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The role of competitive counterion adsorption on the electrolyte induced surface ordering in methyl ester sulfonate surfactants at the air-water interface

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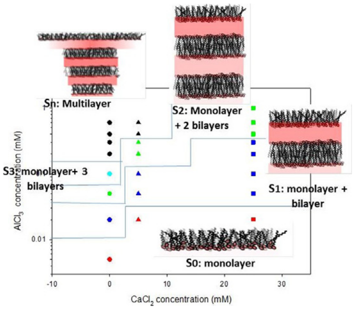
GRAPHICAL ABSTRACT



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ABSTRACT

The strong binding of Al^{3+} trivalent counterions to the anionic surfactants sodium polyethylene glycol monoalkyl ether sulfate and α-methyl ester sulfonate results in surface multilayer formation at the air-water interface. In contrast the divalent and monovalent counterions Ca^{2+} and Na^{+} result only in monolayer adsorption. Competitive counterion adsorption has been extensively studied in the context of surfactant precipitation and re-dissolution, but remains an important feature in understanding this surface ordering and how it can be manipulated.

The α-methyl ester sulfonate surfactants are a promising class of anionic surfactants which have much potential for improved performance in many applications, greater tolerance to extreme solvent conditions such as water hardness, biocompatibility and sustainable production. Hence in this study we have used neutron reflectivity to extend previous studies on the surface ordering of the α-methyl ester sulfonate surfactant, sodium tetradecanoic 2-sulfo 1-methyl ester, in the presence of electrolyte to investigate the role of binary mixtures of electrolytes, $AlCl_3/CaCl_2$, and $AlCl_3/MgCl_2$.

In the mixed electrolytes the evolution of the surface structure, from monolayer to multilayer with increasing $AlCl_3$ concentration, is observed. It is broadly similar to that reported for the addition of only $AlCl_3$. However with increasing $CaCl_2$ concentration the structural evolution is shifted progressively to higher $AlCl_3$ concentrations. Similar observations occur for the $AlCl_3/MgCl_2$ mixtures. However the presence of the $MgCl_2$ results in an additional phenomenon; the partial co-adsorption of a more compact

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lamellar structure which exists until the highest $AlCl_3$ concentrations. The results demonstrate the importance of the competitive adsorption of different counterions in driving and controlling the formation of surface multilayer structures with anionic surfactants. Furthermore it offers a facile route to the manipulation of these surface structures.

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1. Introduction

The structure and function of anionic surfactants, the major ingredient in many household formulations, have evolved to meet the increasing demands for improved performance [1,2]. The development of the alkyl benzene sulfonates, LAS, and alkyl ethoxy ether sulfate, SLES, surfactants has led to improved hard water characteristics, improved detergency, enhanced low temperature performance and improved biocompatibility and biodegradability [1,2]. The desire for further improvements and the developing need for production from sustainable sources has identified the α-methyl ester sulfonate, MES, anionic surfactants as an increasingly attractive option. The MES surfactants are synthesised from renewable palm oil sources and are increasingly seen as a viable alternative to the petroleum derived counterparts [3–8]. Hence the synthesis and purification of MES have been extensively studied [6,7,9], and their basic physicochemical properties and aspects of their surface adsorption and self-assembly have been studied [9–12]. Improved hard water tolerance, greater biodegradability and better cold water detergency have been demonstrated with the MES surfactants [13–17].

Recently Xu et al. [18] described a new laboratory synthesis of MES, based on the direct sulfonation of the methyl ester by SO_3 introduced from the vapour phase. This enabled the use of neutron reflectivity and surface tension to more definitively characterise the surface adsorption, using purer and better defined samples than previously possible. Subsequently Xu et al. [19,20] have demonstrated the ability of MES to form surface multilayer structures with the addition of $AlCl_3$, and characterise the nature of surface and micelle mixing in the eutectic mixture of the C_{16}- and C_{18}-MES surfactants. Surface multilayer formation has also been extensively demonstrated with LAS and SLES for the addition of multivalent counterions. The strong binding of Ca^{2+} to LAS promoted surface multilayer formation [21], and for SLES with the addition of Al^{3+} [22–24]. The strong counterion binding promotes the attractive interaction which results in the adsorption/-formation of a concentrated lamellar structure at the interface from the dilute solution. It occurs in these systems in which the nature of the anionic surfactant structure promotes improved solubility and a degree of tolerance to precipitation in the presence of multivalent counterions. Important aspects that have only been briefly explored are counterion specific effects, the role of hydration, and the competitive adsorption between counterions. Xu et al. [25] explored ion specific effects by exploring the impact of a range of different trivalent counterions on the surface ordering of SLES. The evolution in the surface ordering depended upon the nature of the counterion, its hydrated radius and its strength of binding.

The impact of monovalent electrolytes on anionic surfactant adsorption and self-assembly is well established, resulting in enhanced adsorption [26], reduction in critical micelle concentrations, cmc, [27] and in micellar growth [28]. The impact of multivalent counterions, divalent and trivalent ions such as Ca^{2+}, Mg^{2+} and Al^{3+}, is more significant. The strong binding and complexation leads rapidly to precipitation in many cases. This has been extensively studied in the context of water hardness and the phenomena of precipitation and re-dissolution have been extensively reported [29–32]. It was observed that the addition of NaCl increases the concentration of Ca^{2+} required to promote precipitation [32,33]; where the addition of NaCl reduces cmc values and the associated monomer concentrations. Furthermore this is aided by the competition between Na^+ and Ca^{2+} to bind to micelles and the surface. It was observed that Ca^{2+} binds preferentially, but that the binding decreases as the Na^+/Ca^{2+} ratio increases. Competitive adsorption of multivalent metal ions and their role in flocculation is important in the environmental removal of heavy metals, such as lead and zinc [31,34,35]. Haverd and Warr [36] discussed the role of hydrated ion radius and free energy of hydration on the selective binding of alkali metal ions, and showed an increasing binding strength in the order $Na^+ < K^+ < Rb^+ < Cs^+$. Alargova et al. [37–39] explored the impact of Al^{3+} binding on the micellar growth and surface tension of the alkyloxyethylene sulfate anionic surfactants. They showed how the strong binding or complexation of Al^{3+} results a significant micellar growth which is correlated with the parameter ξ, where $\xi = (c_t - cmc)/z_m c_m$, c_t is the surfactant concentration, z_m the counterion charge and cm the counterion concentration. For $\xi < 1$, where the Al^{3+} charge is in excess, micellar growth occurs. For $\xi > 1$, where the anion charge is now in excess, the micelles are small and globular. The binding of Al^{3+} ions more effectively reduces the inter-headgroup repulsion and preferred curvature, and drives the micellar growth. It was observed that the micellar growth is more significant for the trivalent than divalent ions. Significant differences between ions of the same valence were observed and were related to the ion size, hydration and polarizability. For example, the more strongly hydrated Mg^{2+} was less effective in promoting micellar growth than Ca^{2+}. A simple thermodynamic model, based on the competitive adsorption of Al^{3+} and Na^+ between the monolayer and micelle, provided a good description of the associated surface tension behaviour, and provided an estimate of the greater binding energy of Al^{3+} compared to Na^+.

Clearly selective and competitive counterion binding are important factors in determining the extent of precipitation and re-dissolution of anionic surfactants in the presence of electrolyte, micellar growth and interfacial tension. It has already been demonstrated that interesting surface properties exist for the MES surfactants in the presence of certain multivalent counterions, and the focus of this study is to explore the extent to which mixed electrolytes determine and control the extent and evolution of the surface ordering encountered in the presence of multivalent counterions. To do this neutron reflectivity measurements have been made at the air – water interface for the C_{14}-MES anionic surfactant in the presence of the mixed electrolytes, $AlCl_3/CaCl_2$, and $AlCl_3/MgCl_2$.

2. Experimental details

The neutron reflectivity, R(Q), was measured as a function of the wave vector transfer, Q, perpendicular to the surface (where Q is defined as $Q = (4\pi \sin\theta)/\lambda$, θ is the grazing angle of incidence, and λ the neutron wavelength). The measurements were made on the INTER reflectometer [40] at the ISIS pulsed neutron source in the UK; where the measurements were made at a fixed θ of 2.3° and a λ range of 1–15 Å to cover a Q range of ~0.03–0.3 $Å^{-1}$. The

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