



Non-ionic surfactant interactions with hydrophobic nanoparticles: Impact on foam stability

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ABSTRACT

The interactive behaviour of particles and surfactant at an air–water interface has been investigated, with particular reference to the effect of the interactions on the stability of air–water foams. For a system combining octyl grafted silica particles and Triton X-100, the effects of both individual particles and surfactants with the interface have been considered, along with particle–surfactant interactions. Because of the complexity of the system, the change in aqueous foam stability was inferred from a number of key parameters: namely, the bulk adsorption of surfactant onto the particles, the combined influence on system interfacial tension, the role of surfactant on particle aggregation and the role of interfacial elasticity. It was found that adsorption on the particles occurred in a two-stage process, with an initial Langmuir monolayer being augmented as interactions between surfactant aromatic moieties produced a perpendicular arrangement with head-groups facing into the solution, rendering the particles completely hydrophilic at high concentrations. At low-to-moderate concentrations of surfactant, the foam stability was increased by ~20% in comparison to pure particle systems. The reasons for the improved stability were two-fold. Firstly, in low concentrations, surfactant caused bridging flocculation of the particles at the interface, producing enlarged sterically strong interfacial barriers. Secondly, at moderate concentrations, the surface elasticity was increased by the presence of the surfactant. The maximum interfacial elasticity was higher in composite systems, in comparison to pure surfactant solutions, probably a result of reduction in available interfacial area for adsorption of free surfactant to the air–water interface.

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1. Introduction

The combined behaviour of particles and surfactant molecules at interfaces is an increasingly important topic of research [1], with potential to benefit many industrial systems that contain mixtures of species, as encountered in food colloids [2] and flotation systems [3]. In isolation, particles have proved to be extremely good interfacial stabilisers, as found in both emulsion [4] and foam systems [5–7], but despite the importance of understanding their behaviour in composite systems, the mechanisms by which particles interact with other species at interfaces are still not completely understood [6]. This is brought into particular focus, in systems where mixtures of particles and surfactant have been found to give interfacial synergy [8–21] (in that the resulting emulsion or foam stability is greater than that with either species alone). The potential explana-

tions for this synergy differ markedly between systems [6], and are complicated by the problems of separating individual particle or surfactant interfacial activity from particle–surfactant interactions either in bulk solution or at the interface.

Most previous studies have attempted to simplify interactions by considering three main properties of the system: the effect of particle–surfactant mixtures on surface tension, the effect of surfactant adsorption on particle–interface contact angle, and the nature of any surfactant-induced particle flocculation [22]. When examining the effect of combined interactions on interfacial tension, some have attributed system synergy to a large drop in surface tension [12,14,21], arising from attractive interactions between interfacial particles and bulk surfactant, which augment the surfactant surface excess [14]. Others have focussed on the change in particle contact angle [11,17,19,23], correlating an observed contact angle increase owing to surfactant adsorption with the resultant increase in particle–interface detachment energy [11] (and hence increased interfacial steric strength). Lastly, partial flocculation has been considered as a major contributor to stability of foaming and emulsion systems, either in the form of bulk [8–10,14,19,22] or interfacial flocculation [13,15,16]. However, it is normally stipulated that while

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small scale flocculation leading to increased viscosity [9,20] and rheological [13,15,16] strength is advantageous, large scale flocculation may lead to foam and emulsion destruction [14], and generally low system stability [24].

The work presented here is aimed at providing a fuller understanding of these interfacial mechanisms and their relation to bulk foam stability for a system of hydrophobic particles and non-ionic surfactant. Unlike most previous research (e.g. [9,12,17,19]), the system studied here used particles pre-hydrophobised with a grafted octyl coating yielding a moderately high contact angle [25], which is not expected to be enhanced by surfactant adsorption. This allowed investigations to be focused on the two other important aspects of stability, namely the system surface tension and interfacial surfactant-induced flocculation of particles. A detailed adsorption mechanism for the surfactant was also introduced to help highlight bulk interactions, and resultant interfacial effects. Lastly, interfacial changes were monitored by measuring the surface elasticity. Elasticity has been found to be a key component for stabilisation in composite protein–surfactant systems [26,27], and Ravera and co-workers [28] found that particles may in fact lead to an enhancement of surface elasticity, providing an additional mechanism for system synergy.

2. Experimental

2.1. Materials

The silica used was purchased from FUSO chemicals Japan (SP-0.3B). The particle size was nominally 300 nm, but sizing by light scattering (Malvern Zetasizer ZS) indicated a mean hydrodynamic diameter closer to 260–270 nm (with low polydispersity, PDI ~ 0.05). The BET surface area was given by the supplier as $12 \text{ m}^2/\text{g}$. Triton X-100 (TX100) non-ionic surfactant (Ajax Finechem, given as 97–100%) and 1-octanol (Merck, >99%) were used as received. Acetone (Chem-Supply) was used as a mixing co-solvent for the esterified particles, and all water used was deionized (Millipore Milli-Q). Silicon wafers (Silicon Valley Microelectronics, U.S.A) with a thermal oxide layer of 115 nm were used for contact angle studies.

2.2. Methods

2.2.1. Esterification & dispersion of particle and wafer surfaces

To render the particles hydrophobic (and so cause them to be strong foam stabilisers, [6]), they were subjected to an esterification reaction with octanol [29], as previously detailed in our complementary paper [25]. In brief, dispersions of the particles (50 g) in around 120 g of octanol were mixed and boiled under reflux for a period of 7 h. The esterified particles were centrifuged and rinsed repeatedly in acetone and ethanol before drying. The same process was additionally used to esterify the oxide surface of the silicon wafers. To facilitate mixing and dispersion of the hydrophobic particles in water, acetone was initially used as a co-solvent, but was subsequently removed by boiling at 80°C and progressively replaced with water, again as previously described [25].

2.2.2. Estimation of contact angle changes with surfactant

Owing to the difficulty in directly measuring contact angles with such small particles [30], especially if modification in surfactant is taken into account, changes were simply correlated by measuring captive bubble contact angles beneath an equivalent planar oxidised silicon wafer [24,31]. Using an OCA20 (Dataphysics, Germany) direct contact angle device; the contact angles of bubbles on the esterified wafers (with approximate area $2 \times 1 \text{ cm}^2$) were measured in different concentrations of TX100. Wafers were first left to sit in the given surfactant solutions for a period of 3 hours, to ensure equilibration of surfactant adsorption.

2.2.3. Surface tension & adsorption studies

The surfactant–particle adsorption behaviour was measured using the well-established UV depletion method [32]. Particle dispersions (1 wt%) were mixed with various concentrations of surfactant for a period of 3 h. The dispersions were centrifuged at 2500 rpm for 2 h to ensure complete settling of particle beds. The supernatant was analysed (after being passed through a Gelman $0.2 \mu\text{m}$ filter) in a Shimadzu UV-800 spectrometer, and concentrations of TX100 estimated by comparing the intensity of the aromatic absorbance maximum (at 224 nm [33]) allowing calculation of the amount of surfactant adsorbed onto the particles. The static surface tension was measured with the du Nouy ring method [34] both with pure surfactant solutions and 1% particle dispersions in various concentrations of added surfactant. Initial surface tension values were hence recorded in terms of the surfactant added to the system, however, as the surfactant adsorption to the particles was quantified as above, the surface tension measurements could then be presented in terms of the equilibrium surfactant concentration.

2.2.4. Measurement of foam stability & particle partitioning

The static foam stability was simply measured in 100 mL measuring cylinders. Particle dispersions (4 wt%) were prepared with pure water in four concentrations of surfactant. Dispersion 1 contained 4 wt% particles in water, while Dispersions 2–5 contained 4 wt% particles in $6 \times 10^{-5} \text{ M}$, $3.2 \times 10^{-4} \text{ M}$, $8 \times 10^{-4} \text{ M}$ and $2 \times 10^{-3} \text{ M}$ TX100 solutions respectively. The foam heights were recorded (after vigorous shaking for 1 min) over a 24 h period. It is noted that equivalent addition of $2 \times 10^{-3} \text{ M}$ TX100 in a 4% particle dispersion corresponds approximately to the CMC in water.

The partitioning of particles between foam and liquid phases was monitored via turbidity. Here, the turbidity of 0.9 wt% particle and surfactant dispersions was measured before and after foaming (by vigorous shaking for 1 min) with a HATCH portable colorimeter. Using previously established standards [25], the drop in dispersion turbidity was equated with a loss of particles into the foam phase, and the change in relative concentration of particles partitioned in the foam was calculated as a function of increasing surfactant concentration.

2.2.5. Measurement of surface-pressure isotherms

The surface pressure behaviour of particle monolayers deposited on surfactant solutions was measured using a 500 mL NIMA (UK) Langmuir-Blodgett trough. Particles were first well dispersed in acetone, and an amount equivalent to 7 mg of particles was deposited drop-wise onto a trough sub-phase containing, either, pure water or various solutions of TX100. The trough was compressed at a rate of $50 \text{ cm}^2/\text{min}$, and the resulting pressure–area (Π – A) relationship recorded.

2.2.6. Interfacial elasticity studies

The interfacial dilational elasticity of surfactant solutions with and without addition of 0.5 wt% particles was measured so as to correlate potential changes in oscillatory rheology with foam stability observations. Elasticity was measured with a profile analysis tensiometer (PAT-1) from SINTERFACE (Germany) in a frequency range between 0.005 and 0.1 Hz. Droplets of the dispersions were firstly left to attain a steady surface tension (normally around 6000–10,000 s) whereupon the droplet surface area was oscillated sinusoidally, and corresponding changes in surface tension measured. The changes were analysed in terms of the dilational elasticity as a number of papers have detailed previously [28,35–38]. Corresponding theoretical elasticity limits were calculated by fitting the theoretical elasticity response against oscillation frequency (considering bulk surfactant concentration, c) according to LvT theory [39,40] as generalised by Garrett and Joos [41] (Eqs. (1) and (2)). Here, ε_0 (the theoretical elasticity limit) and ω_0 (character-

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