

CHAPTER I

INTRODUCTION

Surfactants are widely used in many industries, namely detergents and cleaners, cosmetics and other personal care products, paints and other coatings, pharmaceuticals, textiles and fibers, and mining (Myers, 2005). In general, surfactants accumulate at solid-liquid, liquid-liquid, and liquid-gas interfaces and tend to change the properties of those surfaces. The adsorption of surfactants at solid-liquid interface is a phenomenon of practical importance. Some relevant fields include detergency, surface treatment, protection of metal surfaces, and stabilization of solid dispersions (Clint, 1992). Surfactant adsorption at the solid-liquid interface has been studied using a variety of experimental instruments such as quartz crystal microbalance (Knag *et al.*, 2004; Karlsson *et al.*, 2008; Kou *et al.*, 2010), ellipsometry (Tiberg and Ederth, 2000; Denoyel, 2002; Poptoshev and Claesson, 2006), neutron reflection (Vacklin *et al.*, 2005; Yaseen *et al.*, 2005; Wang *et al.*, 2013), and atomic force microscopy (AFM) (Ducker and Grant, 1996; Wall and Zukoski, 1999; Velegol *et al.*, 2000).

This project focuses on the adsorption of surfactant mixtures. Mixed surfactant systems show some promising advantages over single surfactant ones (Esumi *et al.*, 1990; Huang *et al.*, 1996; Sakai *et al.*, 2003; Ivanova *et al.*, 2007; Fainerman *et al.*, 2011). In the case of surfactant mixtures where one surfactant is charged and the other is not, a synergistic effect on properties, e.g. a reduction the critical micelle concentration (CMC) (Zhang *et al.*, 2012), is typically observed. This synergistic effect is due to non-ideal mixing effects in micellar aggregates resulting from the more alternating character of individual surfactant placement as opposed to random placement expected for ideal mixing. Since most surfactant solution characteristics scale with the CMC, less surfactant is typically necessary for a given application when mixtures of this type are used.

The quartz crystal microbalance with dissipation (QCM-D) provides *in situ* measurement of both equilibrium and kinetics of adsorption from liquid systems onto solid surfaces. QCM-D is characterized by high sensitivity and real time data acquisition (Caruso *et al.*, 1995). Studies using QCM on mixed surfactant adsorption

have been detailed in the literature. Liu and Kim (2009) studied the adsorption of the anionic surfactant sodium lauryl sulfate (SLS) and the amphoteric surfactant cocamidopropyl betaine (CAPB), and a mixture of the two, on polyethersulfone-coated quartz crystals. Surfactant adsorption was studied at the respective CMCs. When alone, both SLS and CAPB formed rigidly bound films. The mixed surfactants yield a film of mass adsorbed in between that of the individual surfactants and the adsorption of surfactant molecules was likely strong since desorption did not occur after injection of washing solution. Sakai *et al.* (2010) studied the adsorption of mixtures of cationic surfactants ((dodecyltrimethylammonium bromide (DTAB) and hexadecyltrimethylammonium bromide (HTAB)) and the nonionic octaethylene glycol monododecyl ether ($C_{12}E_8$) with the gemini surfactant 1,2-bis(dodecyltrimethylammonio)ethane dibromide (12-2-12). Adsorption isotherms for the mixed surfactant systems were shifted to lower surfactant concentrations, i.e. more adsorption at less surfactant concentration, when the latter was normalized to the CMC. The mixed adsorbed layer became more rigid when compared with those obtained using single surfactant systems.

Other studies of surfactant mixtures not involving QCM-D have been detailed in the literature. Muherei *et al.* (2009) studied adsorption of mixture of the anionic surfactant sodium dodecyl sulfate (SDS) and the nonionic surfactant polyethylene glycol tert-octylphenyl ether (TX-100) on shale and sandstone. For the single surfactant systems the amount adsorbed of TX-100 was higher than that of SDS on both surfaces, while the adsorption of TX-100 was reduced in the presence of SDS, which was attributed to the lower CMC (and hence a lower monomer concentration) of the mixed system. Overall, in the case with one charged surfactant and the other uncharged where one surfactant adsorbs and the other does not, if the adsorbing surfactant is adsorbed followed by rinsing with a solution of the nonadsorbing surfactant, then the adsorption on the surface decreases because the adsorbed surfactant is pulled into micelles in solution (Kayes, 1976; Bolze *et al.*, 1996; Thibaut *et al.*, 2000). However, a report has been presented where cooperative adsorption can occur leading to a higher amount adsorbed in total (Colombié *et al.*, 2000).

The surfactants used for this study are representative of those used in mixed surfactant systems used as dispersants to clean up oil spills in water, via the formation of small oil droplets that can be degraded by bacteria (Lessard and DeMarco, 2000). COREXIT 9500, an oil dispersant produced by NALCO, was used during the BP Deepwater Horizon spill in the Gulf of Mexico in 2010 (Campo *et al.*, 2013). The two main surfactants used in COREXIT 9500 are dioctyl sodium sulfosuccinate (AOT), and polyoxyethylene (20) sorbitan monooleate (Tween 80) (Place *et al.*, 2010). Li *et al.* (1998) and Li *et al.* (2001) found that AOT adsorbed on hydrophobic silica with a strong interaction of intermolecular AOT hydrocarbon chains, and AOT was also found to adsorb on hydrophilic silica as a lamellar phase at concentrations higher than its CMC. Tween 20 is used in this project instead of Tween 80. Tween 20 and Tween 80 have the same hydrophilic headgroup but different hydrophobic tails. Tween 20 and Tween 80 are derived from monolauric acid and monooleic acid, respectively. Seo *et al.* (2011) studied the adsorption of Tween 20 on lignocellulose. Tween 20 formed a monolayer on the surface because of hydrogen bonding between carboxyl and hydroxyl groups of lignin and ethylene oxygens of Tween 20, and because of hydrophobic interactions between hydrophobic part of surface and Tween 20 tails. To the knowledge, no studies have examined adsorption from a mixture of AOT and polyoxyethylene (20) sorbitan monolaurate (Tween 20) surfactants.

In the present work, AOT and Tween 20 are studied with respect to their adsorption on gold, both individually and as mixtures using QCM-D. The effect of sequential addition of the two surfactants was investigated and compared with the results for the single surfactant systems to better quantify competitive adsorption.