R. D. (2022). Gemini and bicephalous surfactants: A review on their synthesis, micelle formation, and uses. *International Journal of Molecular Sciences*, *23*(3), 1798. https://doi.org/10.3390/ijms23031798 Cited by: 94

[18] Zhuang, W., Wang, X., Zhu, W., Zhang, Y., Sun, D., Zhang, R., & Wu, C. (2021). Imidazoline gemini surfactants as corrosion inhibitors for carbon steel X70 in NaCl solution. *ACS Omega*, *6*(9), 5653–5660. https://doi.org/10.1021/acsomega.0c06103 Cited by: 59

[19] Brycki, B., Szulc, A., Brycka, J., & Kowalczyk, I. (2023). Properties and applications of quaternary ammonium gemini surfactant 12-6-12: An overview. *Molecules*, *28*(17), 6336. https://doi.org/10.3390/molecules28176336 Cited by: 24

[20] Brycki, B. E., Kowalczyk, I. H., Szulc, A., Kaczerewska, O., & Pakiet, M. (2017). Multifunctional gemini surfactants: Structure, synthesis, properties and applications. *Application and Characterization of Surfactants*. https://doi.org/10.5772/intechopen.68755 Cited by: 114

[21] Mechken, K. A., Menouar, M., Talbi, Z., Saidi-Besbes, S., & Belkhodja, M. (2024). Self-assembly and antimicrobial activity of cationic gemini surfactants containing triazole moieties. *RSC Advances*, *14*(33), 19185–19196. https://doi.org/10.1039/d4ra02177k Cited by: 13

[22] Dahal, H., Roy, S., Dey, J., & Bose Dasgupta, S. (2024). Impact of the hydrocarbon chain length of biodegradable ester-bonded cationic gemini surfactants on self-assembly, in vitro gene transfection, cytotoxicity, and antimicrobial activity. *Langmuir*, *40*(5), 2242–2253. https://doi.org/10.1021/acs.langmuir.3c03290 Cited by: 17

[23] Liu, P., Li, X., Li, H., Liu, S., Wang, J., & Zhang, P. (2025). Application and synthesis of gemini surfactant in heavy oil development. *ACS Omega*. https://doi.org/10.1021/acsomega.4c11144 Cited by: 10

[24] Menger, F. M., Keiper, J. S., & Azov, V. (1999). Gemini surfactants with acetylenic spacers. *Langmuir*, *16*(4), 2062–2067. https://doi.org/10.1021/la9910576 Cited by: 309

[25] Kamboj, R., Singh, S., Bhadani, A., Kataria, H., & Kaur, G. (2012). Gemini imidazolium surfactants: Synthesis and their biophysiochemical study. *Langmuir, 28*(33), 11969–11978. https://doi.org/10.1021/la300920p Cited by: 152

[26] Katari, O., Kumar, K., Bhamble, S., & Jain, S. (2024). Gemini surfactants as next-generation drug carriers in cancer management. *Expert Opinion on Drug Delivery*, *21*(7), 1029–1051. https://doi.org/10.1080/17425247.2024.2384037 Cited by: 11

[27] Bombelli, C., Giansanti, L., Luciani, P., & Mancini, G. (2009). Gemini surfactant based carriers in gene and drug delivery. *Current Medicinal Chemistry*, *16*(2), 171–183. https://doi.org/10.2174/092986709787002808 Cited by: 152

[28] Bell, P. C., Bergsma, M., Dolbnya, I. P., Bras, W., Stuart, M. C. A., Rowan, A. E., Feiters, M. C., & Engberts, J. B. F. N. (2003). Transfection mediated by gemini surfactants: Engineered escape from the endosomal compartment. *Journal of the American Chemical Society*, *125*(6), 1551–1558. https://doi.org/10.1021/ja020707g Cited by: 294

[29] Jin, W., Al-Dulaymi, M., Badea, I., Leary, S. C., Rehman, J., & El-Aneed, A. (2019). Cellular uptake and distribution of gemini surfactant nanoparticles used as gene delivery agents. *The AAPS Journal*, *21*(5). https://doi.org/10.1208/s12248-019-0367-1 Cited by: 24

[30] Bhadani, A., Singh, S., & Kaur, G. (2010). Synthesis, Surface Activity, and Antimicrobial Activity of Ester-Functionalized Cationic Gemini Surfactants. Langmuir, 26(18), 14454–14460.