CHAPTER VI

ADSORPTION OF SURFACTANTS ON CARBON BLACK AND PAPER FIBER IN THE PRESENCE OF CALCIUM IONS

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6.1 Abstract

Deinking is an important step in recycling of waste paper and flotation is commonly used in this process. By studying the interaction between added surfactant and the solid surfaces of ink pigment and pulp, the fundamental mechanism of flotation deinking can be better understood. In this work, the adsorption of two anionic surfactants (sodium dodecyl sulfate, SDS and sodium octanoate, C8) on both a model ink (hydrophobic carbon black) and a model fiber (hydrophilic office paper) was studied. The effect of pH on the SDS adsorption and the co-adsorption of calcium and surfactant on both surfaces also were investigated. The SDS adsorbs on carbon black as a tail-down monolayer (hemimicelle) while on paper fiber as a head-down, head-out bilayer (admicelle). The C8 forms admicelles on both carbon black and paper fiber indicating the stronger interaction of the carboxylate group with the carbon surface than the surfactant sulfate group, causing the C8 to adsorb at higher levels than SDS on carbon black. This helps explain why soaps are used widely as the surfactant in flotation deinking operations. Calcium causes surfactant adsorption to increase on carbon black as it adsorbs between negatively charge surface sites and the anionic head group of the surfactant (bridging) especially at low surfactant levels while not enhancing surfactant adsorption on paper fiber, explaining its activation effect in deinking processes. At high surfactant loadings, increasing surfactant concentration can cause calcium adsorption to decrease (calcium exclusion effect), probably due to covering up of negative adsorption sites on the surface.

Keywords: Adsorption isotherm/Surfactant/Carbon black/Paper fiber/Calcium ion

6.2 Introduction

Surfactant adsorption at solid surfaces is crucial in many important processes, such as froth flotation, enhanced oil recovery, detergency and wetting [1]. In general, the adsorption of surfactant at a solid-aqueous interface is governed by several factors, including the nature of the adsorbing surface, the structure of the adsorbed surfactants, properties of the bulk fluid phase, and temperature [2]. For hydrophilic surfaces, surfactants self-assemble in the form of quasi two-dimensional admicelles similar to the aggregate structure observed in bulk aqueous solutions, i.e. spherical or cylindrical micelles or bilayer structures [2]. For hydrophobic surfaces, surfactant aggregates tend to form either monolayer or hemimicellar structure, i.e. hemispherical or hemicylindrical, with the charged or polar group oriented towards the aqueous solution [3]. The geometric structure of admicelles or hemicelles depends on the critical packing factor of the surfactant [4].

The addition of calcium enhances ink removal in flotation-recycling paper processes [5]. In actual flotation processes, calcium and anionic surfactant generally form precipitate. Since adsorption is being probed in this study, conditions are used where the solubility constant (K_{sp}) of the calcium surfactant [6] is not exceeded. The two anionic surfactants, sodium octanoate (C8) and sodium dodecyl sulfate (SDS), were previously found by our group to yield disparities in the flotation efficiency which may correlate to the different molecular structure of dissimilar hydrophilic groups [6]. Costa and Rubio [7] studied the influence of calcium soap and surface-active substances by using calcium oleate, calcium chloride, sodium oleate, SDS, and sodium benzene dodecyl sulfate on the performance of deinking flotation. Their experimental results demonstrated that ink removal was more efficient when SDS was associated with calcium oleate than when these reagents were used separately. Beneventi *et al.* [8] described that a higher surfactant concentration caused a decrease in ink flotation efficiency since both surface tension and contact angle were decreased. The purpose of the work described in this paper is to quantify the adsorption of SDS and sodium octanoate and calcium on model printing ink and paper fibers and understand surfactant-calcium co-adsorption.

From a practical view, this research is aimed to determining if fatty carboxylate surfactants (soap) are so widely used in flotation deinking operations with calcium as an "activator" because of some specific interactions between the surfactant/calcium with ink and fiber, or if some other anionic surfactant could work as well. In our previous study [6, 9], we proved that adsorption on ink particles of soap synergized by calcium was responsible for good flotation, not precipitation of soap as had also been proposed. Also, detailed adsorption studies of surfactants on hydrophobic surfaces are far less common than studies on hydrophilic surfaces. Although SDS contains a 12-carbon hydrophobe, an 8-carbon hydrophobe was chosen rather than a 12-carbon hydrophobe for the carboxylate because of solubility considerations.

6.3 Experimental

6.3.1 Materials

Carbon black (type 400R) used in this study was manufactured by Cabot Corporation. The carbon black was thoroughly washed with distilled water several times in order to remove all ionic salts that may affect the adsorption isotherm results. After that, the washed carbon black was dried at 50°C in stagnant air for 5 d. Paper fiber was prepared by pulping common office papers (Xerox, A4 80 GSM) at 5% consistency for 20000 beats at 3000 rpm in a disintegration machine (pulper) to obtain a pulp slurry. The pulp slurry was then filtered and washed with distilled water several times over a number zero filter funnel (nominal maximum pore size of 160–250 μm) to remove all fillers and extraneous ions. The washing step was repeated until the concentration of calcium in the filtrate was less than 0.1 ppm as determined by an atomic absorption spectrophotometer (Varian, 300). The pulp fiber was then pressed to remove excess water and dried at 50°C for 2 d. The surfactants used in this adsorption study were sodium octanoate (C8, $C_8H_{15}O_2Na$) and sodium dodecyl sulfate (SDS, $C_{12}H_{25}SO_4Na$). The surfactants were purchased from Sigma Chemical Company (St. Louis, MO) with a purity of 99%. Calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$) obtained from Fluka Co., Ltd. (Switzerland) was reagent grade and dried at 90°C for 12 h prior to use due to its hygroscopic nature.

6.3.2 Adsorption Experiments

Adsorption experiments were conducted at 30°C using the solution depletion method in a series of vials with screw caps. A quantity of 2.5 g of carbon black was added into 20 mL of a surfactant solution with different concentrations of C8 or SDS with various calcium ion concentrations, while 1.0 g of the prepared paper fiber was mixed with 25 mL of a surfactant solution. The solution pH was adjusted at 7 or 9 by addition of NaOH. After mixing vigorously by hand, the vials were then allowed to equilibrate for 4 d in a water bath shaker at 30°C. Solutions were then centrifuged at 2500 rpm for 15 min. The obtained supernatants were further filtered by using 0.22 μm cellulose acetate filter membranes to obtain the filtrates for the analysis of surfactant and calcium concentrations. The C8 or SDS concentrations were determined by a total organic carbon (TOC) analyzer (Shimadzu, 5000A) and a high performance liquid chromatograph (HPLC) (Hewlett Packard, 1050) with an electrical conductivity detector (Altech, 550), respectively. The calcium concentration was analyzed by an atomic absorption spectrophotometer (AAS) (Varian, 300). Surfactant and calcium adsorptions were calculated by the concentration difference between initial and equilibrium concentrations. The adsorption isotherms were then generated by plotting the adsorbed surfactant and calcium levels against their equilibrium concentration.

6.3.3 Other Measurements

BET surface areas of the carbon black and paper fiber were measured by a surface area analyzer (Quantachrome, Autosorb-1). The surface areas were calculated by measuring the amount of nitrogen gas adsorbed onto the solid surface at liquid nitrogen temperature (-196°C). The carbon black or paper fiber sample was out-gassed overnight before the nitrogen adsorption step.

Zeta potentials of both paper fiber and carbon black were determined by using a zeta meter (Zeta-meter, 3.0+). A mass of 1.5 mg of carbon black or 0.1 g of the paper fiber was added to 40 mL of distilled water. Then, the pH was adjusted by addition of NaOH or HCl solution. The samples were then placed in an electrophoresis cell maintained at 30°C. The two electrodes placed at the ends of the cell were connected to a power supply, which created an electric field, causing the charged colloids to move. Velocities of individual particles were tracked via a grid in the eyepiece of the microscope. The solution pH showing no net movement of particles indicates the point of zero charge (PZC).

The critical micelle concentration (CMC) of C8 and SDS were deduced from the discontinuity in slope of surface tension vs. log (surfactant concentration). Surfactant tensions were measured by the pendant drop method using a drop shape analysis instrument (Krüss, DSA10).

6.4 Results and Discussion

At 30°C and pH 9, the concentration-based (not activity-based) solubility product constant (Ksp) for dodecyl sulfate and divalent calcium cation is 4.37×10^{-10} M^3 and for C8 and divalent calcium cation is 4.08×10^{-7} M^3 [10]; the concentrations studied were below values necessary for precipitation. For the carbon black and paper fiber, PZCs are 2.3 and 3.6, respectively; i.e. both surfaces were negatively charged under the conditions used in this study to measure adsorption isotherms. The BET surface area of the carbon black is 96 m^2/g. The swelling of paper fiber in water makes BET measured surface areas of dry paper of 1.5 m^2/g [9] inapplicable. Riviello *et. al.* [9] deduced an area of 100 m^2/g for paper fiber prepared in the same manner from the same source according to calcium adsorption densities, so this is the surface area used to calculate surface coverages on paper fiber in this work. Budd and Herrington [11] reported the specific surface area of water-swollen cellulose fiber to be between 50 and 200 m^2/g. The CMC of SDS and of C8 are 8.3×10^3 µM and 3.5×10^5 µM, respectively, similar to literature values [12].

6.4.1 Surfactant Adsorption Isotherms

Figure 6.1 shows adsorption isotherms of SDS and C8 on both paper fiber and carbon black at pH 9 with no calcium ions. This pH was chosen since high pH is most commonly used for flotation processes in deinking of wastepaper [13, 14]. Figure 6.2 shows SDS adsorption on carbon black and paper fiber at pH levels of 9 and 7. An increase in equilibrium surfactant concentration increases the adsorption of both SDS and C8 on either the surface of carbon black or paper fiber. The maximum (plateau) adsorption (above the CMC) of SDS on the paper fiber is approximately 0.5 μmole/m^2 at pH 9 and 0.7 μmole/m^2 at pH 7, while that on the carbon black is 2 μmole/m^2. For C8 on both paper fiber and carbon black, the maximum adsorptions are approximately 7.8 and 7.1 μmole/m^2, respectively, which are much higher than those of SDS. The adsorption areas calculated for paper fiber assuming surfactant monolayers and the fully-occupied surfaces are 330 Å^2/SDS molecule and 21 Å^2/C8 molecule, which can be compared to the close-packed monolayer at the water/air interface of 51 Å^2/SDS molecule and 57 Å^2/C8 molecule calculated using the Gibbs adsorption equation applied to surface tension data [15]. This calculation suggests bilayer formation for C8 on both surfaces. The higher plateau adsorption of C8 than SDS at pH 9 on paper fiber could be due to a stronger affinity of the carboxylate group for the paper fiber (cellulose) surface compared to the sulfate group even in the absence of calcium. Another possibility is that since SDS has 12 carbons vs. 8 for C8, any surface roughness differences should have a larger effect for this longer hydrophobe because of the greater importance of hydrophobic interactions for the longer carbon chain [16].

From Figure 6.2, for SDS on carbon black, there is essentially no difference in adsorption as a function of pH while lower pH enhances adsorption for paper fiber. The surface of the paper fiber has a zeta potential (approximates the electrical potential at the edge of the Stern layer next to the surface) of -28 mV at pH 9 [9] and zero at pH of 3.6 (PZC). The analogous values for carbon black are -29 mV and a pH of 2.3. For highly heterogeneous surfaces like paper fiber or carbon black, there are still positively charged sites on the surface when the zeta potential is negative; in this case negative charges exceed positive charges. As pH decreases, the surface becomes less negatively charged, so adsorption of the anionic sulfate groups will be enhanced. Lack of effect of pH on SDS adsorption on carbon black indicates that the head groups are not adsorbing on the surface and supports tail-down or hemimicelle formation. On paper fiber, pH effects indicate that head groups are adsorbed to the surface in the first layer with a second adsorbed surfactant layer formed with head groups facing the solution to form the admicelle. The plateau adsorption level is about 20% higher at pH 7 than at pH 9. So even though the amount of SDS adsorbed on paper fiber is less than that on carbon black, on the former a surfactant bilayer is formed while on the latter a surfactant monolayer is formed.

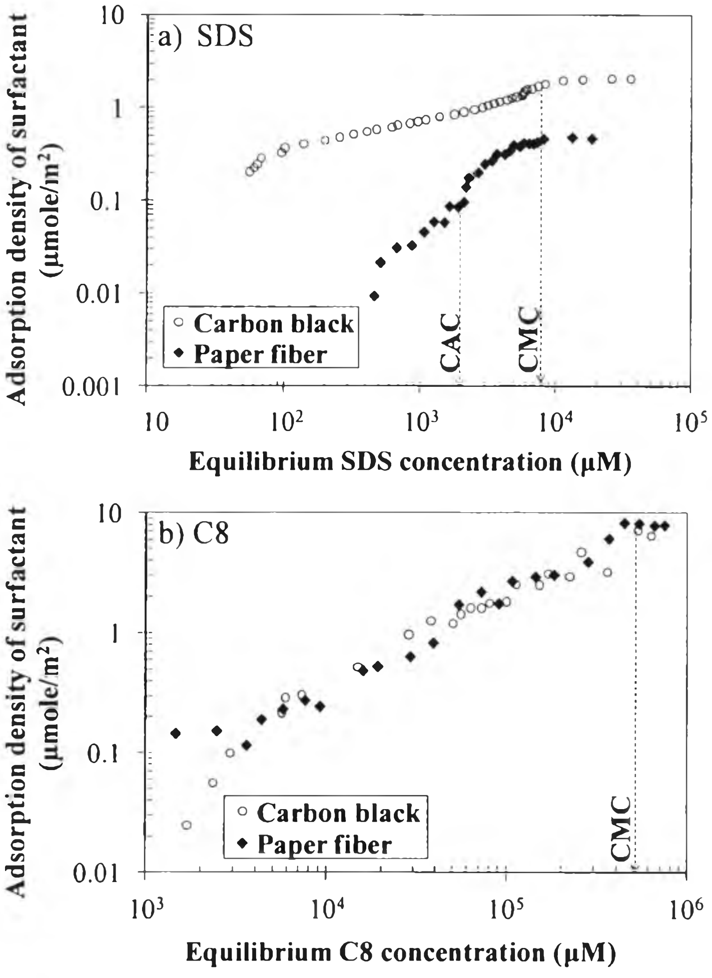


Figure 6.1 Adsorption isotherms of SDS and C8 on carbon black and paper fiber in the absence of calcium ions at pH 9.

C8 is a weak acid with a pKa of 4.89 [17]. So, at pH of 7, the surfactant will be a mixture of the anionic species and the protonated nonionic species, while at pH 9, C8 is almost all anionic. Due to the ambiguity of interpreting results for mixed surfactants, adsorption isotherms were not measured for C8 at pH 7.

Only the adsorption of SDS on the paper fiber shows an abrupt change in slope which is attributed to cooperative adsorption or 2D-phase transitions to bilayered aggregates called admicelles and this concentration is termed the CAC (critical admicellar concentration) [18]; the CAC is about 2x10^3 μM in Figure 6.1. The CAC is often around 10 to 20% of the CMC on metal oxide of mineral surface [15, 18], so this is quite reasonable. The adsorption isotherm below the CAC is known as Region I or the Henry's Law Region where generally adsorption is proportional to concentration (slope of unity on log-log plot as in Figure 6.1). At the CAC, lateral attraction between the surfactant tail groups (also called hydrophobic bonding) induces formation of layered admicelle aggregates on the most energetic patch on the surface. As concentration increases in this Region II of the adsorption isotherm, successively less energetic surface patches fill up. A decrease in slope in region II at higher concentrations indicates the emergence of Region III; this decrease attributed to repulsion between anionic head groups in the admicelles. Above the CMC, adsorption is approximately constant because the chemical potential of the surfactant is nearly constant and this region is known as the Plateau Adsorption Region or Region IV. The slope of the adsorption isotherm in Region II increases with surface homogeneity (e.g. alumina has higher slope than kaolinite). The modest slope in Region II in Figure 6.2b indicates that paper fiber is fairly heterogeneous in energy distribution on the surface.

Surfactant adsorption on hydrophobic surfaces has received much less attention than on hydrophilic surfaces, so probing these regions of anticooperative forces deserves attention. From Figure 6.1, for SDS adsorption on hydrophobic carbon black, a traditional Region I to II transition typical of that seen on hydrophilic surfaces is not observed. Surfactant tail groups presumably have attractive Van der Waal interactions with the carbon black surface at low concentrations. The slope of SDS adsorption isotherm on carbon is nearly constant at about 0.3. So, instead of cooperative attraction between surfactant molecules as hemimicelles form, there are repulsive forces causing a slope to be less than unity even at relatively low adsorption levels. The environment in the surface aggregate is no more favorable than that of a horizontally adsorbed molecule at low adsorption densities (no significant surfactant-surfactant interactions). There is a hint of a Region I in Figure 6.2a with a slope of 1 for SDS on carbon black, but it is difficult to have high precision under these conditions; a Henry's Law Region with a slope of unity would probably be attained at low enough concentrations below those experimentally accessible in this work. In the case of C8 adsorption on both carbon black and paper fiber (Figure 6.1b), the slope of the isotherms are close to one. The C8 does not exhibit a Region I to II transition on paper fiber unlike SDS on paper fiber probably due to lower lateral attraction between surfactant tail groups since there are 8 carbons vs. 12 carbons for SDS.

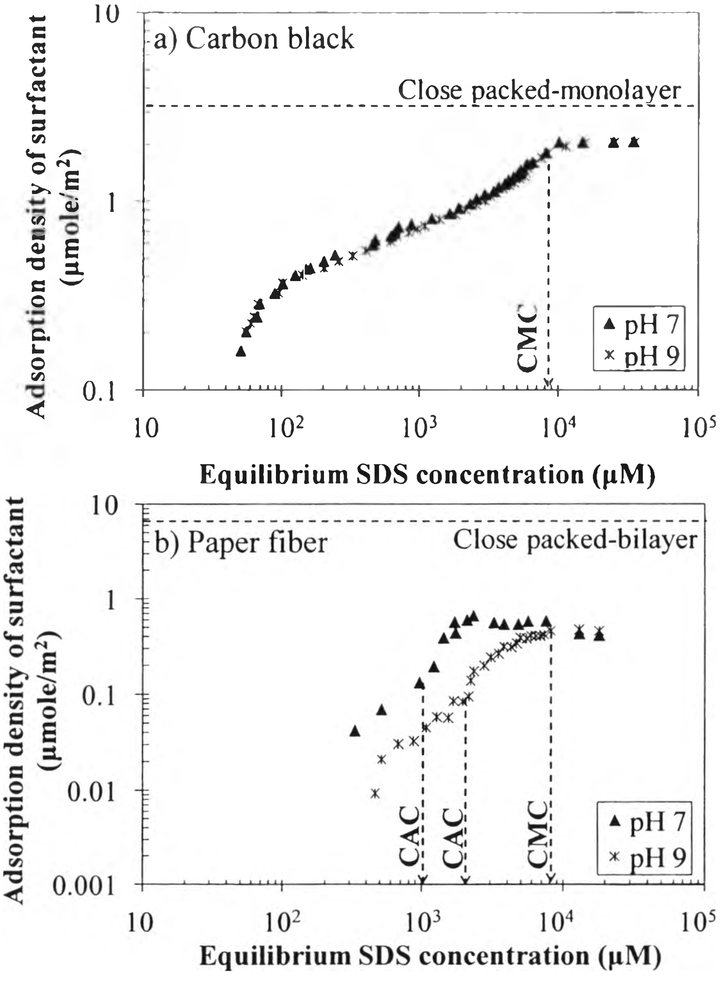


Figure 6.2 SDS adsorption on carbon black and paper fiber in the absence of calcium ions at pH of 7 and 9.

In the absence of calcium, from plateau adsorption densities and pH effects at high enough surfactant concentrations for surface aggregates to form, we conclude that C8 adsorbs as a bilayer on both carbon black and paper fiber as does SDS on paper fiber. However, SDS adsorbs as a tail-down monolayer on carbon black.

6.4.2 Calcium Adsorption Isotherms

Adsorption isotherms of calcium ions on carbon black and paper fiber are shown in Figure 6.3. The calcium ions are attracted by the negatively charged sites on the surfaces. For the carbon black surface, the negatively charged sites may result from surface oxidation, while, for the paper fiber, the negative charges on the surface are likely from the ionization of carboxylates and hydroxyls of the cellulosic structure [6]. Calcium adsorption on paper fiber approximately obeys Henry's Law (slope of unity on log-log plot) while on carbon black the slope is less than unity. This indicates that charge-charge repulsion between adsorbed calcium cations leads to anticooperative adsorption on carbon black. Positive sites may be spatially correlated to a higher extent on carbon black than on paper fiber. Based on a close-packed density of 3.92 Å^2/molecule [19] for calcium, even the highest adsorption levels in Figure 6.3 correspond only to a few % of maximum monolayer coverage.

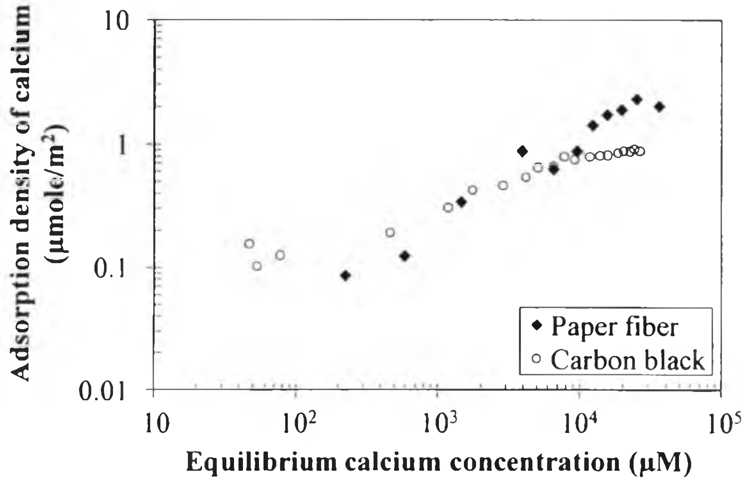
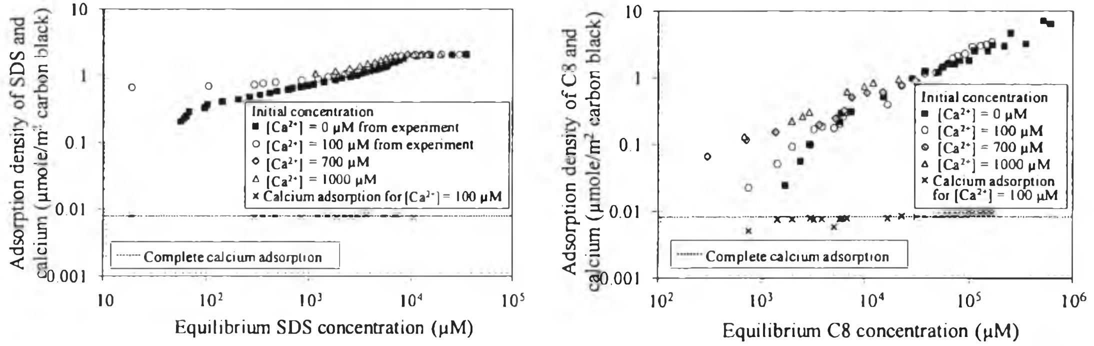


Figure 6.3 Calcium adsorption on carbon black and paper fiber in the absence of surfactant at pH 9.

6.4.3 Co-adsorption of Surfactant and Calcium

Figure 6.4 shows adsorption isotherms of SDS and C8 on carbon black at various initial calcium ion concentrations. Also shown is calcium adsorption for an initial calcium concentration of 100 μM (Figures 6.4a - 6.4c) or 1000 μM (Figure 6.4d). As calcium ion concentration increases, the adsorption of either SDS or C8 on the carbon black surface increases. The surfactant adsorption increase is more pronounced at low surfactant concentrations and for C8 as opposed to SDS at these low concentrations. The slope of the adsorption isotherm decreases with increasing calcium concentration, particularly for C8. The horizontal lines in Figures 6.4a and 6.4b on carbon black correspond to quantitative (complete) adsorption of all the calcium added when the calcium added was 100 μM. To explain adsorption at low surfactant and low calcium concentrations on carbon black, we hypothesize a two-state adsorption model for SDS (monolayer adsorption in absence of calcium) and for C8 (bilayer adsorption in absence of calcium). Calcium adsorbs on negative sites on the surface on which the negatively charged head groups would not adsorb due to charge repulsion. The calcium acts like a bridge between the surface and negatively charged surfactant head groups. Two monovalent anionic head groups adsorb onto the adsorbed calcium and presumably a second layer of surfactant adsorbs through hydrophobic bonding onto these bridged surfactant molecules. At these low surfactant adsorption densities on the surface, it is assumed that this bridging adsorption mechanism operates independently from either the monolayer (carbon black) or bilayer (paper fiber) adsorption and the calculated adsorption curves shown in Figures 6.4a and 6.4b assume additivity of these two contributions to surfactant adsorption and describe the observed results very well for C8 and SDS, except at the lowest initial calcium concentration (100 μM) for SDS. Four monovalent surfactant molecules are assumed to adsorb for every co-adsorbed divalent calcium molecule. From Figures 6.4a and 6.4c, the SDS concentration corresponding to the Region III to Region IV transition decreases at the highest calcium concentration used due to decreasing CMC with increasing divalent counterion (calcium) solution concentration.

a) SDS on carbon black b) C8 on carbon black



c) SDS on paper fiber d) C8 on paper fiber

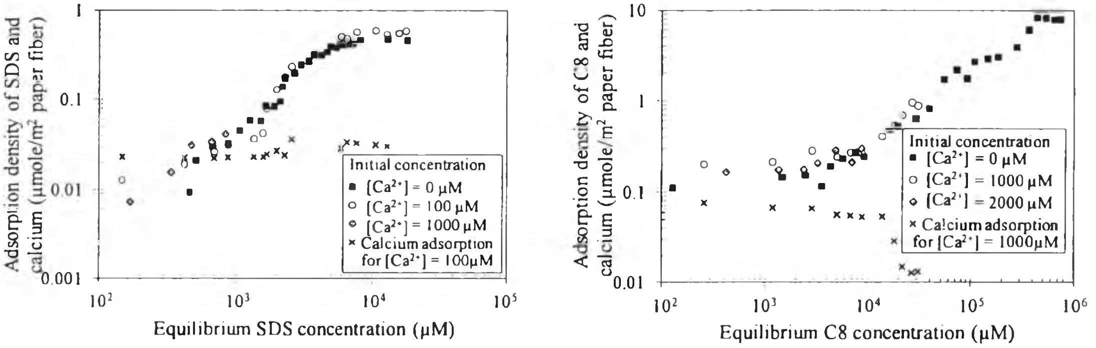
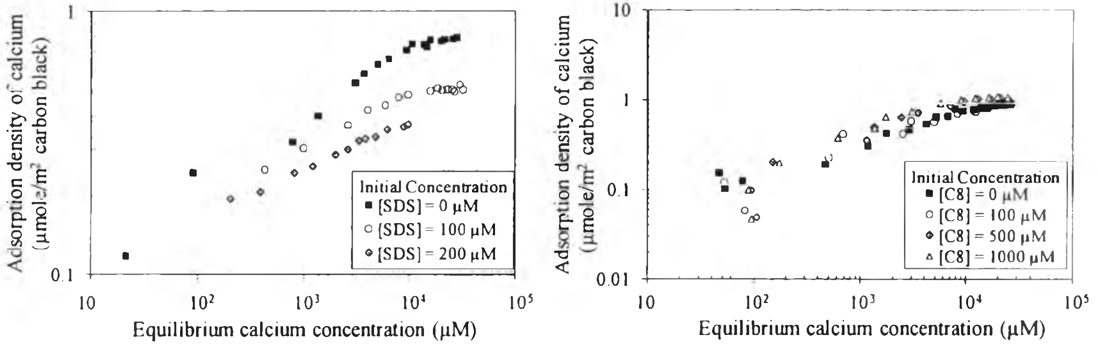
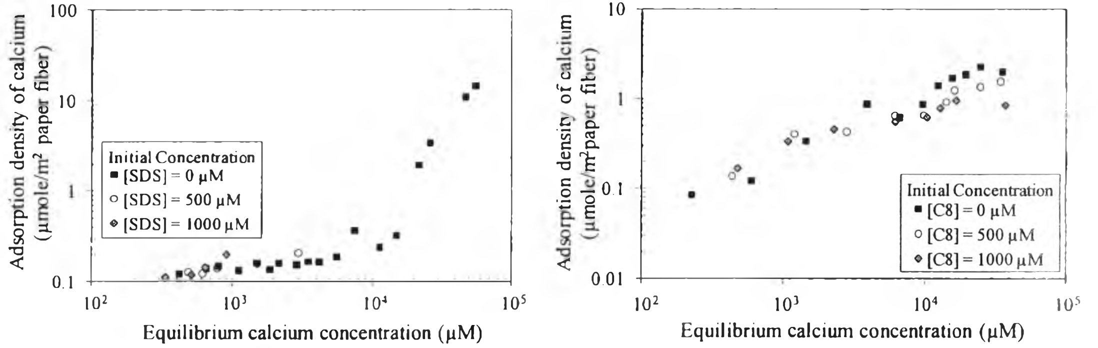


Figure 6.4 SDS and C8 adsorption isotherms on carbon black and paper fiber at various initial calcium concentrations and calcium adsorption isotherm on carbon black and paper fiber (initial calcium concentration 100 µM) at pH 9.

On paper fiber, the calcium is almost quantitatively adsorbed for initial calcium concentrations of 100 µM with SDS, but less is adsorbed in the presence of C8 as seen in Figures 6.4c and 6.4d. For SDS, the effect of calcium on surfactant adsorption on paper fiber is so small that trends are not apparent. As surfactant concentration increases, there is a critical concentration at which calcium adsorption decreases dramatically for C8, but not for SDS on paper fiber. This calcium adsorption trend is not observed for either surfactant on carbon black. This same unexpected "calcium exclusion" effect was observed by Riviello *et al.* [9] only on C8/paper fiber as in this work. One incentive driving the work was to confirm and probe this calcium exclusion effect in more detail.


a) SDS on carbon black

b) C8 on carbon black


c) SDS on paper fiber

d) C8 on paper fiber

Figure 6.5 Effect of surfactant concentration on calcium adsorption on carbon black and paper fiber at pH 9.

Figure 6.5 shows calcium adsorption with low constant surfactant concentrations on both carbon black and paper fiber. For SDS on carbon black, increased surfactant concentration causes a reduction in calcium adsorption, while the opposite effect of surfactant concentration is observed for C8 on carbon black, at least at higher calcium concentrations. From Figure 6.5c, SDS has little effect on calcium adsorption on paper fiber, consistent with the lack of effect of calcium on surfactant adsorption in Figure 6.4c. From Figure 6.5d, increasing C8 concentration causes calcium adsorption to decrease, consistent with the calcium exclusion effect seen in Figure 6.4d at lower calcium concentrations.

A summary of effects of calcium and surfactant on each other's adsorption is shown in Table 6.1. As a framework to understand the complex interactions observed, there are two contradictory effects which are present. The calcium bridging causes both SDS and C8 adsorption to increase with increasing calcium concentration at low calcium concentrations (Figure 6.4a and 6.4b). From Figure 6.5b on carbon black, increasing C8 concentration causes a small increase in calcium adsorption. At high surfactant concentrations, the surface patches are increasingly filled, covering up potential calcium adsorption sites, causing a reduction of calcium adsorption for SDS on carbon (Figure 6.5a) or C8 on paper fiber (Figure 6.5d). But, the greatest effect of added surfactant on calcium adsorption is to decrease it on carbon black for SDS, the only system for which calcium-free surfactant adsorption is tail-down monolayer or hemimicelle formation. So, the hemimicelles are presumably more effectively than admicelles in covering up sites onto which calcium would otherwise adsorb. Another possible explanation for the calcium exclusion effect for C8 is that water soluble surfactant/calcium complexes form in solution, reducing free calcium concentration and calcium adsorption at high C8 concentrations.

Table 6.1 The effect of co-adsorption of surfactant and calcium adsorption on carbon black and paper fiber

Surfactant / **Substrate**	**Effect of increasing $[Ca^{2+}]$ on surfactant adsorption**		**Effect of increasing [surfactant] on calcium adsorption**	
	SDS	**C8**	**SDS**	**C8**
Carbon black	↑ at low [SDS]	↑ at low [C8]	↓ at high $[Ca^{2+}]$	↑ at high $[Ca^{2+}]$
Paper fiber	↔	↔	↔	↓ at high $[Ca^{2+}]$

6.4.4 Relevance of Results to Flotation Deinking of Paper

From the perspective of flotation deinking of wastepaper, the most relevant findings from this study are that calcium can substantially improve surfactant adsorption on carbon black (cause of calcium activation effect), while not enhancing surfactant adsorption on paper fiber. Another finding is that the carboxylate head group (C8) has higher surfactant adsorption onto carbon black than the sulfate head group (SDS) even with a shorter hydrophobe. Finally, carboxylates or soaps are more popular as flotation surfactants than sulfates is that carboxylates adsorb head-down on carbon black instead of tail-down for sulfates. Presumably, when the rising air bubble in the flotation cell collides with the carbon black particle, the tail group of the adsorbed surfactant sticks into the air phase; such an effect is only possible for the carboxylate because of its head-down adsorption. This mechanism of particle/air bubble attachment has been hypothesized by our group to explain ore flotation [20]. Since high molecular weight carboxylate surfactants which are insoluble at room temperature are used in industrial flotation deinking processes. The actual concentrations at which synergisms between calcium and the low molecular weight carboxylate in this work are not directly translatable to industrial systems. The relevance of this work is to demonstrate that there is a range of calcium/carboxylate surfactant concentrations over which adsorption synergisms are observed.

6.5 Conclusions

In the absence of calcium, at a high enough concentration for aggregates to form, C8 adsorbs as a bilayer on both carbon black and paper fiber as does SDS on paper fiber. However, SDS adsorbs as a tail-down monolayer on carbon black. When calcium is added to the surfactant solutions, in addition to these bilayer or monolayer surfactant aggregates, surfactant adsorption is synergized due to calcium adsorption on negative surface sites and co-adsorption of the anionic surfactant on the positively charged cation (calcium bridging effect). At high surfactant concentrations, the surface patches are increasingly filled, covering up potential calcium adsorption sites, causing a reduction of calcium adsorption for SDS on carbon or C8 on paper fiber. These results help explain why calcium is an effective activator and carboxylate surfactants are more effective than alkyl sulfates in flotation deinking of paper.

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