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Adsorption and self-assembly in methyl ester sulfonate surfactants, their eutectic mixtures and the role of electrolyte

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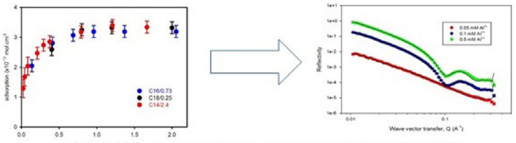
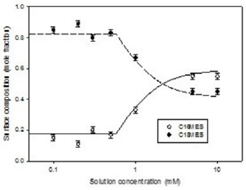
GRAPHICAL ABSTRACT



Transition from monolayer to multilayer adsorption with the addition of $AlCl_3$ for C16-MES



Eutectic C16-MES / C18-MES mixture rich in C16-MES in limit of high concentrations

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ABSTRACT

The α-methyl ester sulfonate, MES, anionic surfactants are a potentially important class of sustainable surfactants for a wide range of applications. The eutectic-like Kraft point minimum in the C_{16} and C_{18}-MES mixtures is an important feature of that potential. Understanding their individual adsorption properties and the surface mixing of the eutectic mixtures are key to their wider exploitation.

Neutron reflectivity has been used to investigate the adsorption at the air–water interface of the C_{16} and C_{18}-MES surfactants and the eutectic mixture of C_{16} and C_{18}-MES, in aqueous solution and in electrolyte. The micelle mixing of the eutectic mixture is investigated using small angle neutron scattering.

The adsorption isotherms for C_{14} to C_{18}-MES are found to scale with their critical micelle concentration value. The surface and micelle compositions of the C_{16} and C_{18}-MES eutectic mixture differ from the eutectic composition; with compositions in the limit of high concentrations richer in C_{16}-MES. The mixing properties are described by the pseudo phase approximation with a repulsive interaction between the two surfactants. The impact of the multivalent ions Al^{3+} on the adsorption at the air–water interface results in a transition from monolayer to multilayer adsorption.

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1. Introduction

The major surface active ingredients in most household detergents are anionic surfactants [1,2]. The increasing demand for improved formulations to provide better detergency, enhanced performance at lower temperatures and greater tolerance to hard water has resulted in the development of a range of new anionic surfactant structures and the optimisation of anionic/non-ionic surfactant mixtures [1–4]. The alkyl sulfates, especially for the longer alkyl chain lengths, precipitate readily due to the strong binding and complexation with the multivalent ions in hard water [5–7]; a common problem in limiting hard water tolerance. This can be partially mitigated by co-adsorption and self-assembly with a non-ionic co-surfactant [7]. The development of the alkyl benzene sulfonate, LAS, [2,8], and the alkyl ethyoxy ether sulfate, SLES, [9–11] surfactants has greatly improved hard water detergency properties. LAS has for example demonstrated both improved detergency properties and biodegradability [1,2].

To meet the sustainability agendas of the major detergent manufacturers there is a greater drive towards the use of surfactants prepared from renewable sustainable sources, instead of petroleum based materials [12], for greater biocompatibility and biodegradability, and for efficient operation at lower temperatures. The α-methyl ester sulfonates, MES, anionic surfactants, prepared from renewable palm-oil based sources, have been promoted as attractive alternatives to the petroleum based counterparts [13–17]. Improved hard water tolerance, greater biodegradability and better cold water detergency have been demonstrated [18–22]. Hence the synthesis and purification of MES has been extensively studied and reported [15,16,23], and the basic physicochemical properties, surface adsorption and self-assembly have been studied [23–26].

Xu et al. [27] have recently reported the adsorption properties of C_{14}-MES at the air-water interface; evaluated by surface tension, ST, and neutron reflectivity, NR, and using a synthetic route to provide better defined samples. This resulted in an adsorption isotherm and limiting adsorption amounts freer from the impact of impurities, but consistent with surface divalent counterion impurities. Xu et al. [28] have reported the impact of electrolyte on C_{14}-MES adsorption at the air-water interface. In NaCl, $CaCl_2$ and low concentrations of $AlCl_3$ slightly enhanced adsorption is observed, but at higher $AlCl_3$ concentrations surface multilayer formation occurs, ranging from a single bilayer beneath the initial monolayer at the surface to multiple bilayers. This is consistent with the more extensive studies of surface multilayer formation with the addition of multivalent counterions with LAS and SLES at low surfactant concentrations and outside the regime of precipitation [29–32]. This was demonstrated with the addition of Ca^{2+} for LAS and Al^{3+} for SLES, in which the evolution of the extent of the surface multilayers is controlled by surfactant, and counterion concentration, and the surfactant structure. The surface multilayer formation results in persistent wetting of hydrophobic solid surfaces, substantially enhanced adsorption at interfaces, and the opportunity to deliver and provide an effective surface reservoir for other surface ingredients, such as perfumes [33].

The MES surfactants can exist with a range of alkyl chain lengths, typically from C_{12} to C_{18}. Xu et al. [27,28] have focussed on the characterisation of the C_{14}-MES at the air-water interface. In this paper the focus is on the adsorption of the C_{16} and C_{18}-MES surfactants, and their eutectic mixture. One of the issues associated with the longer alkyl chain lengths is their relatively high Krafft temperatures, 28 and 40 °C for C_{16}-MES and C_{18}-MES respectively; which would suggest that the pure MES solutions would not be very effective detergents, especially at lower temperatures [18,34]. However the Krafft temperature of the C_{16}/C_{18}-MES mixture goes through a minimum at a temperature ~15 °C at a composition of 65/35 mol ratio C_{16}/C_{18}-MES [35], and this mixture exhibits good detergency properties. A minimum in the Krafft point was reported in other anionic surfactant mixtures, in sodium dodecyl sulfate/bivalent metal dodecyl sulfate mixtures [36], in the sodium and calcium salts of other anionic surfactants such as the linear alkyl benzene sulfonates [37], in different alkyl benzene sulfonate mixtures [38,39], and in myristic/palmitic acid mixtures [40]; and has been likened to a eutectic point.

However little is known about the adsorption and self-assembly of such eutectic mixtures. In light of their potential importance in a range of applications the focus of this paper is on the adsorption of the eutectic mixture of C_{16}/C_{18}-MES, the individual component surfactants, and the impact of electrolyte on the adsorption, using primarily neutron reflectivity, NR. Furthermore small angle neutron scattering, SANS, is used to characterise the self-assembly of the C_{16}/C_{18}-MES eutectic mixture to primarily determine the micelle composition. The NR and SANS data are analysed and evaluated using the Pseudo phase approximation, PPA, to model the eutectic mixing behaviour. The combination of the surface and micelle compositions provides a more rigorous examination of the thermodynamics of the mixing in such systems.

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 [41] 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 to 15 Å to cover a Q range of ~0.03–0.3 $Å^{-1}$. The reflectivity was converted to an absolute scale by normalisation to the incident beam intensity and the reflectivity of a D_2O surface. The measurements were mostly made in null reflecting water, nrw, (8.8 mol% D_2O/91.2 mol% H_2O, with a scattering length density, ρ, of 0.0, matched to air), and using deuterium labelled or a combination of deuterium labelled and unlabelled surfactants. The measurements were made in sealed Teflon troughs, with sample volumes ~25 mL. The NR measurements for C_{16}-MES and C_{18}-MES were made at 30 °C and 40 °C respectively, and at 25 °C for the eutectic 65/35 mol ratio C_{16}-/C_{18}-MES mixture. Each measurement took ~20 to 30 min; measured sequentially on a 7 position sample changer, and repeated ~2–3 times (for a total lapse time of up to 3 to 6 h) until the reflectivity profile reached a steady state.

In the kinematic approximation [42] the neutron reflectivity is related to the square of the Fourier Transform of the scattering length density distribution, ρ(z), normal to the surface; where $\rho(z) = \sum_i b_i n_i(z)$, $n_i(z)$ is the number density distribution of species i and b_i is the scattering length (the $\sum b$ values of the different components studied are listed in Table 1). As the neutron scattering lengths of H and D are quite different (-3.75×10^{-5} and 6.67 $\times 10^{-5}$ Å respectively) ρ(z) can be manipulated for organic species by D/H isotopic substitution. Hence deuterium labelling enables the reflectivity from different components at the interface to be isolated. This is the basis of the measurements here, as the

Table 1
$\sum b$ values for different components in study (used to evaluate adsorbed amounts).

Component	$\sum b$ ($\times 10^{-3}$ Å)
d-C_{16}MES	3.37
h-C_{16}MES	0.25
d-C_{18}MES	3.77
h-C_{18}MES	0.23
nrw	0.0