Chapter 5

Force Measurements between Silanated Silica Surfaces in Aqueous $CuSO_4$ Solutions at Various pHs

5.1 Introduction

It is well known that adsorption density of a multivalent metal ions (M^{z+}) on a variety of substrates increases sharply only at pHs where the concentration of the singly-charged hydroxo complex ($M(OH)^{+}_{(z-1)}$) is appreciable (1-4). In Chapter 4, a new mechanism was proposed to explain why adsorption of these hydroxo-complexes may be thermodynamically more favorable than that of the unhydrolyzed metal ions. This mechanism will be explained here briefly; for a more detailed description, the reader is referred to Chapter 4. We proposed that the free energy of adsorption (ΔG^{o}_{ads}) of a hydroxo-complex is given by the sum of coulombic (ΔG^{o}_{elec}) and specific chemical (ΔG^{o}_{chem}) contributions:

$$\Delta G^{o}_{ads} = \Delta G^{o}_{elec} + \Delta G^{o}_{chem} \qquad (1)$$

Further, it was suggested that ΔG^{o}_{chem} may be represented as:

$$\Delta G^{o}_{chem} = \Delta G^{o,H}_{chem} + \Delta G^{o,l}_{chem} \qquad (2)$$

where $\Delta G^{o,H}_{chem}$ represents the free energy of hydrogen bonding interactions between the hydroxo complex and the substrate and $\Delta G^{o,l}_{chem}$ is the free energy gained by lateral interactions between adsorbed hydroxo complex molecules on the surface. In general, $\Delta G^{o,H}_{chem}$ for any H-bonding reaction is ≈-10 kJ/mole. For the adsorption of $CaOH^{+}$ on silica, $\Delta G^{o,l}_{chem}$, was estimated by fitting experimental adsorption isotherms of Ca(II) on silica and was noted be much larger ≈-32 kJ/mol. Therefore, it was concluded that the lateral interactions between adsorbed hydroxo-complexs are the major driving force for the adsorption of these species on a substrate.

The fact that $\Delta G^{o,l}{}_{chem}$ is so large suggests that specific adsorption of the singly-charged hydroxo-complexes may occur even if $\Delta G^{o,H}{}_{chem}$=0 kJ/mole. This should be the case for nonpolar/inert substrates, which may not be capable of forming H-bonds with adsorbing molecules. Indeed, there is experimental evidence to suggest that this may happen. For example, force measurements (5) have revealed that secondary hydration forces between mica surfaces at pH 10.1 (caused by adsorption of Na^+ ions introduced to the system to adjust the pH) are destroyed due to the preferential adsorption of $CaOH^+$ ions. Note here that the basal plane of mica consists of siloxane bonds, which are chemically inert and cannot H-bond with $CaOH^+$. ζ-potential measurements (6) conducted on isooctane droplets in water show that the surface charge is reversed at pHs where the concentrations of $Cr(OH)_2{}^+$ and $Al(OH)_2{}^+$ reach a maximum, suggesting specific adsorption of these species on the nonpolar surface. Matijevic *et al*. (4) showed that hydrolyzed thorium and aluminum species are more effective in coagulating the lyophobic AgI, AgBr and AgCl sols than unhydrolyzed Th(IV) or Al(III) cations. Finally, it has been noted that the flotation recoveries of sphalerite (7) and methylated quartz (8) are depressed (0% flotation recovery) in the presence of $CuSO_4$ in the pH ranges where $CuOH^+$ species are dominant. These evidences suggest that the adsorption of the singly-charged hydroxo-complexes may be favored even on substrates that are not capable of H-bonding interactions with an adsorbing molecule.

In the present communication, we have used an Atomic Force Microscope (AFM) to conduct direct force measurements between Octadecyltricholorosilane (OTS) coated silica surfaces in $CuSO_4$ solutions at various pHs. The objective of the experiment was to observe if $CuOH^+$ adsorbs on the nonpolar silica surface and thereby reduces its hydrophobicity, causing a decrease in hydrophobic force.

5.2 Experimental

5.2a *Materials*

Optically smooth fused silica plates were obtained from Haraeus Amersil, Inc. They were cleaned by boiling in a nitric acid solution for 12-15 hours, and then equilibrated in conductivity water obtained from a Barnstead Nanopure II water treatment unit. Clean silica plates thus obtained exhibited equilibrium contact angles (θ_{eq}) of less than 5^o, as measured using a Rame-Hart Model 100 goniometer. Glass spheres of radius 10-30 μm were obtained from Duke Scientific. HPLC grade cyclohexane was obtained from Aldrich Chemical Co. and dried overnight over 3-12 mesh Davidson 3 A^o molecular sieves. Octadecyltrichlorosilane (OTS) was obtained from Aldrich at 96% purity and used without further purification. Epon R Resin 1004 from Shell Chemical Company was used as an adhesive. $CuSO_4$ (99.9% purity) was obtained from Fischer Scientific. A stock solution of 0.01 M was prepared using an aliquot of the salt.

5.2b *Sample Preparation*

All operations involving OTS were carried out in a nitrogen-filled glove bag to minimize exposure of the OTS solutions to atmospheric water vapor. A silica plate and a glass sphere (mounted on an AFM cantilever tip using an Epoxy resin (9,10)) were silanated in a freshly prepared $1x10^{-3}$ M OTS solution contained in a PTFE beaker, which in turn was placed in an ultrasonic bath. After 3 minutes of silanation time, the θ_a of the silica plate was measured to be 91^o. This is in agreement with the result of Flinn *et al.* (11), who varied the silanation time as a means of controlling hydrophobicity. Since the silica plate and glass spheres were silanated in the same OTS solution for the same period of time, its may be reasonable to assume that both have the same hydrophobicity.

5.2c *Methods and Apparatus*

A Nanoscope III AFM from Digital Instruments Co. was used to measure the forces between a silanated silica plate and a glass sphere mounted on a TESP cantilever tip. The stiffness of the cantilever was measured using the technique of Senden and Ducker (9). This technique consisted of placing a heavy tungsten sphere on a cantilever tip, turning the cantilever upside down, and measuring its deflection from the AFM signals. Force measurements were conducted in Nanopure water and in solutions containing known amounts of $CuSO_4$. The measurements were conducted by varying the pH of the $CuSO_4$ solution. Prior to each measurement, the two surfaces, i.e., silica plate and glass sphere, were equilibrated in a given solution for 15 minutes. The pH was adjusted by adding aliquots of NaOH and HCl solutions. The radii of the glass spheres used in the force measurements were determined using a Kontron SEM-IPS image processing system.

5.3 Results and Discussions

Figure 5.1 represents the species distribution diagram of a $2x10^{-4}$ M $CuSO_4$ solution. It was constructed using the thermodynamic data given in reference (12). As shown, as the pH increases, Cu^{2+} ions are hydrolyzed to produce various hydroxo-complexes. The concentration of the $Cu(OH)^+$ and $Cu_2(OH)_2^{2+}$ species reach maximum at pH 6.6. At higher pHs, $Cu(OH)_{2(s)}$ precipitates. It is expected that some of these species may adsorb on the surfaces of the hydrophobic silica plate and glass sphere and change their hydrophobicity. As noted earlier, the silica plates silanated under conditions employed in the present work exhibited $\theta_a=91^o$. AFM surface force measurements were conducted at three different pHs, namely, 3.0, 6.2 and 9.0. It should be noted, however, that the contact angle measurements conducted in the presence of $2x10^{-4}$M $CuSO_4$ showed no change in θ_a. It is possible that the changes in θ_a was too small to be detected by the goniometer that was used for the contact angle measurement.

The results obtained at pH 3.0 in a $2x10^{-4}$ M $CuSO_4$ solution are given in Figure 5.2. The measured forces (F) were normalized by the radius of the sphere (R), and are plotted versus the separation distance (H). As shown, the force data obtained both in the presence and absence of $CuSO_4$ lie on the same curve. The measured forces are attractive at all separations and show no evidence for double-layer repulsion, suggesting that surface potential (ψ_o) is zero. This is not surprising because the pH at which the force measurements were conducted was close to the point of zero charge (p.z.c.) for silanated silica (≈pH 2.0) (13). The dashed lines represent the van der Waals force, which has been calculated using the Hamaker constant (A_{131}) of $6x10^{-20}$ J. This value is close to what is expected of two silica surfaces interacting across water (10). As

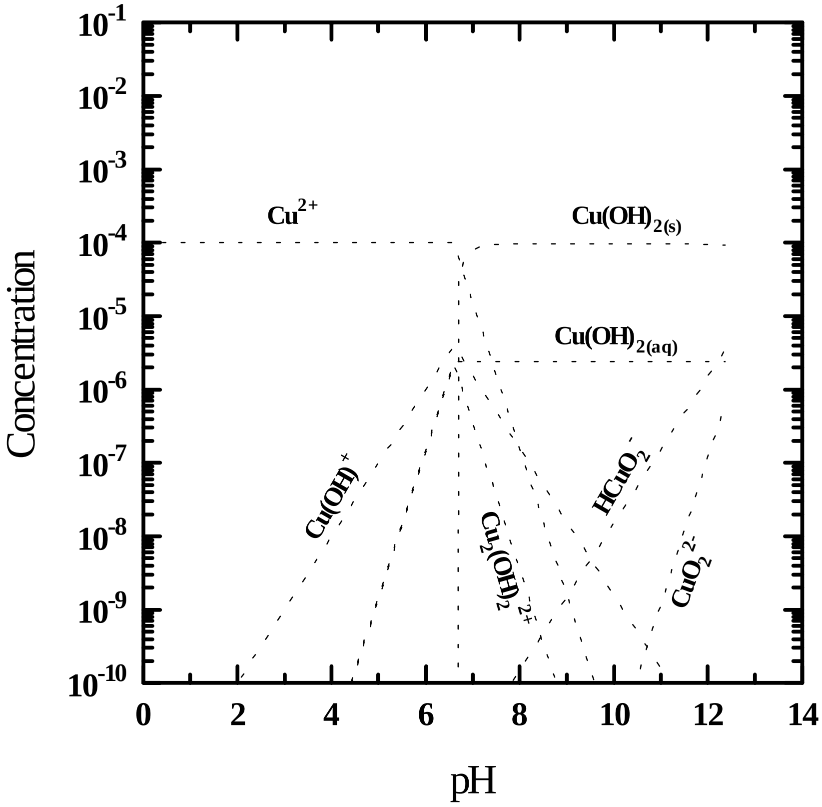

Figure 5.1. Species distribution diagram of $2x10^{-4}$ M $CuSO_4$.

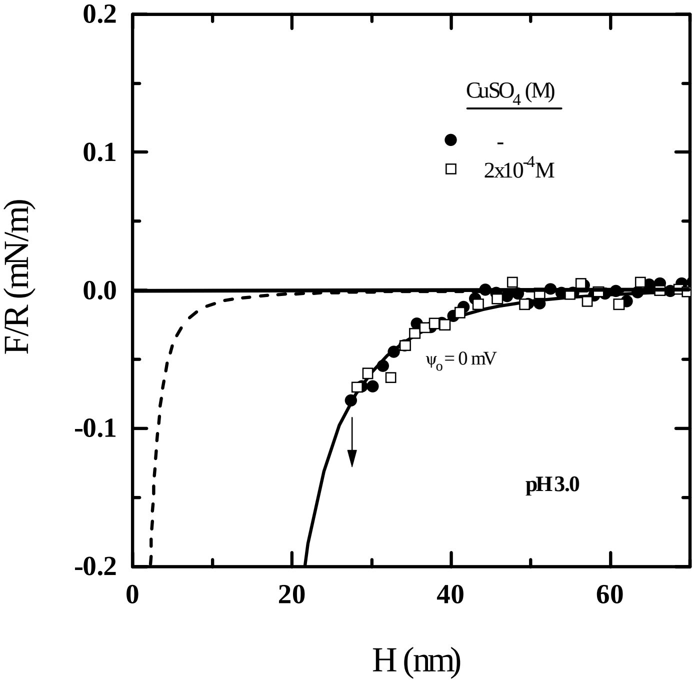

Figure 5.2. F/R vs H curves obtained between slianated silica plate and glass sphere in (i) pH 3.0 (●) and (ii) 2x10^{-4} M CuSO$_4$ at pH 3.0 ( ). The dashed lines represents the van der Waals force calculated using a Hamaker constant (A_{131}) = 6x10^{-21}J. The solid lines represent the extended DLVO theory (Eq.2), incorporating a hydrophobic force term.

shown, the measured forces are stronger than the van der Waals force, which suggests the presence of a hydrophobic force. The solid line represents the experimental data fitted to the extended DLVO theory:

$$F_t = F_e + F_d + F_h \tag{3}$$

which includes contributions from the hydrophobic force (F_h) in addition to those from electrostatic (F_e) and dispersion (F_d) forces already considered in the DLVO theory (16,17). The following expression was used to represent F_h (14):

$$\frac{F_h}{R} = C_1 \exp\left(\frac{-H}{D_1}\right) + C_2 \exp\left(\frac{-H}{D_2}\right) \tag{4}$$

where C_1, C_2, D_1 and D_2 were used as adjustable parameters. Table 5.1 shows the values of these parameters that were used to fit the data. The value of the long-range decay length of D_2=10.1 nm obtained from fitting the measured forces to the extended DLVO theory (Eq. [3]) is comparable to those obtained by other researchers (15) with surfaces exhibiting similar θ_a values. Recall from Figure 5.1 that at pH 3.0, Cu^{2+} ions are the predominant species in solution. The fact that strong hydrophobic force are observed in a Cu(II) solution at this pH suggests that Cu^{2+} ions do not adsorb on the silanated silica surface.

Figure 5.3 compares the results obtained in the absence and presence of Cu(II) species in solution at pH 6.2. The upper force curve shows the results obtained in Nanopure, with the dashed line representing the constant charge model of the DLVO theory fitted to the data using the algorithm of Chan *et al.* (18). The data obtained at H>30 nm can be fitted to the DLVO theory with ψ_o=-52 mV. This value is close to that obtained for untreated hydrophilic silica at pH 5.7 (19). It seems, therefore, that silanation does change the surface potential of silica significantly. Similarly, Laskowski and Kitchner (13) showed that silanation does not change the ς-potentials of silica. However, the two silanated surfaces jump into contact at H=31 nm, which is larger than predicted by the classical DLVO theory. This finding suggests the presence of an attractive hydrophobic force, not considered in the DLVO theory. Therefore, the

Table 5.1

Surface Force Data obtained with silanted silica in the presence of $2\text{x}10^{-4}$M $CuSO_4$ at different pHs

pH	$CuCl_2$ (M)	ψ_o (mV)	κ^{-1} (nm)	C_1 (mJ/m^2)	D_1 (nm)	C_2 (mJ/m^2)	D_2 (nm)	H_j (nm)
3.0	0	0	-	100	3.1	1.0	10.3	28
3.0	$2\text{x}10^{-4}$	0	-	100	3.1	1.0	10.3	28
4.0	0	-36	38	100	3.1	1.0	10.8	33
4.0	$2\text{x}10^{-4}$	-22	13	100	3.1	1.0	10.1	26
5.0	0	-43	56	100	3.1	1.0	10.5	33
5.0	$2\text{x}10^{-4}$	-17	11	100	3.1	1.0	10.1	23
6.2	0	-52	90	85	3.1	1.2	10.1	31
6.2	$2\text{x}10^{-4}$	26	14	90	3.2	1.1	7.7	24
9.0	0	-49	69	92	3.3	1.0	9.8	31
9.0	$2\text{x}10^{-4}$	0	-	88	3.0	1.3	6.6	27

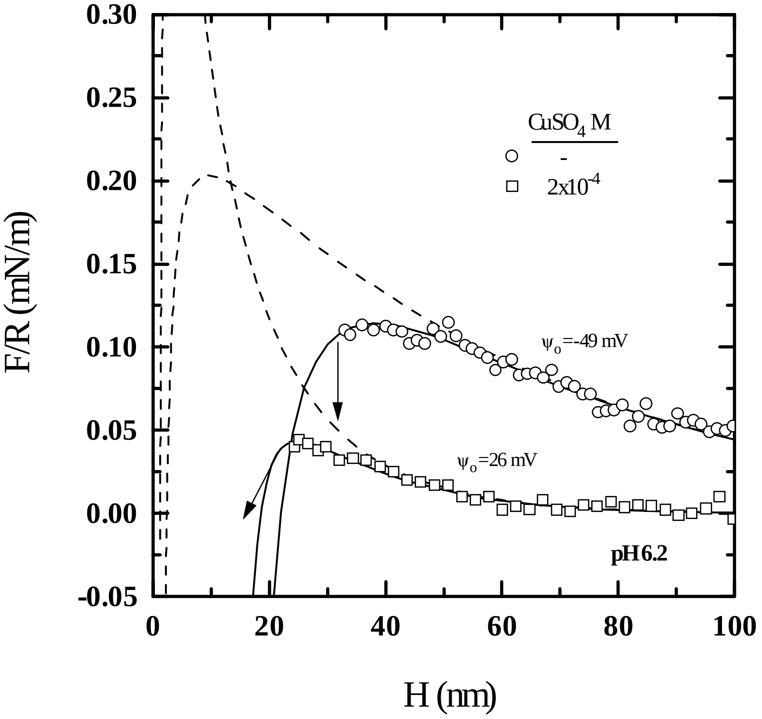

Figure 5.3. F/R vs H curves obtained between a silica plate and glass sphere in (i) pH 6.2 (○) and (ii) $2x10^{-4}$ M $CuSO_4$ at pH 6.2 ( ). The dashed lines represent the constant charge model of the DLVO theory fitted to the data using the parameters listed in Table 5.1. The solid line represents the extended DLVO theory (Eq.[3]). The arrows indicate the position at which the surfaces jump into contact.

experimental data were fitted to the extended DLVO theory, with the solid line representing the theoretical fit. Table 5.1 gives the values of the C_1, D_1, C_2 and D_2 of Eq. [4] that were used to fit the data. It may be worthwhile to note here that the hydrophobic force parameters obtained at pH 6.2 are the same as those at pH 3.0, which suggests that hydrophobic force is independent of surface charge (or potential).

The lower force curve in Figure 5.3 was obtained in a $2\text{x}10^{-4}$ M $CuSO_4$ solution at pH 6.2. At H>40 nm, the force data can be fitted to the constant charge model of the DLVO theory with $|\psi_o|=26$ mV. Although it is not possible to know the sign of the potential from the surface force measurement, it is likely to be positive. It has been shown that the ζ-potentials of non-polar surfaces can be reversed in solutions of hydrolizable cations at a pH where the concentration of singly charged hydroxo-complexes is high (6). In Cu(II) solutions, the concentration of $CuOH^+$ ions reaches its maximum at pH 6.6 as shown in Figure 5.1; therefore, it is likely that these ions adsorb on the silanted silica surfaces at pH 6.2 and reverse their surface charge. Note that the two surfaces jump into contact at 24 nm, which is larger than predicted by the classical DLVO theory, indicating the presence of hydrophobic force. Therefore, the data were fitted to the extended DLVO theory with the values of C_1, C_2, D_1 and D_2 given in Table 5.1. As shown, the first three of these parameters are very close to those obtained in the absence of $CuSO_4$. However, the D_2 value has decreased substantially. The main reason for this decrease may be the adsorption of $CuOH^+$ ions on the surface. Since these are hydrophilic species, their adsorption on the surface should decrease the hydrophobicity.

Figure 5.4 shows the results of the force measurements conducted at pH 9.0. In the absence of $CuSO_4$, the force data exhibit double layer repulsion. The data obtained at H>50 nm can be fitted with $\psi_o=-49$ mV. The two silanated silica surfaces jump into contact at H=31 nm, indicating the presence of a hydrophobic force. Therefore, the data have been fitted to the extended DLVO theory using the values of C_1, C_2, D_1 and D_2 given in Table I. These hydrophobic force parameters are practically the same as those obtained at pH 3.0 and 6.2 in the absence of $CuSO_4$. The data obtained in the presence of $2\text{x}10^{-4}$M $CuSO_4$, on the other hand, show no repulsive forces. The force data obtained at H<30 nm are net attractive indicating the presence of a hydrophobic force. As shown in Table 5.1, the value of D_2 decreased to 6.6 nm,

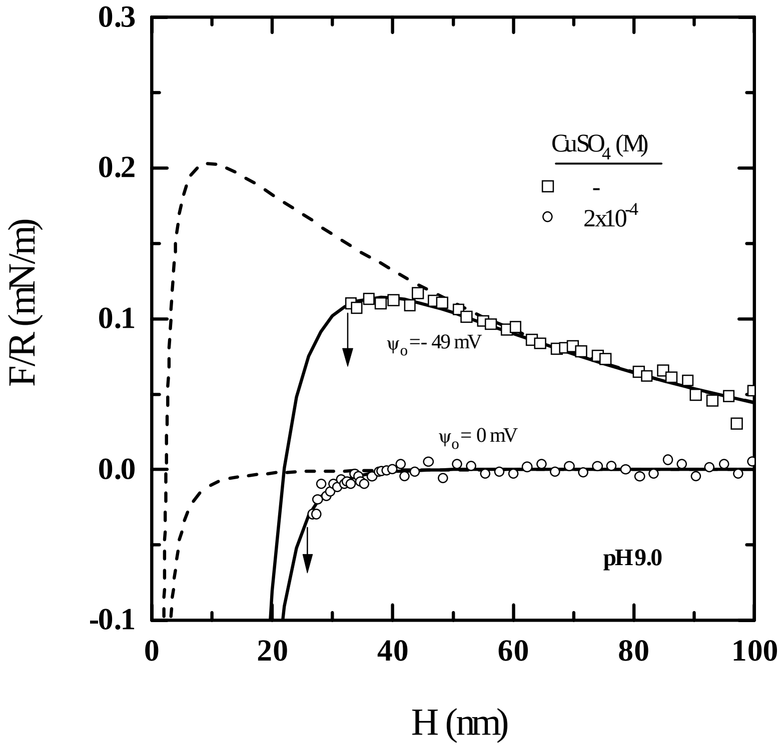

Figure 5.4. F/R vs H curves obtained between a silica plate and glass sphere in (i) pH 9.0 ( ) and (ii) $2x10^{-4}$ M $CuSO_4$ at pH 9.0 (○). The upper dashed line represents the constant charge model of the DLVO theory whereas the lower dashed line is the vDW force calculated using $A_{131}=6x10^{-20}$J. The solid line represents the extended DLVO theory. The arrows indicate the position at which the surfaces jump into contact.

which is lesser than those obtained lower pHs. This sharp decrease may be attributed to the adhesion of $Cu(OH)_2(s)$ precipitate on the surface of silica. Since the precipitate is hydrophilic, the silica surface coated by it should decrease the hydrophobic force. Evidence for the presence of $Cu(OH)_2$ precipitate is that the force curve can be fitted to the extended DLVO theory with ψ_o=0 mV, which can be ascribed to the fact that $Cu(OH)_2(s)$ has its p.z.c. at pH 9.4 (20).

The results presented heretofore showed that the repulsive double-layer forces observed between silanated silica plate and glass sphere change substantially with pH in the absence of Cu(II) species. On the other hand, the attractive hydrophobic forces observed between them remain more or less constant over a wide range of pH investigated in the present work. However, the hydrophobic forces change with pH considerably in $CuSO_4$ solutions, which can be attributed to the adsorbability of the various Cu(II) species present in solution on silanated silica surfaces. Figure 5.5 shows the changes in D_2 versus pH. Also shown is the distribution diagram for the various Cu(II) species at a total concentration of $2x10^{-4}$ M. It can be seen that D_2 remain constant at pH<6.0, and that their values are the same as obtained in Nanopure water. Since Cu^{2+} ions are the predominant species at this pH range, a conclusion that can be drawn from these observations is that either Cu^{2+} ions do not adsorb on silanated silica surfaces, or if they do, the presence of the Cu^{2+} ions on the surface does not affect the hydrophobicity. The former is more likely. As shown by many investigators, various divalent cations such as Ca^{2+}, Mg^{2+}, Co^{2+}, Mn^{2+}, Pb^{2+} and Cu^{2+} ions do not adsorb on oxides unless they are hydrolized (1-3). This is so even on non-polar substrates such as isoctane droplets (6).

At pH 6.2, where the concentration of the hydroxo-complex approaches its maximum, D_2 decreases by ≈27%. At this pH, $CuOH^+$ ions adsorb on the surface of silanated silica and decrease the hydrophobic force. Ability of these hydroxo-complexes to form H-bonds with water molecules may be responsible for the decrease in hydrophobic force. At pH 9.0, D_2 decreases further due to the adhesion of $Cu(OH)_2(s)$ on the surface, which is also capable of forming H-bonds with water. Evidence for the presence of the precipitate on the surface of the silanated silica is given by the fact that ψ_o=0 mV at pH 9.0, which agrees well with the fact that the p.z.c. of $Cu(OH)_2(s)$ is pH 9.4.

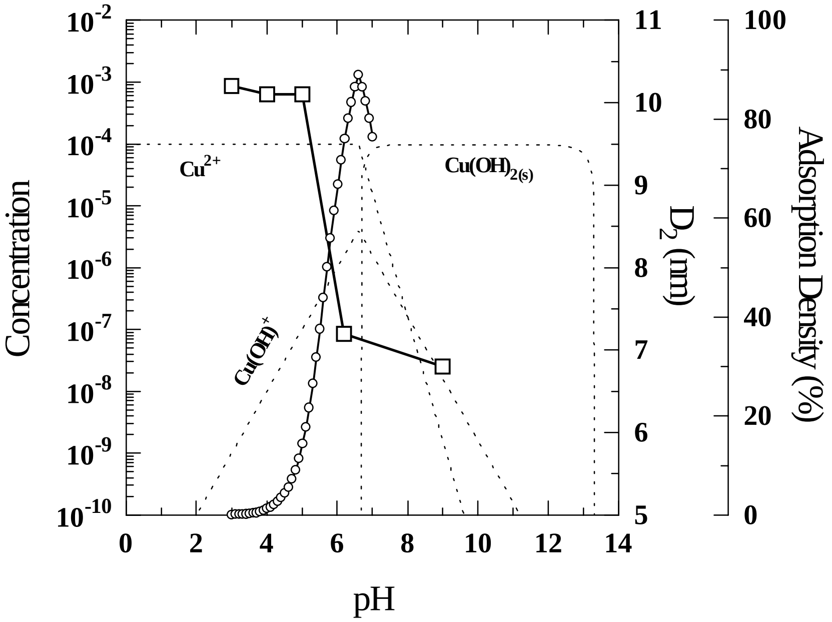

Figure 5.5. Decay lengths (D_2) of hydrophobic force at 2x10^{-4}M CuSO$_4$ ( ) as a function of pH. Also shown is the fractional coverage (o) by CuOH$^+$ species on the silanated silica surface obtianed using the model described in the text. The dotted lines represent the concentration of the different species in solution at 2x10^{-4} M CuSO$_4$.

It has been shown in Chapter 4 that $CuOH^+$ ions can also adsorb on hydrophilic silica. The free energy change associated with this process can be given by Eq. [1]. The free energy change due to electrostatic interaction can be calculated using the following relationship:

$$\Delta G^o_{elec}=zF\psi_o \qquad (5)$$

where z (=1) is the valence of the $CuOH^+$ ions adsorbing on the surface, F the Faraday's constant, and ψ_o is the surface potential of the substrate. For their adsorption on hydrophilic silica, the free energy change due to chemical interaction has been subdivided into two components, as shown by Eq. [2].

In the present work, Eqs. [1] and [2] were used to obtain the values of ΔG^o_{ads} for the adsorption of $CuOH^+$ ions on silanated silica. The values of ΔG^o_{elec} were calculated using Eq. [5]. The experimental values of ψ_o given in Table I were used for the calculation. The values of ψ_o not available from the AFM force measurement were calculated by interpolation. In calculating ΔG^o_{chem}, it was assumed that $\Delta G^{o,H}_{chem}=0$, because the substrate is non-polar and, hence, cannot form H-bonds with $CuOH^+$ ions. The values of $\Delta G^{o,l}_{chem}$ were calculated from the free energy change associated with the following reaction:

$$2CuOH^+ = Cu_2(OH)_2^{2+} \qquad (5)$$

whose standard free change is -32.2 kcal per mole of $CuOH^+$ ions, according to the thermodynamic data given ref. (19).

The values of ΔG^o_{ads} obtained in the manner described above were used to calculated the equilibrium constant (K) for the adsorption of the $CuOH^+$ ions on silanated silica using the following relationship:

$$K = \exp(-\Delta G^o_{ads}/RT) \qquad (6)$$

where R is the universal as constant and T is the absolute temperature. The adsorption of the $CuOH^+$ ions may be given by:

$$(1-\theta) + CuOH^{+} \overset{K}{=} \theta \tag{7}$$

where θ is the fractional surface coverage, which in turn can be given by the following relationship:

$$\theta = \frac{KC}{1+KC} \tag{8}$$

where C is the concentration of the $CuOH^+$ ions in bulk solution. The values of C can be readily determined using the thermodynamic data given in literature and as shown in Figures 5.1 and 5.5.

In Figure 5.5, θ has been plotted versus pH. As shown, D_2 begins to decrease at the pH where θ begins to increase sharply. At pH 6.6, where the concentration of $CuOH^+$ ions reaches a maximum, θ begins to decrease. However, D_2 continues to decrease with increasing pH, which can be attributed to the adhesion of $Cu(OH)_2(s)$ on the surface of the silanated silica.

5.5 Conclusions

Force measurements were conducted between silanated silica plate and silanated glass sphere to study the effect of $CuSO_4$ on the hydrophobic forces at various pHs. In the absence of $CuSO_4$, the measured hydrophobic forces at all pHs can be fitted to a double-exponential function with D_2 in the range of 9.8 to 10.3 nm. In 2×10^{-4} M $CuSO_4$ solutions, D_2 varies significantly with pH. At pH<6.0, where Cu^{2+} ions are the predominant species in solution, it remains unchanged. At pH 6.2, where the concentration of $CuOH^+$ reaches maximum, D_2 decreases to 7.7 nm, which can be attributed to the specific adsorption of $CuOH^+$ ions on the silanated silica surface. It is possible that these species form H-bonds with the water molecules in the vicinity of the surface and render the surface hydrophilic.

A model for the adsorption of the $CuOH^+$ ions was developed. It was based on calculating the free energies of adsorption, which consist of contributions from electrostatic and chemical interactions. The values of the former were calculated based on the surface potentials determined from the AFM force measurement, while the latter was assumed to be -32.2 kJ/mole which is the free energy change associated with the dimerization of $CuOH^+$ ions. The hydrophobic force continues to decrease above the pH (=6.6) where the model predicts the adsorption of the $CuOH^+$ ions to be maximum. This can be attributed to the adhesion of the hydrophilic $Cu(OH)_2(s)$ species on the silanated silica surfaces.

5.6 References

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