



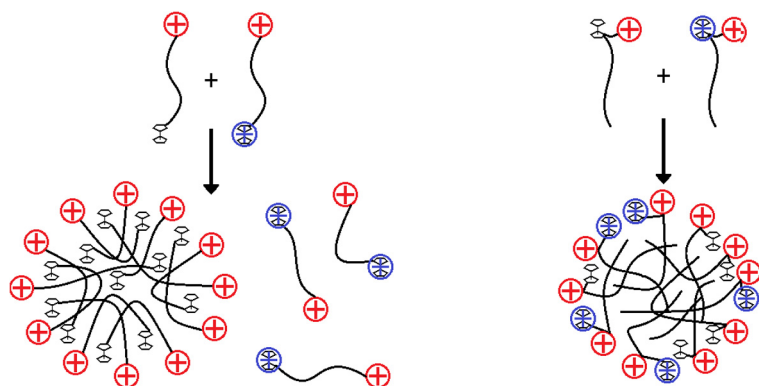
Redox-triggered mixing and demixing of surfactants within assemblies formed in solution and at surfaces



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GRAPHICAL ABSTRACT



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ABSTRACT

We report experiments that test the hypothesis that redox-triggered changes in the architectures of surfactants permit control of mixing of surfactants within assemblies. Specifically, we describe surface tension, light scattering, atomic force microscopy, and quartz crystal microbalance measurements that characterize the redox-dependent behaviors of cationic surfactants with a ferrocene group located either at the surfactant terminus (11-ferrocenylundecyl-trimethylammonium bromide; FTMA) or head (*N,N*-dimethylferrocenylmethyldecylammonium bromide; DMFA). In bulk solution, we find that reduced and oxidized FTMA do not mix within micellar assemblies but that reduced and oxidized DMFA do form mixed micelles. Because oxidized FTMA has the architecture of a bolaform surfactant whereas oxidized DMFA has a conventional surfactant architecture with a divalent head group, these results suggest that redox-triggered changes in molecular architecture permit control of the extent of mixing of surfactants in micellar assemblies in bulk solution. This conclusion receives further support from measurements performed with mixtures of dodecyltrimethylammonium bromide and FTMA, with FTMA in either reduced or oxidized states, and was found to extend to hemimicellar assemblies formed at hydrophobic solid surfaces but not to mixed monolayers formed at the surface of water. The latter is attributed to differences in the conformations of surfactants within monolayers and micellar assemblies. Overall, these results provide insight into the design of surfactant assemblies within which mixing can be controlled reversibly using redox processes.

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1. Introduction

Surfactant mixtures are widely used to tune the structure and properties of micellar assemblies formed by surfactants in bulk solution or at interfaces [1–12]. Surfactant mixtures can form assemblies with a range of morphologies, including vesicles (e.g., by binary mixtures of conventional cationic and anionic surfactants) [1–5], various lyotropic liquid crystalline phases [6,7], and giant worm-like micelles [8–10]. Surfactant mixtures can be exploited also to design systems that minimize the concentration of surfactant monomer present in bulk solution through favorable interactions between unlike surfactants in the mixture (i.e., minimizing the critical aggregation concentration (CAC)) [11]. Alternatively, the interactions between some surfactant mixtures can be sufficiently unfavorable that the surfactants form two coexisting micelle populations that do not mix [13–17]. For example, mixtures of conventional (hydrogenated) and fluorinated surfactants [13,14], ternary mixtures of cationic, anionic and nonionic surfactants [15], or mixtures of conventional and bolaform surfactants can form coexisting populations of micelles [16,17]. In this study, we report on the mixing of surfactants that contain the redox-active group ferrocene. Specifically, we test the hypothesis that redox-triggered changes in molecular architecture can be used to control the mixing of these surfactants within micellar assemblies formed in bulk solution and at interfaces.

The properties of switchable surfactants containing the ferrocene moiety have been explored in a number of past studies [18–21]. These past investigations revealed that oxidation of ferrocene to ferrocenium changes the properties of aqueous solutions of ferrocenyl surfactants in a manner that is strongly dependent on whether the ferrocene moiety is located near the head group or the terminus of the tail of the surfactants [22–24]. Herein we focus on the mixing behavior of two ferrocenyl surfactants (Fig. 1): 11-ferrocenylundecyl-trimethylammonium bromide (FTMA) and *N,N*-dimethylferrocenylmethyldecylammonium bromide (DMFA). Both surfactants possess cationic head groups (trimethylammonium), but the ferrocene of FTMA is located at the terminus of the aliphatic tail whereas the ferrocene of DMFA is located adjacent to the head group [25]. Upon oxidation of ferrocene to ferrocenium, FTMA is transformed to an ionic bolaform surfactant. Past measurements at the air-water interface of solutions of FTMA have shown that this transformation can lead to an increase in surface tension of as much as 23 mN/m [22]. In contrast, because the ferrocene group of DMFA is located adjacent to the trimethylammonium head group of the surfactant, oxidation of ferrocene in DMFA results in the formation of a surfactant with a conventional architecture and divalent head group. Past measurements performed with DMFA at the air-water interface have revealed the surface tensions of aqueous solutions of DMFA to increase by only 3 mN/m when DMFA is oxidized [23]. In this paper, we contrast the behavior of FTMA and DMFA in the context of understanding how redox-triggered changes in molecular architecture affect their tendency to form mixed assemblies in solution and at interfaces.

As context to the study reported herein, we note that prior studies have proposed mixing rules for conventional and bolaform surfactants within micellar assemblies. For example, the formation of mixed micelles in bulk solution by conventional and bolaform surfactants was investigated by Zana et al. [16,17], using mixtures of alkyltrimethylammonium bromide (C_n TAB) and alkane- α - ω -bis(trimethylammonium) bromide (TABC $_m$ TAB) amphiphiles. These studies concluded that, due to chain packing constraints, mixed micelles only form with C_n TAB and TABC $_m$ TAB when the values of m and n satisfy $2n-5 \approx m$. This conclusion was also supported by studies of the dynamics of micellization of bolaform surfactants [26–28], which conclude that bolaform surfactants adopt a looped

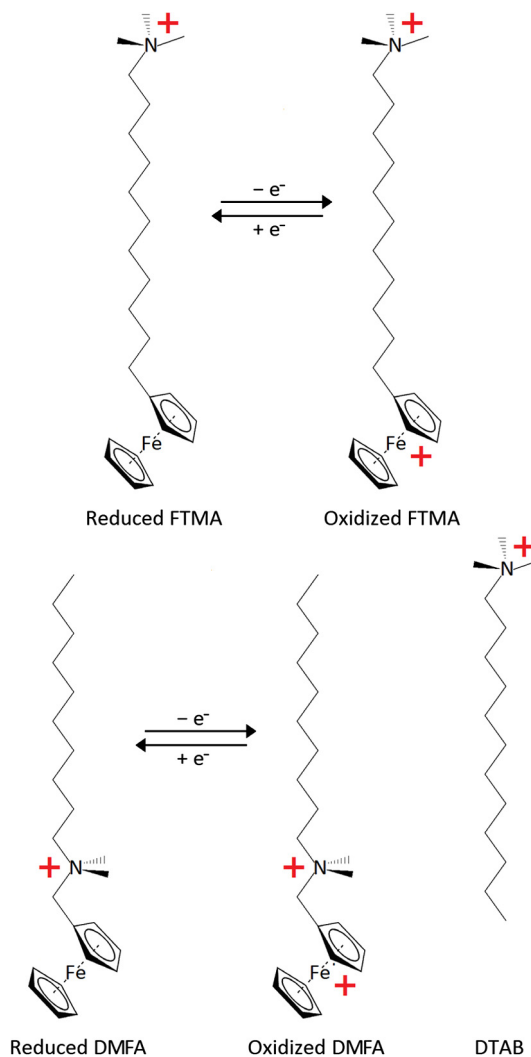


Fig. 1. Molecular structures of surfactants used in this study.

configuration in mixed micelles. In this paper, we explore the applicability of these mixing rules to ferrocenyl surfactants such as FTMA and DMFA. For example, if reduced FTMA behaves as a conventional surfactant ($n \approx 14$), the above-described mixing rules predict that reduced FTMA will not form mixed micelles with oxidized FTMA ($m = 11$). We note, however, that the applicability of these mixing rules to a ferrocenyl surfactant such as reduced FTMA was not obvious to us in advance of this study. For example, reduced FTMA differs from conventional surfactants such as DTAB because the ferrocene group is bulkier and more polarizable than a methyl group (terminus of a conventional surfactant) [29,30]. Both of these factors can impact chain-packing statistics.

Zana and coworkers proposed that the mixing rules outlined above arise from constraints on the packing of surfactant chains in micellar assemblies. Accordingly, the applicability of the mixing rules is predicted to depend on the morphology of the assembly, as the morphology of an assembly impacts chain packing statistics. In this paper, we explore mixing within surfactant assemblies formed in three environments: (i) in bulk solution, (ii) at the air/water interface, and (iii) at hydrophobic solid surfaces. Past studies have found that reduced FTMA forms micellar and hemimicellar assemblies in bulk solution [31,32] and at hydrophobic solid surfaces, respectively [33]. This behavior is similar to DTAB. In contrast, at the surface of water, reduced FTMA has been inferred to form a monolayer comprised of molecules in a looped configuration

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