

SURFACE ENERGY CHARACTERIZATION AND COMPETITIVE SURFACE
EQUILIBRIA USING CONTACT ANGLE

By

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ABSTRACT

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Surface energy measurements are usually difficult to assess when not considering a solid-air or liquid-air interface. Contact angles was used as a method of obtaining the interfacial energy of a silanol-water surface using carbon tetrachloride as a probing liquid. The theory for this work operated under the assumption that the pKa of a silanol surface could be measured by obtaining a titration like curve as a function of pH. A decrease in contact angle of about 7° was observed at a pH (pKa) of 3.5. This corresponds to an energy difference of 2 mN/m.

Additionally, the effect of competing equilibria was investigated using this technique. The above result was see at an ionic strength of 0.1M NaCl but the effect was not observed at 0.01M. This lead to the assertion that there is a competition between H^+ and Na^+ for the deprotonated silanols. At these conditions the association constant for Na^+ with the surface, K_{Na} , was found to be 7×10^{-3} .

ACKNOWLEDGMENTS

Special thanks is given to my research group who helped with ideas and theory for this work, to Jillian Mutcher whose question sparked this investigation, Scott Bankroff who helped with modifying the substrates used, and to Dr. Gary Blanchard for the opportunity to work under him throughout the project.

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Chapter 1

Introduction

Interfaces are ubiquitous in chemical reactions and separations, and their physical and chemical properties determine their utility. Interfaces are defined by the contact between two or more immiscible phases of matter. Surfaces provide a wide variety of supports on which physical and chemical processes can happen. Due to the wide variety and often complex nature of surfaces, it is typically difficult to characterize them adequately. In this document, fundamental surface characteristics are examined using chemical equilibria and contact angle measurements to address questions that remain to be fully understood regarding silica surfaces.

Phospholipid membranes provide a medium for reactions to happen in biological systems and exhibit a range of physical and chemical properties depending on the function(s) they are specialized for.¹ Such membranes show distinct reactivity and selectivity and this has been an attractive target for scientists to replicate. Model lipid bilayer interfaces are typically formed on planar supports, composed of a limited number of components, and placed on support surfaces that are suited for the intended application (*e.g.* electrochemistry, spectroscopy). The interaction of the lipid molecules with the surface (*e.g.* silica, mica, gold, ITO) has been examined previously.² Bilayer fluid properties have been investigated for their potential utility as biomimetic systems.³ Monolayers and bilayers can be placed on supports with metal ions that are used to modulate the strength of the interaction with the surface. The identity, charge and ionic radius of these metal ions affect their interaction not only with the surface but with the lipids through the phosphate head group.

The interactions between metal ions with either surfaces or functional groups can be characterized. These associations are characterized by their characteristic free energy, in the same manner as covalent bonds. Bond strengths are well documented through quantities such as lattice strength and solubility products, depending on the system. If we consider sodium chloride, the body dissociation energy is about 411 kJ/mol.⁴⁻⁵ In solution there is an electrostatic interaction that changes based on the distance between the molecules. This is similar to what would be expected on the surface. The metal ions are attracted to the surface and as such have their own attraction/association energies. Among the differences between surface and solution phase interactions between specific metal ions and complexing species is the difference in solvation energies for the complexing species in bulk solution and surface environments. While difficult to model owing to the complexity and transient nature of the solvation process, such interactions are certainly amenable to experimental evaluation.

Ionic and other associative interactions depend on factors such as pH, temperature, concentration, and charge. These system properties affect both the metal ion and the surface. The groups with which metal ions can complex are characterized by acid dissociation constant(s), rendering the complexation process pH-dependent.

Metal and conducting oxide surfaces are employed in experiments that require conductive surfaces. Insulating oxide surfaces, such as silicon dioxide or titanium dioxide, are used extensively in energy storage and conversion, and separations, for example. Transition metal oxides and semi-metal oxides have also been used in certain applications.⁶

Energy conversion and storage is an area of current and long-term interest. As the population continues to grow and countries continue to develop technologically, fossil fuels will at some point become depleted, and energy demands will rise. Solar energy is an attractive target

for energy generation. In the late-20th century, solar cells were used as a method to convert solar radiation to electrical energy.

In a chemical separation technique such as high performance chromatography, silica serves as the support material on which chemical functionality is attached to facilitate the separation. The silica surface contains reactive silanols that can be modified to suit the proposed target analyte(s).⁷ The interaction of the analytes with the surfaces mediates the separation process but the molecular-scale details of these processes remain to be understood fully.

Oxide surfaces such as silica or titania can exhibit a wide range of surface morphologies, from microcrystalline to amorphous, and the bulk surface structural features can likewise vary widely. Among the consequences of this structural variability over a range of length scales is the non-uniform accessibility of surface chemically-active species. For example, surface hydroxyl functionality will exhibit different dissociation behavior when on an open surface region versus when located deep within a pore or crease. Such morphology-dependent chemical properties further complicate attempts to characterize and model such materials.

Dye-sensitized solar cells take advantage of surface-adsorbed optical absorbers (dyes) to effect carrier injection into the conduction band of the acceptor semiconductor (TiO_2). The dye is typically a transition metal complex such as $\text{Ru}(\text{bpy})_3^{2+}$. Titanium dioxide, as a mesoporous material (pore diameter < 50 nm), can be coated with a usefully large amount of $\text{Ru}(\text{bpy})_3^{2+}$ due to its relatively large surface area. Titania is capable of supporting electron diffusion across its surface. Its band gap is also suitable for absorption of ultraviolet (UV) radiation. Incident UV (solar) photons excite the chromophore on the TiO_2 surface which then transfer electrons to the semiconductor, with subsequent carrier diffusion within the bulk material. A better understanding of electron injection at the semiconductor surface is essential, although the limiting factor to

efficiency in such solar cells is recombination, and it is not clear that the semiconductor surface is capable of functioning to make electron transport asymmetric across the interface. Substantial fundamental work remains to be done.

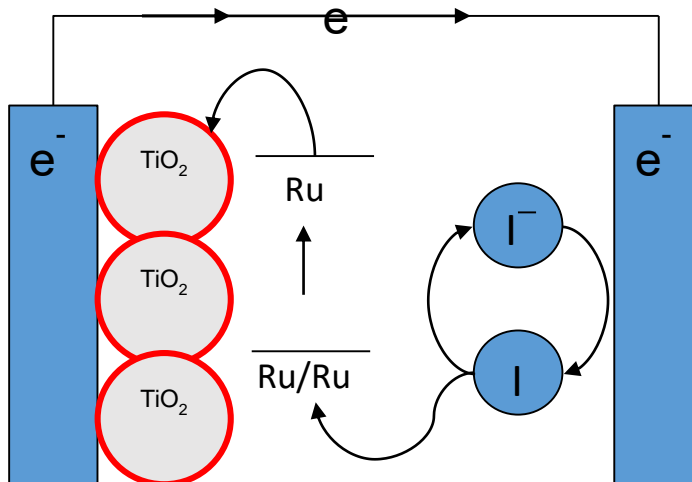


Figure 1. Dye Sensitized Solar Cell. A schematic of a dye (red line) sensitized solar cell that is used for energy conversion. Titanium dioxide is used as the electron transfer material from the dye to the electrode.

The chemical nature of these surfaces can also vary from sample to sample and depending on the method in which they are prepared. The terminal groups on a silica surface are hydroxyls, but there can be more than one type of hydroxyl group. Silanol groups are classified as Q^1 through Q^3 , with the superscript indicating the number of hydroxyl groups bonded to a parent silicon atom. Silicon atoms that are bonded exclusively to other Si-O functionalities are designated Q^0 . The distribution of the groups Q^1 through Q^4 in silica depends on the morphology and porosity of the bulk material.⁸⁻⁹

Characterizing and mapping the distribution of Q¹ to Q³ surface functionalities has been attempted by others based on the different pK_as characteristic for each type of hydroxyl group. A complicating factor, as indicated above, is that in addition to the structural differences in different silanol functionalities (Q1 through Q3), the local environment of the silanols can serve to alter the effective dissociation constant(s) for these groups. Effects such as hydrogen bonding with neighboring silanols and access to bulk aqueous solvent can alter the effective pK_a of a silanol group significantly.

The spatial distribution of the different types of silanol groups is also not understood well nor characterized easily. This is partly a matter of the length scales involved and partly because of the wide morphological variability in silica. While there is limited data available indicating the spatial variability in the distribution of surface silanol groups, making such a determination requires significant surface modification chemistry to be observable.¹⁰

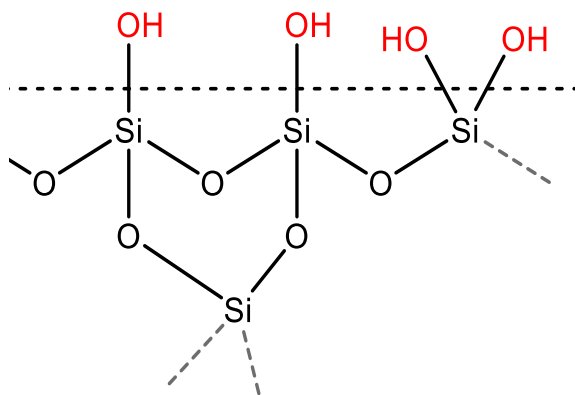


Figure 2. Representative Silica Surface. Example image of a silica surface. Q¹ and Q² silanols are shown on the surface as well as siloxane bridges under the surface. These bridges can also be above the surface.

The pKas of these silanol groups are generally accepted to be between 4.5 and 8.5,¹¹ depending on both structural form ($Q^1 - Q^3$) and local morphology. Hydrogen bonded silanols, and Q^2 and Q^3 silanols are thought to have higher pKa values due to stabilizing effects such as hydrogen bonding between neighboring OH groups. Due to the distribution of silanol pKa values, the silica surface will exhibit partial dissociation, with the extent of the dissociation extending over several pH units. It is well established that at neutral pH a silica surface is characterized by a net negative charge.

The surface charge of silica is exploited effectively in electrophoretic separations. The charge on the surface interacts with the overlaying solution.¹² In the presence of a potential gradient, the fixed charges on the inside of a silica capillary and mobile charge carriers in the solution contained within the capillary give rise to electroosmotic and electrophoretic flow. In the absence of fixed surface charges, electrophoretic flow would not proceed and only electroosmotic flow of solution phase ions would occur. In practice, there are multiple charged components in solutions that are analyzed using electrophoresis due to the use of buffer(s), and the cationic solution phase species (*e.g.* H^+ , Na^+ , K^+ , etc.) will compete for the silica surface (anionic) siloxide sites. The details of these competitive equilibria have not been considered in detail to this point, and we present a means in this Thesis to evaluate these competing processes.

The experiments described in this thesis focus on two phenomena that operate at a silica interface. First, the surface-charge interacts with cations in an overlaying media. Even though the surface is protonated to some extent there remains associative interactions between solution phase cations from the buffer and the negatively charged siloxide functionality. The solution phase ions are attracted to the surface and form an electric double layer. The competitive equilibria between

protons and specific metal ions in solution and the surface determines the properties of the interface.

Because the extent of surface charge varies with experimental conditions such as cation concentration (*i.e.* ionic strength) and pH, the surface energy varies. Surface energies can be challenging to quantitate and we use several techniques in concert to evaluate them for the systems reported in this work. We employ a variant of contact angle measurement in conjunction with Wilhelmy plate measurements to characterize the constituent surface energies of the systems we study, and in particular, we monitor how the surface energy for the silica surface varies with experimental conditions. Contact angle measurements are described using the same physics used to describe meniscus phenomena, and is based on the balance of energies between three phases of matter. In the case of contact angle measurements, the liquid drop, the solid surface, and the overlying medium (usually air), interact with each other and achieve a balance of forces (surface energies) that determines the contact angle of the drop with the (solid) surface as described by Young's Equation.¹³ In 1805 Thomas Young developed a qualitative theory to explain surface tension and the rise of liquids in capillaries.

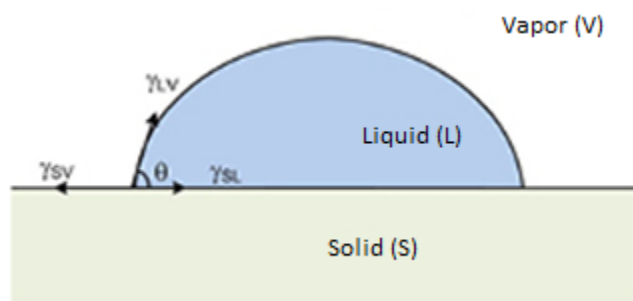


Figure 3. Liquid Drop on Solid Surface. Schematic of a contact angle image. A liquid is placed onto the surface and the balanced forces create the profile of the drop.

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

Figure 4. Young's Equation. Relating contact angle (theta) to the balancing of forces where γ_{SV} is the solid-vapor energy, is the γ_{SL} solid-liquid energy, and γ_{LV} is the liquid-vapor energy.

Young's Equation relates the contact angle (θ in Fig. 3) to the surface energies, γ , where γ_{SV} is the solid-vapor interface energy, is the γ_{SL} solid-liquid interface energy, and γ_{LV} is the liquid-vapor interface energy.¹³ Changes in one or more of these energies is manifested as a change in the measured the contact angle. For a silica surface, there is a change in surface charge associated with the chemical composition of the (aqueous) overlayer, and changes in ionic interactions that involve the (silica) surface will produce changes in γ_{SV} and γ_{SL} . It is these changes that we sense as a function of the chemical composition of the aqueous overlayer. The work contained in this Thesis demonstrates a method for measuring and quantitating the interfacial energy of a solid surface in an aqueous medium, with a specific focus on the competitive equilibria that determine the effective properties of the (silica) interface. Such data have not been reported widely and knowledge of this information can be of direct use in chemical sensing and separations applications.

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Chapter 2

Abstract

Characterizing the composition of an oxide surface is critical to a range of applications in separations and reaction chemistry. For silica surfaces, among the key issues is the competition for occupancy of the siloxide (SiO^-) sites by H^+ and other cations. We have studied the competition between H^+ and Na^+ for surface siloxide occupancy as a function of the concentrations of each cation using the contact angle of a droplet of CCl_4 on a silica surface immersed in aqueous solution as the probe of surface energy. We find the dissociation constant for SiONa to be larger than the SiOH dissociation constant, and with knowledge of the surface energy for CCl_4 in contact with H_2O , we are able to determine the surface energies of the SiOH -water, SiONa -water and CCl_4 - SiOX interfaces.

Introduction

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Oxide interfaces are among the most widely used surfaces in the chemical sciences. Silica and alumina, for example, have found wide use in chemical separations, ranging from plate chromatography to electrophoresis. Titania has found use in solar energy conversion and heterogeneous catalysis applications. These interfaces share the common challenge of characterization owing to their complex, and for some systems, amorphous structure.

In many instances, a key parameter in the utilization of an oxide surface is the extent to which its chemically (re)active –OH functionalities are dissociated and what chemical species are present in the system for the –O⁻ sites to interact with. For liquid phase measurements, it is a simple matter to measure the *pH* of a solution, but for oxide surfaces, gauging the extent of protonation and/or occupancy by other (cationic) species poses a much greater challenge.¹¹ Among the reasons for this challenge is the inability to use electrochemically-based techniques, and the fact that the surface silanol functionalities can interact with multiple different chemical species.^{11, 14} It is for these reasons that we have devised an experimentally simple means of evaluating competitive equilibria at an oxide surface.

We focus on silica in this work as an illustrative oxide surface, and consider the competition for its accessible silanol groups in aqueous solution under conditions of variable [H⁺] and [Na⁺]. We measure the contact angle of a droplet of CCl₄ on a silica surface immersed in aqueous solution. Our data show that the contact angle of the CCl₄ droplet changes with the *pH* and the *pNa* of the aqueous solution, with both equilibria contributing to the observed *pH*-dependence of the droplet contact angle.¹⁵⁻¹⁷ We describe these data in the context of competing equilibria and based on the contact angle data and the known surface energy of the H₂O-CCl₄ interface, we can determine the surface energies for the SiOH-water, SiONa-water and CCl₄-SiOX interfaces. These data are, to our knowledge, the first reports of the surface energies of these systems.

Experimental Section

Chemicals and preparation: For all measurements, the silica surface used was fused silica in the form of a cuvette (ThorLabs). The aqueous solutions were prepared using 18 M Ω -cm water (Milli-Q). Carbon tetrachloride (CCl₄, 99.9%, Sigma-Aldrich), sodium chloride (J.T. Baker), potassium chloride (Spectrum) and hydrochloric acid (CCI) were used in the highest purity grade available, as received. The CCl₄ droplets used were colored with 10⁻⁵ M Solvent Red 7335 dye (Koch Colors) to provide contrast for the contact angle measurements. All glassware used in this work, including the fused silica cuvette, was cleaned with Piranha solution (*Caution! Strong oxidizer!*).

Contact angle measurements: Contact angle measurements were performed on a VCA 2000 Visual Contact Angle System. Dye-containing CCl₄ drops were added to buffered solutions using a micro-syringe. The volume of the drops was kept near 5 μ L. With the drop resting on the cuvette, a picture was taken using the camera and the contact angle was analyzed using commercial software (VCA).

Surface energy measurements: The interfacial tension between CCl₄ and water (ionic strength 0.1M, pH 4.5) was measured using a platinum Wilhelmy plate. The plate was flamed using a handheld propane torch and then submerged into CCl₄. Aqueous solution was added slowly to the crystallizing dish and the plate was slowly pulled through the interface until half of it was in water and half remained in CCl₄. Pressure readings were recorded using commercial software (KSV NIMA).

Results and Discussion

The surfaces we are concerned with in this work are complex structures that are characterized by irregular distributions of surface functionalities and a non-uniform, highly featured physical structure. There are known to be multiple structural forms of silica, ranging from Q^0 through Q^3 , with the superscripted number referring to the number of silanol groups per silicon atom. The compositional distribution of silica among the forms Q^0 through Q^3 depends on the physical format and processing history of the material.⁸⁻⁹ For these reasons, the equilibria that describe the chemical properties of such oxide surfaces are complex and in systems that contain multiple associative species it is important to understand the competition between these processes. We have focused on the competition between H^+ and Na^+ association with the (accessible) surface siloxide functionalities in this work because of the importance of understanding the various reactions that the surface experiences, and the many systems where this competition is operative.

The characterization of oxide surfaces is hampered by the intrinsic complexity of the material, its inability to be addressed electrochemically and the small number of chemical functionalities that determine the surface properties. A typical silica surface has a silanol density of 4-8 $\mu\text{mol}/\text{m}^2$ and the “molecular” surface area can vary widely relative to the geometric surface area, depending on the physical form of the silica.⁹ The characterization of surface silanol groups by NMR and other techniques has provided a great deal of insight, especially in terms of the pK_a s that characterize the silica surface.¹⁸ Among the properties of surfaces that determine their utility is their surface energy. We have chosen to examine changes in the surface energy of the silica surface using contact angle measurements. Despite the outward simplicity of this measurement, the results contain information on the relative surface energies of the interfaces involved in the

measurement and such measurements are amenable to being performed *in situ*, under ambient conditions.

Initially, the goal of this work was to characterize the $pK_a(s)$ of a silica surface *in situ*, using contact angle measurements of a CCl_4 droplet immersed in aqueous solution of controlled pH. Initial results of this work produced results that were not consistent with the known pK_a values of silica, and, the pH-dependence of the CCl_4 contact angle data changed with the ionic strength of the aqueous solution (Fig. 9).¹⁹⁻²⁰ These inconsistencies required further examination.

As noted above, we interrogate the silica surface with a droplet of CCl_4 where both the droplet and the silica surface are immersed in an aqueous medium containing known amounts of H^+ and Na^+ . The contact angle of a droplet of a liquid on a surface is determined by the balance of surface energies between all of the interfaces involved, as described by Young's equation,

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} = \frac{\gamma_{SiOX-H_2O} - \gamma_{SiOX-CCl_4}}{\gamma_{CCl_4-H_2O}} \quad [1]$$

Where the surface energies γ are for the interfaces indicated. For the purposes of this work we consider that the $SiOX-CCl_4$ surface energy changes to a limited extent at most (*i.e.* $\gamma_{SiOH-CCl_4} \sim \gamma_{SiONa-CCl_4}$, *vide infra*) and $\gamma_{CCl_4-H_2O}$ changes negligibly with changes in aqueous solution composition. The dominant change in surface energy for this system is for the $SiOX-H_2O$ interface, where $X = H^+, Na^+$. In order to maintain these conditions and vary the pH of the aqueous solution, the ionic strength of the aqueous solutions is held constant, and for this situation to obtain the ionic strength is determined by the lowest pH solution used. In other words, for a solution of HCl at pH = 1, the $[H^+] = [Cl^-] = 0.1$ M, and $[Na^+] = 0.0$ M. For the measurements reported here, the ionic strength was maintained at either 0.1 M or 0.01 M.

For the system under consideration, where the silica surface is in equilibrium with an aqueous solution containing, in general, both Na^+ and H^+ , the competitive equilibria of interest are given by



The surface species of interest in this work are SiOH, SiO^- and SiONa. We assert that the association of H^+ and Na^+ with SiO^- is sufficiently favorable (*i.e.* small K_{dis}) that the steady state concentration of SiO^- is small for our experimental conditions. In this case, the ratio of surface coverage by SiOH to SiONa is given by

$$\frac{[\text{SiONa}]}{[\text{SiOH}]} = \frac{[\text{Na}^+]K_a}{[\text{H}^+]K_{Na}} \quad [3]$$

The ratio of siloxide sites associated with Na^+ to those associated with H^+ is directly relevant to the surface energy of the macroscopic silica surface. As noted above, knowledge of the exact density and distribution of silanol (and siloxide) sites is not known, and consequently the evaluation of absolute surface concentrations of each species is not feasible. We can, however, normalize the ratio to fractional monolayer coverage of each species, with $[\text{SiOH}] = \alpha$ and $[\text{SiONa}] = 1 - \alpha$. Substituting these quantities into Eq. 3,

$$\frac{K_a[\text{Na}^+]}{K_{Na}[\text{H}^+]} = \frac{1 - \alpha}{\alpha} \quad [4]$$

The surface energy of the silica surface is the weighted average of the surface energies for the SiOH and SiONa components of the surface, and this expression of surface energy can be related to the contact angle of a CCl_4 droplet on the silica surface through Eq. 1, where

$$\gamma_{\text{SiOX-H}_2\text{O}} = \alpha\gamma_{\text{SiOH-H}_2\text{O}} + (1-\alpha)\gamma_{\text{SiONa-H}_2\text{O}} \quad [5]$$

The quantities α and $(1-\alpha)$ can be calculated as a function of $[\text{H}^+]$, $[\text{Na}^+]$, K_a and K_{Na} , and all of these quantities are known, save for K_{Na} . Using Eq. 5 to determine the surface energy of the SiOX-H₂O interface as a function of pH, and with the assumptions provided above, we can model the pH-dependence of the contact angle data for this system.

The experimental data show a change in contact angle between pH 3 and pH 4 for the CCl₄ droplet on silica, immersed in an aqueous NaCl solution with ionic strength of 0.1 M (Fig. 5a). When these measurements are performed using an aqueous NaCl solution with ionic strength of 0.01 M, there is no discernible pH dependence in the range of pH 2 to pH 5 (Fig. 5b). It is known from NMR studies that the pK_a for silanol is 4.5 ($K_a = 3 \times 10^{-5}$) and it is the K_a and K_{Na} values that determine the position of the change in contact angle.¹⁸ The experimental data are consistent with a value of $K_{\text{Na}} = 7 \times 10^{-3}$ and we report the calculated pH-dependence of the contact angle in Fig. 6a for a fixed $[\text{Na}^+] = 0.05$ M as a function of K_{Na} . The SiONa moiety thus dissociates more readily than the SiOH moiety, and this is not a surprising result. The comparison is between a polar bond with some covalent character (O-H) and an ionic association (O⁻ - Na⁺). This model predicts that the position of the change in contact angle should be pH dependent and we observe this to be the case for measurements performed in 0.01 M NaCl (*aq*) (Fig. 5b). We show the corresponding calculated results for $K_{\text{Na}} = 5 \times 10^{-3}$ as a function of $[\text{Na}^+]$ (Eqs. 4 and 5) in Fig. 6b.

With the value of K_{Na} established, and the predicted $[\text{Na}^+]$ -dependence verified experimentally, we consider the information available from the contact angle data. The value of θ implies a negative value for $\cos\theta$, which obtains for $\gamma_{\text{SiOX-CCl}_4} > \gamma_{\text{SiOX-H}_2\text{O}}$. The magnitude of the difference between $\gamma_{\text{SiOH-H}_2\text{O}}$ and $\gamma_{\text{SiONa-H}_2\text{O}}$ determines the change in contact angle that we observe

(Fig. 7). Young's equation (Eq. 1) involves the ratios of surface energies, and the pH-dependence of the contact angle is not, by itself, sufficient to determine the surface energies of the interfaces comprising the system. We have measured using a Wilhelmy plate balance that the surface energy $\gamma_{\text{CCl}_4\text{-H}_2\text{O}}$ is 45 mN/m, and this value is in agreement with literature reports.²¹ With this value and the contact angle data, we can determine that the quantity $(\gamma_{\text{SiOX-H}_2\text{O}} - \gamma_{\text{SiOX-CCl}_4}) \approx 40$ mN/m. Without further information on either quantity separately, we are not able to further elucidate these terms. There are two factors that allow us to determine these surface energies, however. The first is through the use of a Zisman plot (Fig. 8), which yields an estimate of 23.3 mN/m for $\gamma_{\text{SiOX-air}}$. (It should be noted that $\gamma_{\text{SiOX-air}}$ was estimated by using several liquids whose contact angles on quartz are known. A series of plots, each plot with a different combination of liquids, was used to estimate the energies. These plots were averaged together. It is also well established in the literature that the surface tension of water, $\gamma_{\text{H}_2\text{O-air}}$, is 72 mN/m. Taking the difference between these surface energies yields $\gamma_{\text{SiOH-H}_2\text{O}} \approx 49$ mN/m. The extraction of an interfacial energy by taking the difference between two surface energies of surfaces with a common phase is justified based on the finding that $\gamma_{\text{H}_2\text{O-air}} - \gamma_{\text{CCl}_4\text{-air}} = (72 \text{ mN/m} - 26.4 \text{ mN/m}) = 45.6 \text{ mN/m}$, in excellent agreement with experimental data. We note that, while it is feasible to estimate $\gamma_{\text{CCl}_4\text{-H}_2\text{O}}$ from $\gamma_{\text{CCl}_4\text{-air}}$ and $\gamma_{\text{H}_2\text{O-air}}$, because there is not a substantial chemical interaction between CCl_4 and H_2O , the use of this approximation is slightly more open to question for the estimation of $\gamma_{\text{SiOX-H}_2\text{O}}$ because silica and water interact more strongly. It appears based on anecdotal information, however, that this means of estimating $\gamma_{\text{SiOX-H}_2\text{O}}$ does not give rise to large errors. Using these values for the several interfaces, we find that the best agreement between experiment and data are for and $\gamma_{\text{SiOH-H}_2\text{O}}$ and $\gamma_{\text{SiONa-H}_2\text{O}}$ are 48 mN/m and 50 mN/m, respectively, and $\gamma_{\text{CCl}_4\text{-SiOX}} = 90$ mN/m.²¹⁻²³ These data are

summarized in Table 1. It is significant to note that $\gamma_{\text{SiOH-H}_2\text{O}}$ is slightly smaller than $\gamma_{\text{SiONa-H}_2\text{O}}$. Differences in the nature of aqueous solvation of these two species likely plays a role in determining these values.

These findings are the result of competitive equilibria between H^+ and Na^+ for accessible SiO^- sites on the silica surface. It is useful to consider the competition between H^+ and other cations, such as K^+ . Our initial data were acquired using NaCl to maintain constant ionic strength. Using KCl to maintain constant ionic strength allows for a comparison between two different cations. Na (ionic radius 116 pm) and K (ionic radius 152 pm) were found to exhibit the transition in contact angle at the same pH, to within the resolution of our measurements. This finding suggests that K_{K} and K_{Na} are similar, which is not surprising.

Our experimental data show that the contact angles for the CCl_4 droplet are the same for $I = 0.1 \text{ M}$, whether NaCl or KCl is used to establish the ionic strength. This finding suggests that the identity of the cation (Na^+ or K^+) does not alter the solution phase charge screening of the silica surface charge significantly. While it could be argued that the identity of the compensating cation may influence the surface energy of the $\text{SiO}_x\text{-H}_2\text{O}$ interface, the absence of a cation dependence indicates that the density of surface silanol groups is sufficiently low to avoid contributions from steric crowding or charge repulsion. This experimental finding also underscores that it is the physical charge screening effect that is more important than ion-specific effects associated with Na^+ or K^+ .

Conclusions

We have reported on the existence of competitive equilibria exhibited by siloxide groups on a silica surface for association with H^+ and Na^+ cations. We measure the contact angle of a carbon tetrachloride droplet on the silica surface immersed in aqueous solution to gauge changes in the

surface energies of the SiOX-H₂O interface, the SiOX-CCl₄ interface and the CCl₄-H₂O interface, and how these relative energies depend on pH and the ionic strength of the aqueous solution. Our data demonstrate that the pH dependence of the CCl₄ droplet contact angle does not correspond simply to the measurement of the silica surface pK_a, but depends on the competitive equilibria between H⁺ and Na⁺ association. The pK_a of the silanol groups in this pH region is known to be 4.5 (K_a = 3x10⁻⁵) and we find that K_{Na} = 7x10⁻³ by fitting the experimental data to a competing equilibria model.

In addition to measuring the effect of competitive equilibria, when our experimental contact angle data are analysed in conjunction with Wilhelmy plate measurements of the CCl₄-H₂O surface energy and the known values of SiOH-air and H₂O-air surface energies, we can determine the surface energies for both the SiOH-H₂O and SiONa-H₂O interfaces (Table 1). A significant piece of information emerges from these data, that the surface energies of the SiOH-H₂O and SiONa-H₂O interfaces differ by 2 mN/m, or *ca.* 5%. In order to elucidate this information measurement of the CCl₄ droplet contact angle has to be accurate and reproducible to ±2°, a level that challenges the capabilities of the instrumentation used for this work.

This approach to the characterization of competitive equilibria at oxide surfaces offers the opportunity to examine a number of important materials as well as an opportunity to evaluate the effect of surface modification chemistry (*e.g.* phosphorylation) on such surfaces.²⁴ In such experiments, the contact angle of a non-polar liquid droplet can be used to evaluate relative surface energies and competitive equilibria, and contact angle hysteresis measurements can be used to characterize the homogeneity of the surface modification chemistry applied to the interface.²⁵⁻²⁷ That work is presently underway.

APPENDIX

$\gamma_{\text{SiOH-H}_2\text{O}}$	48 mN/m
$\gamma_{\text{SiONa-H}_2\text{O}}$	50 mN/m
$\gamma_{\text{SiOX-CCl}_4}$ ²²	90 mN/m
$\gamma_{\text{CCl}_4\text{-H}_2\text{O}}$ ²¹	45 mN/m

Table 1. Surface Energy. Surface energy values calculated from the contact angle measurements and Wilhelmy plate measurements.

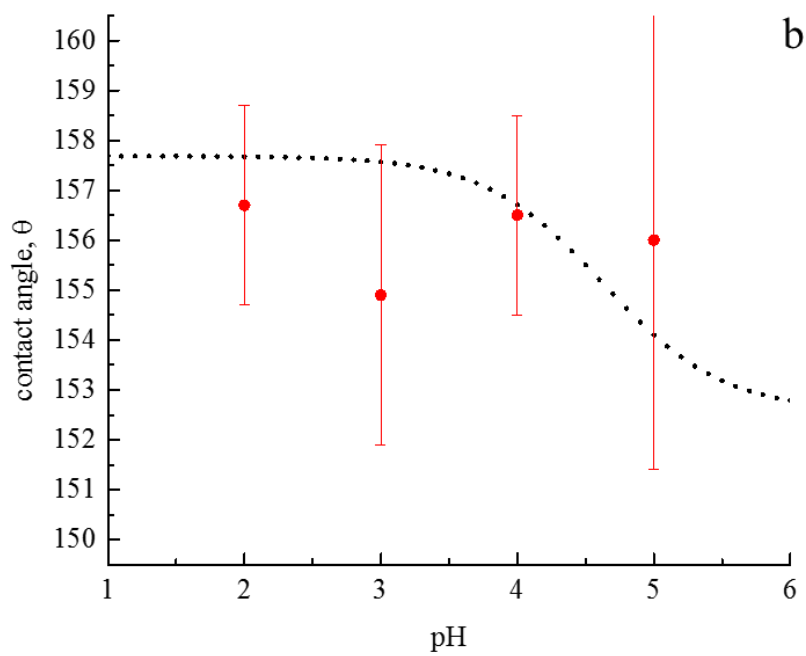
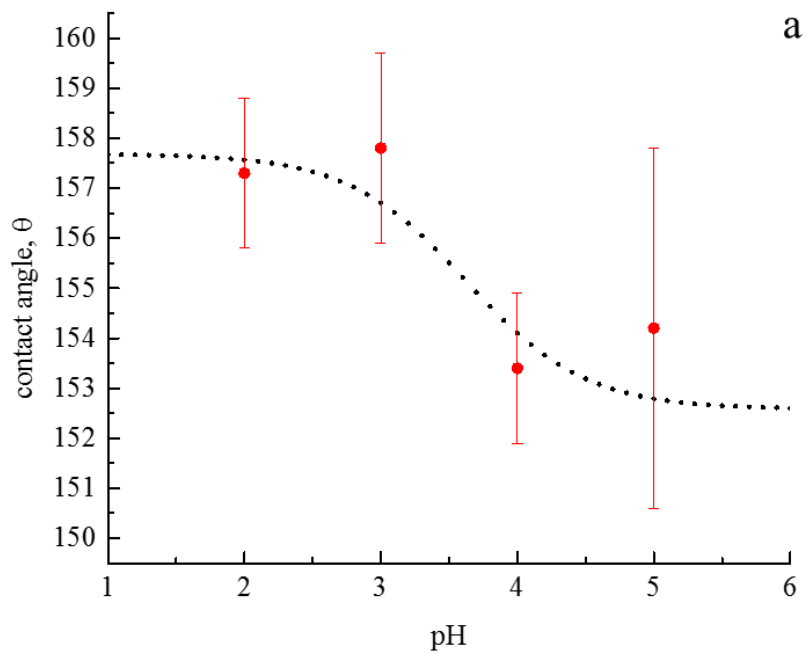


Figure 5. Contact angle measurements. Contact angle measurements as a function of pH at 0.1M ionic strength (a) and 0.01M ionic strength (b).

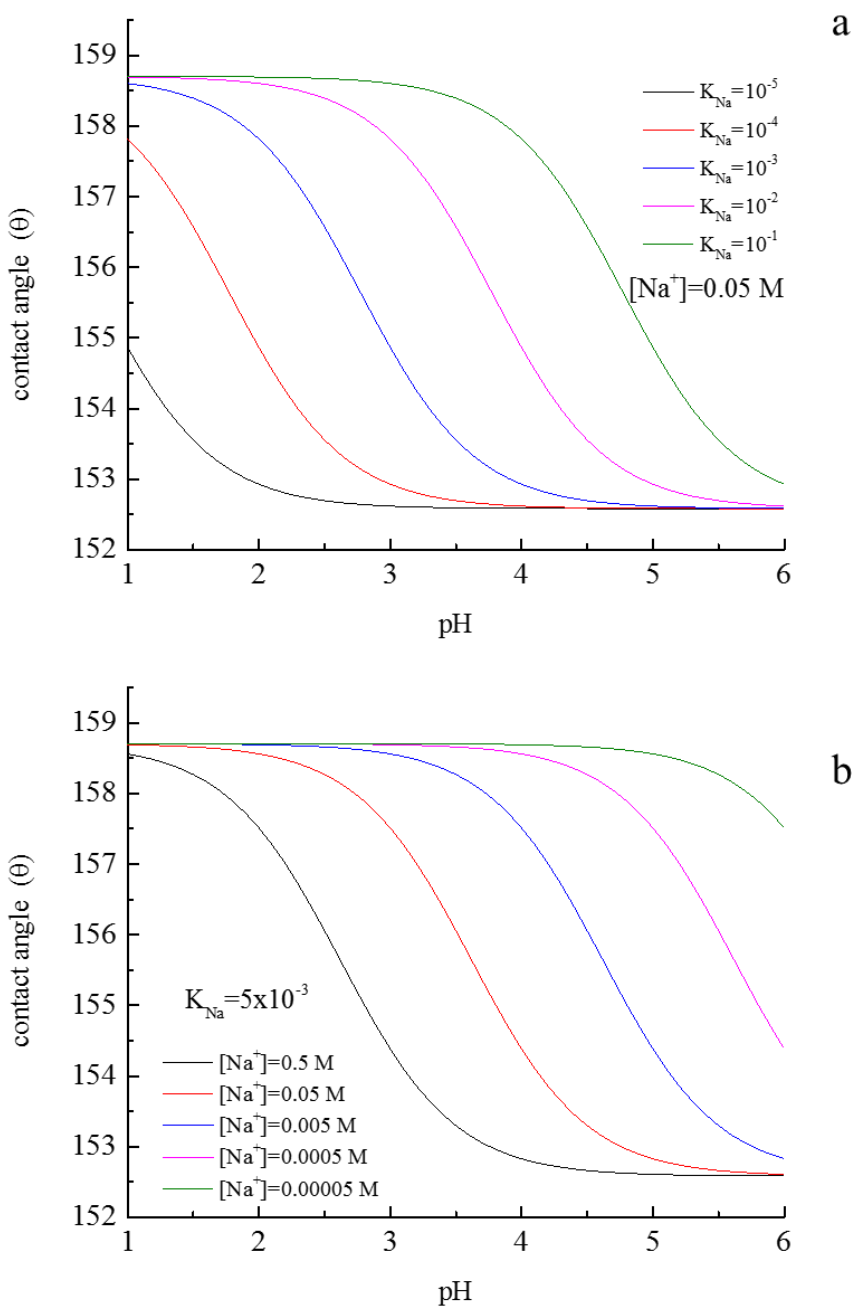


Figure 6. Association Constant Model. The apparent pKa transition was modelled as a function of association constant (a) and of sodium concentration (b). The contact angle is shown as a function of pH.

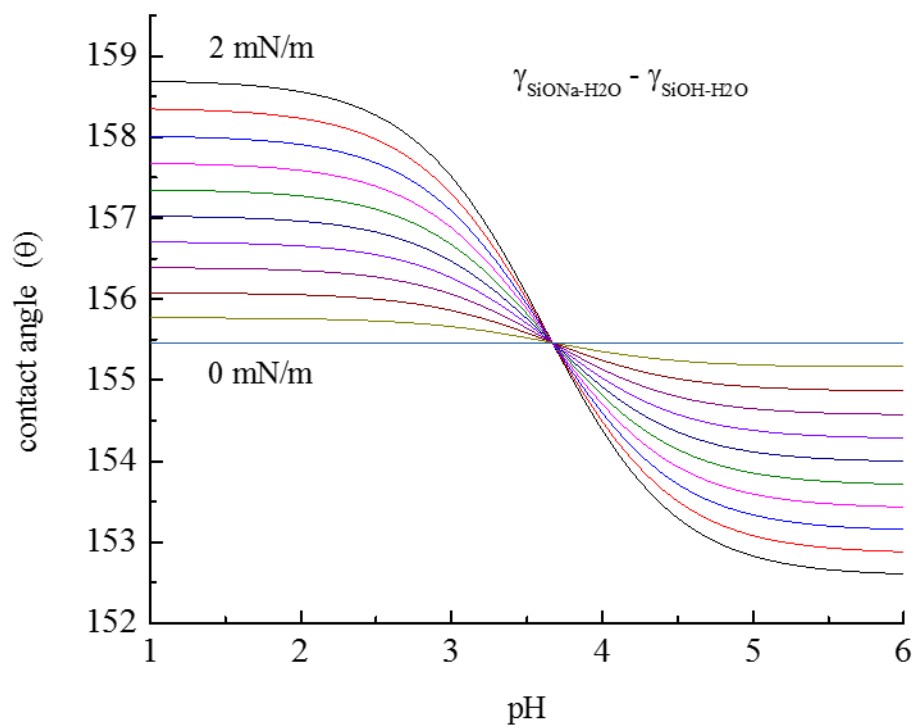


Figure 7. Surface energy difference. The change in surface energy affects the magnitude of the contact angle change. This model shows energy changes from 0 mN/m to 2 mN/m

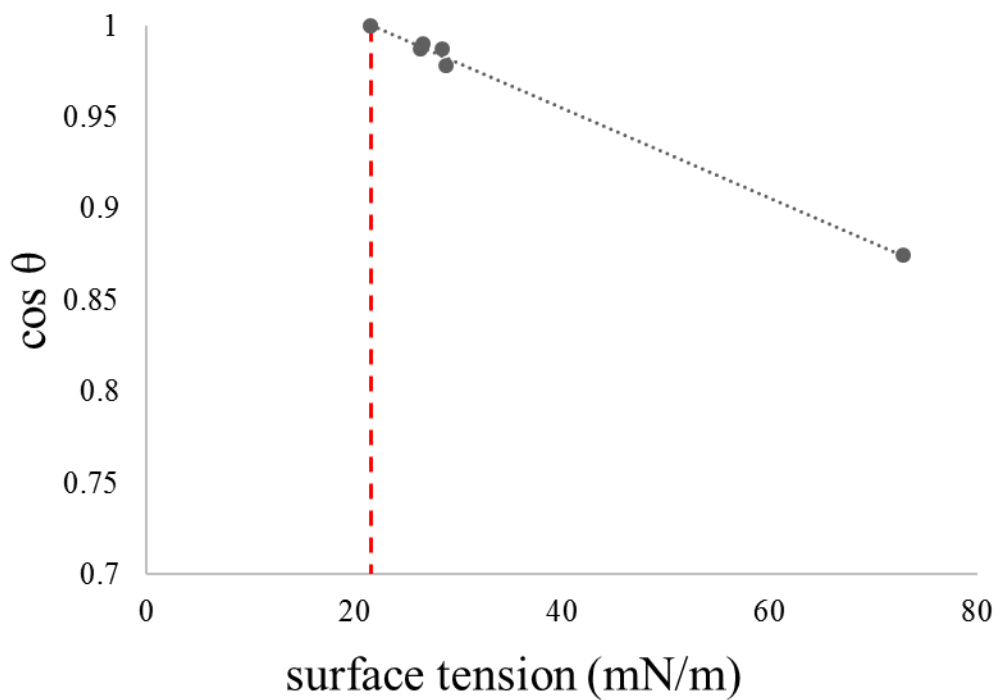


Figure 8. Zisman Plot. Zisman plot approximation used to determine the surface energy of silanol in air.

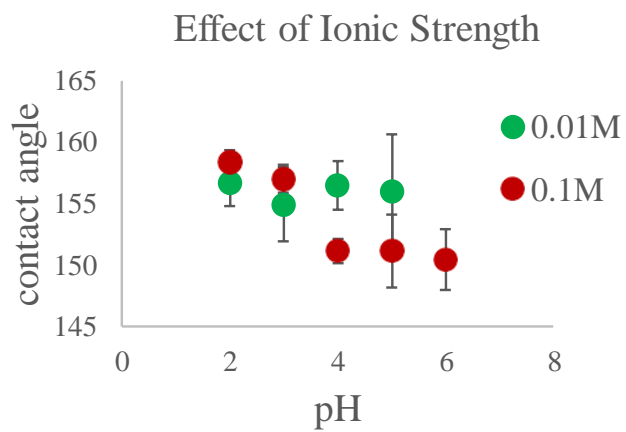
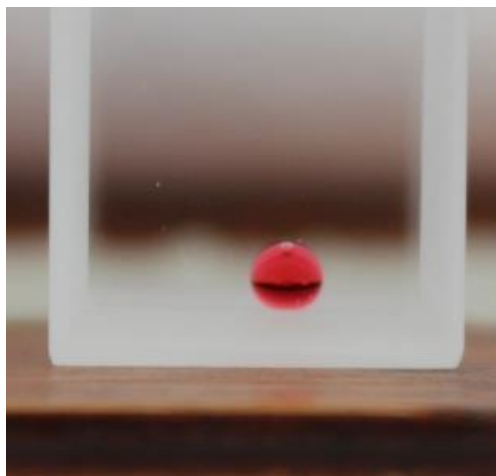


Figure 9. Ionic Strength on Buffer shape. The contact angle was measured at different pH values under two different ionic strength. The image left shows the set-up of the experiment.

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Chapter 3

Conclusions and Future Directions

The competitive equilibria presented in this paper serves to show the inherently dynamic system present at any charged interface. Driven but a tendency towards neutrality, a charged surface will associate with counterions in solution. The strength of this interaction is driven by the relative concentrations of any counterion species present in the buffer. We have established a relationship between sodium concentration and proton concentration on the magnitude of contact angle and the change on the interfacial surface energy. By relying on the fact that the dominate interaction is that between the surface and the buffer we can establish the equilibrium constants for cationic species on the silica surface. The K_{Na} of this system is on the order of 7×10^{-3} and is the first such reported value.

The ability to extract such constants from contact angle measurements is a useful tool as a measure of finding association constant of various metal ions to functionalized surfaces. The impact of this work could see applications in work that involves membrane stability on planer substrates or any system that needs facile diffusion as well as reproducible binding data. By also showing the relationship between apparent binding constant for metal with the surface as a function of pH, greater control over the reactions occurring at the surface can be obtained.

We have also shown a method of determining the surface the magnitude of the interfacial energy of the system. By knowing the contact angle of various liquids on the quartz surface and by knowing the interfacial energy of those liquids in air, the energy of the quartz surface in water can be known. Interfacial energy values are hard to come by for solid interfaces. Zisman plot provide a method of estimating the energy of a surface in air but since this was only an estimate

and depends greatly on the contact angle of the liquids used, a more robust method was developed. While still using a Zisman estimation, the energy of the silanol surface was water was found. This was done taking into consideration that the difference between the interfacial energy surface A and surface air and the interfacial energy between surface B with air gives the interfacial energy between surface A and surface B. This was used to estimate the quartz-air interface and then calculate the quartz-water interface. The original contact angle data was used to measure the difference between silica-carbon tetrachloride and silica-buffer (~40mN/m).

By using both the Zisman approximation and the contact angle measurements, the value of the silica-buffer interfacial energy was found in both pH regions. This was a value of 48mN/m at low pH and 50mN/m at high pH. Care must be taken to remember that this result was seen at an ionic strength of 0.1M and as such the sodium ions were able to outcompete the protons for the surface. The change in contact angle is not apparent at ionic strength 0.01M.

Surface energy values are typically hard to come by as these values have not before been reported to the best of our knowledge. These surface energy values are not often known and are important in techniques that rely on changes in surface energies. It is also shown that the change in surface energy with protonation, 2 mN/m, is small but has a noticeable effect on the contact angle of the system.

Future Work

This work has laid the ground for a wide variety of experiments moving forward, some of which has been investigated during the course of this work. It establishes not only equilibria processes for surfaces and metal ions but also competitive equilibria between the metal ions and protons for the surface. By modulating the ionic strength of the solution the equilibria of the surface towards either the proton or the metal ion can be manipulated.¹⁹⁻²⁰ This has implications in the

field of separations where the quality of the separation is dependent on the affinity of the analyte for the surface. This means that factors such as pH, ionic strength, and ion identity play large role in the separation. Refining such separations is possible knowing the equilibrium constants for the analytes with the surface.²⁸

More complicated surfaces can also be investigated with this technique. For example, since a quartz surface has such a wide distribution of morphologies and reactivities, it would be good to modify the surface in such a way that gives a more dependable surface. An exhaustive phosphorylation was attempted and this the measurements were repeated. It was presumed that the phosphate moiety would give two contact angle changes as there are two acidic protons. The following data set was from a preliminary experiment with a modified surface. It was done before the method was completely refined and as such will be revisited in the future. It is hard to draw any conclusion from this data but there does seem to be a transition between pH 1 and pH 2 and then again being pH 8 and pH 10. The nature of these equilibria are different than the initial experiment and deserve more attention.

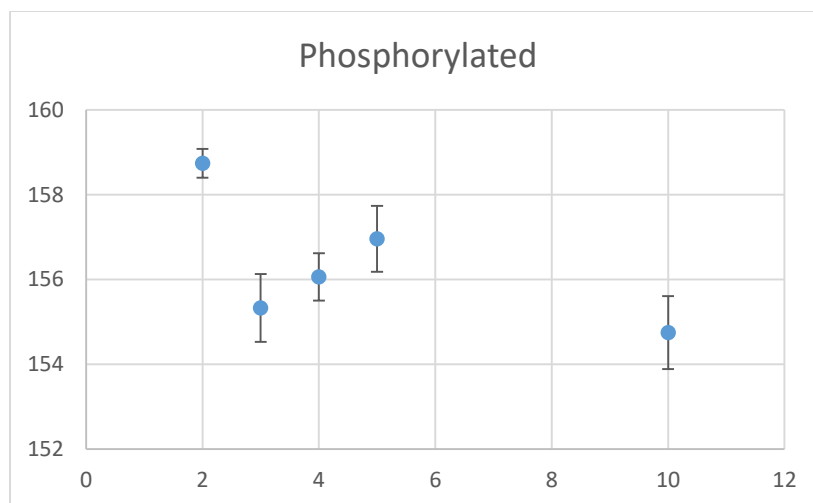


Figure 10. Phosphorylated surface data. pKa values are 7.2 and 12.3. The first proton, pKa 2.2, is the one that is reacted when the phosphate group is attached to the surface.

In addition, bilayer dynamics could be investigated with this method. Complex systems with different metal ions with multiple association constants could be investigated for change in bilayer fluidity as a function of pH. It could be possible to change the identity of the metal ion currently bound to the surface while the other is free to diffuse throughout the system.

These effects as seen provide insight into the fundamental nature of surfaces that has not been dealt with in a thorough manner. The future experiments planned seeks to fill the apparent hole in the literature.

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