Chapter 6

Summary and Conclusions

1. The results of the present investigation show the effect of various reagents on the hydration and hydrophobic forces. The major findings of this work may be summarized as follows:

2. Hydrophobic forces between mica surfaces in DOAHCl solutions are longer ranged than those in solutions of single-chained surfactants such as DAHCl and CTAB. This may be attributed to the likelihood the double-chain DOAHCl can create more closely-packed monolayers of hydrocarbon chains than the latter. Evidence for this was given by the hydrocarbon chain area densities of the double- and single-chain surfactants, which were determined on the basis of the adsorbed layer thickness measured using the Mark IV SFA. It appears, therefore, that the decay lengths of hydrophobic forces are determined by the degree to which hydrocarbon chains of surfactants are close-packed on a surface. It should be noted, however, that there may be other factors affecting the range of the hydrophobic forces.

3. Hydrophobic forces were measured for the first time between silica surfaces in anionic surfactant solutions. Since silica is negatively charged at alkaline pHs, the force measurements were conducted in solutions of Ca(II) and Mg(II) salts so that the charge on the surface is reversed. In the present work, an AFM was used to measure the surface forces between glass sphere and silica plate in sodium oleate solutions. It was found that hydrophobic forces are observed only at pHs where the concentration of the singly charged hydroxo complexes (CaOH⁺ or MgOH⁺) reach maximum, which suggests that that CaOH⁺ and MgOH⁺ are the activating species for silica. Oleate interacts with these species adsorbed on the surface, forming basic calcium oleate (CaOHOI) and basic magnesium oleate (MgOHOI), which are probably held by H-bonding to the silanol groups on the surface.

4. The primary hydration forces observed between silica surfaces may be considered to originate from the strong water structure in the vicinity of silica. Because Si⁴⁺ ions are
highly polarizable, the silanol groups on the surface of silica (SiO₂) are acidic and water molecules are strongly bonded on them via H-bonding as base. Therefore, solutes of stronger basicity than water can displace water from the silica surface, thereby weakening the water structure and destroying the hydration force. This is evident from the fact that in 15% methanol solutions, the hydration force between silica surfaces is destroyed completely. Methanol is a stronger base than water, hence, it is thermodynamically favorable for it to displace the water molecules from the hydration sheath around silica. In 10-20% ethanol solutions, on the other hand, the hydration force decreases but is not completely destroyed. This finding suggests that ethanol is less effective than methanol in displacing the water molecules from the silica surface. The hydration force did not change in the presence of TFE, which can be attributed to the fact that this reagent is less basic than water. Pyridine, on the other hand, is more basic than water but the hydration force of silica did not decrease in pyridine solutions. This may be attributed to the steric hindrance.

5. It has been found that the primary hydration force of silica can disappear completely in MgCl₂ and CaCl₂ solutions. However, this is observed only at pHs, where the concentration of MgOH⁺ and CaOH⁺ ions are maximum. This finding suggests that these are the species adsorbing on the silica surface, and that their presence on the surface weakens the H-bonded network of water molecules on the surface and, hence, the water structure. Since the singly charged hydroxo-complexes are basic, they may adsorb on the silanol groups via acid-base interactions. The disappearance of the hydration force at the pH where the adsorption of the MgOH⁺ and CaOH⁺ ions is most favored suggests that the silica surface coated with these species are not as strongly hydrated as bare SiO₂ surface.

6. A model for the adsorption of the singly charged hydroxo-complexes on silica has been developed. This model is based on the premise that the adsorption free energy (ΔG°_ads) for these species is determined by the sum of the free energy change due to electrostatic interaction (ΔG°_elec) and the same due to chemical interaction (ΔG°_chem). The values of ΔG°_ads were determined from the adsorption isotherms of reported by James and Healy (1972) for Ca(II) on silica, while the values of ΔG°_elec were calculated from the values of the surface potentials determined from the AFM surface force measurements conducted in the
present work. It was found that the values of $\Delta G_{\text{chem}}$ determined by difference are -42 kJ/mole, which is too large to be accounted for by H-bonding of the CaOH$^+$ ions on the silanol groups. It is, therefore, suggested that the adsorption mechanism of the hydroxo-complexes is controlled by lateral interaction between the neighboring CaOH$^+$ ions on the surface. The lateral interaction could involve covalent and H-bonding mechanisms.

7. AFM surface force measurements were conducted with silanated hydrophobic silica surfaces in CuCl$_2$ solutions. The results show that the hydrophobic force decreases, at pH 6.2, where the CuOH$^+$ ion concentration reaches maximum. Thus, the decrease in hydrophobic force may be attributed to the adsorption of the singly charged hydroxo-complex on silica. This finding may be attributed to the fact that CuOH$^+$ ions are hydrophilic species, which mitigate the hydrophobicity of the substrate. The lateral interaction mechanism proposed for the adsorption of singly charged hydroxo-complexes on hydrophilic silica may also play a significant role for the adsorption of CuOH$^+$ on the hydrophobic silica.