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The Effects of Relative Humidity and Valency on Water Absorption and Structure in Polyelectrolyte Brushes

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Honors Project in Polymer Science

PLYS 497-802

Andrea Klima

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Executive Summary

How does the structure of water on a polyelectrolyte brush change when exposed to different levels of humidity? How does the water structure and absorbance change when different counterions are present? How does the water structure respond to a change in ion valency? These are a few of the questions that guided the direction of study over the course of the project where water absorption in polyelectrolyte brushes was measured as a function of humidity.

Polyelectrolyte brushes offer a wealth of possibilities for many environments where a surface is exposed to either vapor or liquid. Such polymer brushes are formed through initiating a surface and polymerizing it to attach high density macromolecules that stretch away from the surface.⁴ Polyelectrolyte brushes are polymer brushes that contain a charge, which provides additional functionality to allow the structure of the brush to change in response to pH levels, counterions, and the surrounding environment.⁴ These responses can affect macroscopic surface properties, such as friction and wettability. Previous reports have drawn conclusions between increased vapor absorption and reduced friction on a surface.³ To gain a better understanding of this relationship, positively and negatively charged polyelectrolyte brushes were synthesized using Activators Regenerated by Electron Transfer Atom Transfer Radical Polymerization, or ARGET ATRP and soaked in a variety of 0.1 molar solutions containing either a monovalent or multivalent ion. The brushes were then dried using nitrogen flow and were exposed to a range of relative humidity.

Attenuated Total Reflection Infrared (or ATR IR) spectroscopy was used to collect spectra of both the positively and negatively charged brushes at various humidity levels. These spectra provided a way to visualize the water peaks resulting from humid vapor absorption by the brush, examples of which are provided in Figures 23 and 24. As humidity increased, the

water peak present at approximately 3400 cm^{-1} increased in intensity and shifted towards lower wavenumbers. The shift in the water peak could be explained by an increase in more strongly bonded ice-like water.³ MATLAB programs provided in the appendix were used to calculate the fraction of ice-like, liquid-like, and free water present under the water peak. Analysis presented in Figures 2, 3, 4 for PSPMA and Figures 11, 12, 13 for PMETAC showed that the area of ice-like, liquid-like, and free water increased in response to increasing relative humidity. Likewise, multivalent ions produced larger water fractions at all humidity levels than monovalent ions regardless of whether the ion was positively or negatively charged. These results were compared alongside literature to ensure accuracy and draw conclusions between the experimental findings and previous research.

Completing this research project provided an opportunity for hands on learning through mastering synthesis of polyelectrolyte brushes and developing a better understanding of polymerization techniques. Additional skills related to operating, reading, and identifying peaks using ATR IR spectroscopy were also improved over the length of the project. Completing the analysis and understanding the reasoning behind increasing and shifting water peaks allowed for a better grasp on the differences in humid vapor absorbance for different counterions. These results could inspire future research to determine how water structure on a brush when a multivalent counterion is used affects the friction or wettability of a polyelectrolyte brush's surface. Additionally, spectra could be collected when the brush is exposed to different pH values to determine the effects of pH on water structure and absorption on the brush surface. Since polyelectrolyte brushes can be used in a variety of applications, understanding the behavior under different conditions can provide insight on how to tailor the counterion on the brush to achieve the desired vapor absorbance or water structure. This project offered a unique

opportunity to explore both polymerization techniques and spectroscopy analysis to understand how manipulating both relative humidity and the counterion affect humid vapor absorbance and water structure on polyelectrolyte brushes.

Introduction

The ability to select a material for a specific use is a critical engineering skill that must be considered before the development of any new process. Material selection typically involves investigating the properties of the intended material to ensure that it is compatible with its environment. Failure to ensure compatibility between materials could have disastrous consequences such as leaks, over pressurization, or corrosion. To ensure compatibility, material properties such as solvent resistance, abrasion resistance, and temperature capacity can be tested. Material properties are largely influenced by what structures make up the surface of a material. Changing the chemical structure present at the interface between a material's surface and its surroundings can impact how the material behaves when it interacts with another solid, liquid, or gas. Polymers are large macromolecules comprised of smaller, simpler chemical units called monomers.¹ Monomers can be either natural or synthetic, and multiple different monomers can be bonded together to form copolymers.¹ Due to the chemistry of the monomer, polymers have unique chemical and physical properties that allow them to aid in changing surface behavior. One way to modify a surface is to initiate and perform a polymerization reaction where polymer chains are chemically adhered to a surface. The new surface formed by the polymer chains is called a polymer brush, and depending on the monomer used, the chains carry a positive or negative charge. Since the polymer brush contains charges, it is referred to as a polyelectrolyte brush. The material property that was studied throughout this project was humid vapor absorption, or how much water was absorbed by the polymer chains on a silicon crystal's surface

when exposed to varying humidity levels. Two different monomers were used, [2-(methacryloyloxy)ethyl] trimethylammonium chloride (METAC) to form positively charged brushes, and 3-Sulfopropyl methacrylate (SPMA) to form negatively charged brushes. To measure vapor absorption by the polymer, the brushes were submerged in different solutions containing either monovalent or multivalent ions that were attracted to the polyelectrolyte brush. Depending on the ion used, the water content and water structure inside the polyelectrolyte brushes differed. The results were used to develop a better understanding of how different ions affect water structure and can be expanded upon to determine how water structure in a polymer brush affects properties such as friction or wettability of a surface.

Background

The motivation behind measuring the water content and absorption on the polyelectrolyte brushes containing different ions stems from the wide range of brush applications in both aqueous and air environments. Similarly, water on the surface of the brushes contains liquid, free, and ice-like regions. The fraction of each type of water present on the surface depends on the counterion used. The ice fraction is of particular interest since ions are heavily involved in the ice formation process, which is limited by the rate of ice nucleation.⁵ Reports have demonstrated that ion exchange can be used to control the surface dynamics and water structure on the polyelectrolyte brush, since the structure of water on a solid surface largely influences ice nucleation.⁵ Likewise, changing the ion present on the polyelectrolyte brush only affects microscopic properties of the surface, leaving all macroscopic surface properties constant for all trials. Polyelectrolyte brushes provide an opportunity to exchange ions while also controlling the thickness and grafting of the polymer chains on the brush surface, which are heavily stretched when exposed to water.⁵ The swelling and stretching of chains in prior research provided a

source of motivation to study the effects of water structure and absorbance of the polyelectrolyte brush when exposed to water vapor present in air. In the article presented by Zhiyuan He, both PMETA and PSPMA brushes were used alongside various ions to draw conclusions between fraction of ice-like water in the sample and ice nucleation. The halide ions (Fluorine, Chlorine, and Iodine) presented an additional relationship between charge density and ice nucleation. As the charge density decreased, the hydrogen bond making rate increased, thereby increasing the number of ice-like water molecules in the sample.⁵ Using this prior research as a guide, the PMETAC and PSPMA brushes used for humid vapor experimentation were tested using several of the ions presented in the Zhiyuan He article. However, the ice fraction and area for the various ions were measured by changing relative humidity rather than temperature, since the chains swell and stretch in the presence of water vapor in air.

The brushes used in the research paper *Tuning ice nucleation with counterions on polyelectrolyte brush surfaces* were prepared on a gold surface, and ions were exchanged by placing the brushes in 0.1 Molar solutions for 60 minutes. The polyelectrolyte brushes used to measure ice fraction and area as a function of relative humidity were prepared on silicon crystals. Counterion exchange was achieved by placing the brushes in 0.1 Molar solutions for approximately 5 minutes.

Experimental Methods

The methods and procedures used to synthesize and examine brush structure closely resemble the techniques described in the article titled “Humidity-Induced Glass Transition of a Polyelectrolyte Brush Creates Switchable Friction in Air”. Polyelectrolyte brush synthesis was performed using Activators Regenerated by Electron Transfer Atom Transfer Radical

Polymerization, or ARGET ATRP. Since the polymerization process occurs at the surface, special care must be taken to ensure all glassware is clean of contaminants prior to use. To ensure all glass was clean, each piece was placed in a base bath containing potassium hydroxide for at least an hour before being rinsed several times with deionized water and drying in an oven. All glassware was covered with aluminum foil to prevent further contamination once cleaned. The following processes described below were followed to synthesize the polyelectrolyte brushes.

Cleaning the Crystals

Before polymerization can occur, the surface of the silicon crystals must be cleaned to remove any surface impurities. To clean the surface, sulfuric acid and hydrogen peroxide were mixed to create piranha solution, a highly corrosive mixture that removes any layers of dirt or polymer from the surface of the crystal. Since piranha solution is extremely corrosive, this part of the procedure occurred in a fume hood and chemicals were handled using rubber gloves in addition to nitrile gloves, safety glasses, and a lab coat to avoid contact with the skin. All silicon crystals that needed to be cleaned were placed inside a Teflon dish, which was then placed inside a larger glass dish for additional containment inside the hood. To begin making the piranha solution, 50 ml of sulfuric acid was added to a glass beaker inside the fume hood. The beaker was then placed on a hot plate inside the hood and the contents were allowed to heat until fume vapors became visible. Using rubber gloves to avoid contact with sulfuric acid, the heated beaker was poured into the Teflon dish with the crystals. 20 ml of hydrogen peroxide was then poured into the dish containing both the crystals and sulfuric acid to start the piranha treatment. The fume hood was closed completely, and all gloves were washed thoroughly. The piranha solution was left to clean the crystals for approximately 20 minutes or until the reaction completed. During treatment, the solution bubbles violently as gas is released. Once all bubbling has

completed, it is safe to rinse the crystals with deionized water to wash the solution off the crystals. The wet crystals were then dried using nitrogen and were plasma treated for 5 minutes before beginning initiation.

Initiation

The initiation for the polymerization of both PSPMA and PMETAC brushes involved the vapor deposition process. To complete initiation, the crystals were placed in a desiccator alongside the initiating liquid under a vacuum pressure less than 140 mTorr, and then placed in an oven under vacuum pressure at 90 degrees Celsius for 4 hours. To begin this process, the desiccator was treated with a base bath, rinsed, and plasma treated for 5 minutes. Once treated, the crystals were placed inside and 5 μm of the initiator, 3-(triethoxysilyl)propyl 2-bromo-2-methylpropanoate, was placed inside the desiccator in a small glass cup beside the crystals. An o-ring was placed between the top and bottom section of the desiccator, and a valve was attached to the top section, which was then closed completely to form a seal. To hold the pieces in place at room pressure, a support clamp was fitted around the glass and secured to prevent the pieces from moving. Next, the desiccator was attached to the vacuum setup and a piece of rubber tubing was secured to the neck of the chamber. An example of the experimental setup is pictured in Figure 1. All valves on both the desiccator and vacuum line were then checked to be closed. Next, the vacuum pump was switched on, and the valves on the vacuum line and desiccator were opened to allow flow to the glassware. To seal the desiccator under vacuum, the top valve was closed. All the other valves were then closed, and the pump was shut off. The rubber hose was then removed. If the metal clamp around the glassware was no longer tight, the sample was confirmed to be under vacuum. The desiccator was then placed in the oven, which was set to 90 degrees Celsius. Once the door to the oven was closed, the heat and vacuum were turned on, and

vapor deposition commenced. After 4 hours, the glassware was removed, and the crystals were sonicated in toluene for a few minutes. Following sonication, the crystals were rinsed with deionized water and dried with nitrogen. After initiation, the surface of the brush should be hydrophobic. The crystals were then stored in clean, plastic vials until the reaction was performed.



Figure 1. The experimental setup pictured above shows the process for placing the desiccator under vacuum. The silicon crystal is positioned alongside the initiator, which was placed in the small vial. The valve on top of the desiccator is open, and the orange tubing is connected to draw vacuum in the vessel. The green clamp ensures a tight seal between both glass pieces.

Reaction

The general recipes for both the PSPMA and PMETAC brushes provided below were used to synthesize the polyelectrolyte brushes. Both recipes provided enough solution to submerge one crystal in the liquid for the allotted reaction time. The general recipes provided can be increased or decreased by a scalar multiple depending on the number of desired brushes.

Table 1. PMETAC General Recipe

Reactant Name	Target Quantity (Moles)
50/50 Mixture of Methanol and Water	8.95E-02
METAC Monomer	1.11E-02
Copper (II) Bromide	2.09E-06
Bipyridine	2.13E-05
Ascorbic Acid	2.12E-05

Table 2. PSPMA General Recipe

Reactant Name	Target Quantity
50/50 Mixture of Methanol and Water	3.22E-01
SPMA Monomer	1.46E-02
Copper (II) Bromide	2.91E-06
Bipyridine	2.93E-05
Ascorbic Acid	2.92E-05

When synthesizing both the PMETAC and PSPMA brushes, Copper (II) Bromide, Bipyridine, and Ascorbic Acid were added in excess to individual vials. The 50/50 mixture of methanol and water was also made in excess to provide enough solution to dilute the powder components. The concentration of Copper (II) Bromide, Bipyridine, and Ascorbic Acid could then be calculated to determine the volume required for the reaction. Any volume of those components was subtracted from the target quantity of methanol and water to ensure the ratio of reactants was consistent with the general recipe.

Since the reaction is sensitive to oxygen, all reactants were added to a vial or round bottom flask using a needle under the flow of nitrogen. Once all reactants were added, a second needle was used to transfer the reaction contents to a separate sealed tube containing the silicon crystal. The crystals were then left to react for the designated reaction time: PMETAC, 1 hour and PSPMA, 30 minutes.

Once the reaction completed, the vial contents were poured out into a beaker and the crystal was rinsed and sonicated for a few minutes, first using methanol, and then using deionized water. Following the rinsing cycle, the crystals were dried using nitrogen to remove any water from the surface. The silicon crystals should appear to have a bluish color on the surface and are hydrophilic if polymerization was successful. Ellipsometry was used to measure the thickness of the brush on the surface of the crystal, and the brush lengths for both PSPMA and PMETAC polyelectrolyte brushes synthesized for this length of time were found to be approximately 160 nm.

Measuring the Spectra

To measure the structure of the polyelectrolyte brush on the silicon crystal, Attenuated Reflection Infrared (or ATR-IR) Spectroscopy was used. The silicon crystal was placed in a sample tray with an O-ring and a cover with two ports, one to flow liquid or air in, and another to flow liquid or air out, over top of the crystal. The initial background scan of the crystal was collected using a ThermoFisher Scientific spectrometer with the following settings on the OMNIC software:

Table 3. Summary of the Experimental Set Up Conditions for Collecting Spectra

Detector:	MCT
Window:	Silicon
Aperture:	80

Number of Scans:	100
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The background scan was then saved as a reference for both the PSPMA and PMETAC brushes.

To determine which counterion was present on the brush, the brushes were submerged in 100 mM solutions containing the desired ion. The ion exchange process occurred for approximately 5-10 minutes before the brushes were removed from the solutions and dried by Nitrogen flow. The samples containing the desired ion were then placed in the crystal accessory for the spectrometer to be exposed to various levels of humidity. The experimental set up for humidity testing contained a control panel with a port for nitrogen, knobs to control the wet and dry air, and an outlet tube that was placed over one of the cover ports on the sample. Another tube was placed on the outlet of the cover and placed in a covered vial alongside a hygrometer to measure the relative humidity passing over the silicon crystal. Dry air was passed over the crystal for 15 minutes before humidity testing began to ensure most of the moisture held by the polyelectrolyte brush was released. After the 15 minutes interval passed, a spectrum was collected at 0% relative humidity. Then, the flow of moist air was increased on the control panel to humidify the air passing across the crystal in intervals of approximately 5% humidity. Once the readings stabilized, the spectra were captured. A typical data set completed using this experimental setup ranged from 0% humidity to approximately 85% humidity. Once a complete data set was collected, the information was normalized using the “Auto baseline” feature on the OMNIC software and saved as a csv file to be further analyzed.

Data analysis was then conducted using three separate MATLAB programs to plot the spectra from all humidity measurements on the same axes and measure the location of the water peaks on the spectra at various humidities. The water peak typically appeared around 3400 cm^{-1} and the fractions of the peak corresponding to ice-like water and liquid-like water could be

determined based on the shift in peak. The MATLAB code used to complete the data analysis for this project is provided in the Appendix.

Data and Results

Since the purpose of the experiments performed was to determine how the structure of water on a polyelectrolyte brush changes as a function of relative humidity for different counterions on both PSPMA and PMETAC brushes, three different water areas were considered: ice-like water, liquid-like water, and free water. Ice-like water was characterized by the water area between 3061 and 3265 cm^{-1} . Liquid-like water was characterized by the water area between 3265 and 3520 cm^{-1} . Free water was characterized by the water area between 3500 and 3742 cm^{-1} . The water area is proportional to the quantity of water held by the polyelectrolyte brush, and the water fraction represents the percentage of each water type present on the brush's surface. Comparing the water fraction allows the results from each ion experiment to be compared on the same scale regardless of the total water absorbed by the brush. Experiments were completed twice for ytterbium, magnesium, sodium, chlorine, and sulfate counterions. For the repeated ions, the standard deviation between measurements was calculated and presented alongside the figures. The results from the experiments are provided below.

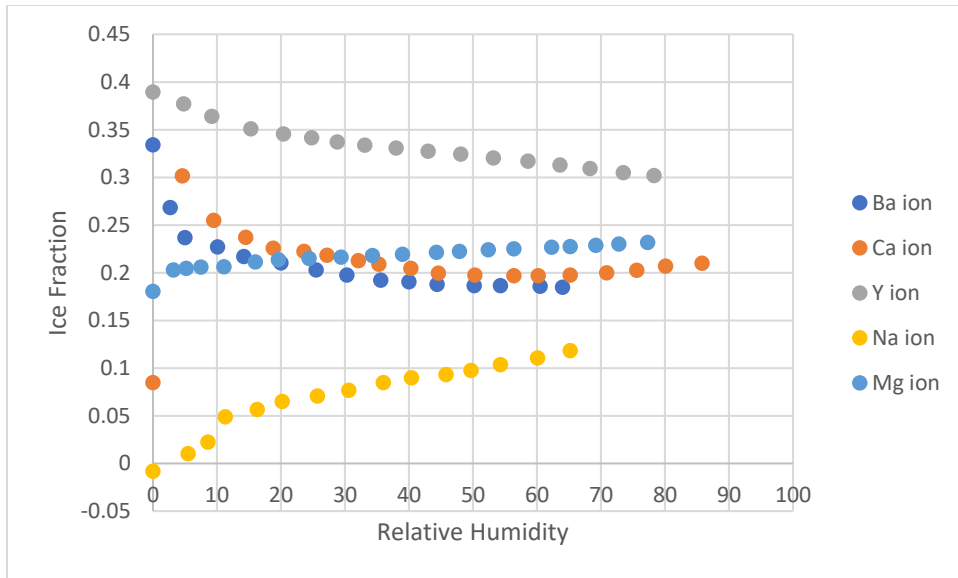


Figure 2. The plot above shows the fraction of ice-like water present on the PSPMA brush when different counterions are present as a function of relative humidity. The error associated with ice fraction was as follows: ytterbium ± 0.011 , magnesium ± 0.013 , sodium ± 0.075 .

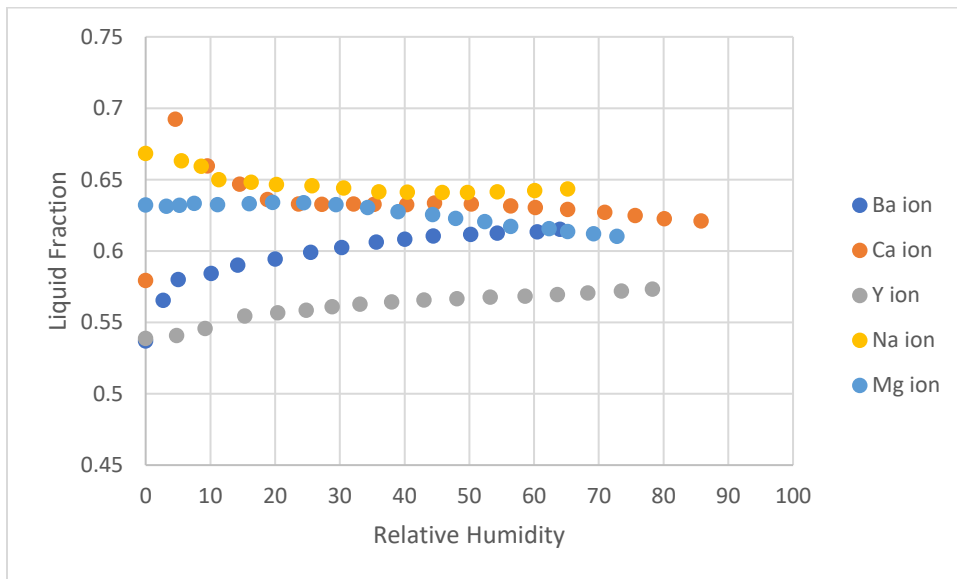


Figure 3. The plot above shows the fraction of liquid-like water present on the PSPMA brush when different counterions are present as a function of relative humidity. The error associated with liquid fraction was as follows: ytterbium ± 0.011 , magnesium ± 0.007 , sodium ± 0.070 .

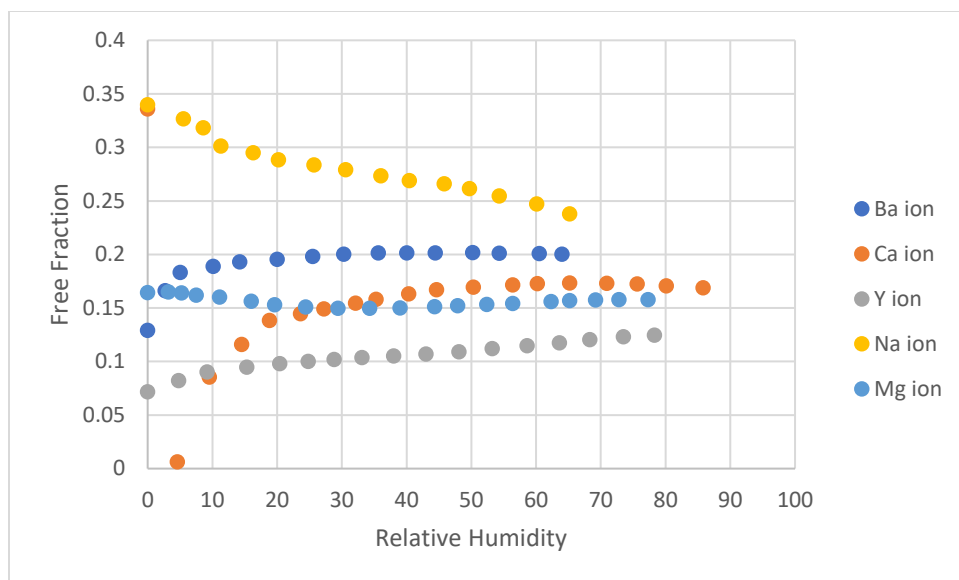


Figure 4. The plot above shows the fraction of free water present on the PSPMA brush when different counterions are present as a function of relative humidity. The error associated with free fraction was as follows: ytterbium +/- 0.008, magnesium +/- 0.007, sodium +/- 0.019.

Looking at Figure 2, the ytterbium ion seems to produce the largest fraction of ice-like water at all values of relative humidity compared to the other counterions studied. From Figure 3 and Figure 4, the fraction of liquid-like and free water are much lower than the fractions of the other ions. Using ytterbium as the counterion on the PSPMA brush produces a water structure that is closest to that of ice, where the molecules are closely packed and highly organized. To confirm the trend in fraction for each water type, an additional trial was conducted, and the data was plotted on the same graph to determine experimental accuracy.

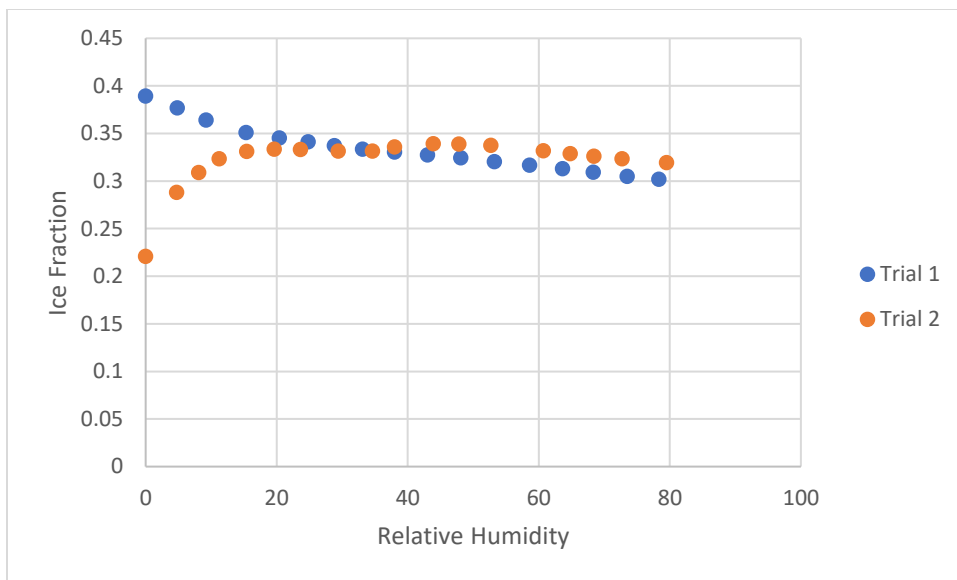


Figure 5. The plot above shows the results of the fraction of ice-like water present on the PSPMA brush containing the ytterbium counterion for each trial as a function of relative humidity. The standard deviation between data points was found to be +/- 0.011.

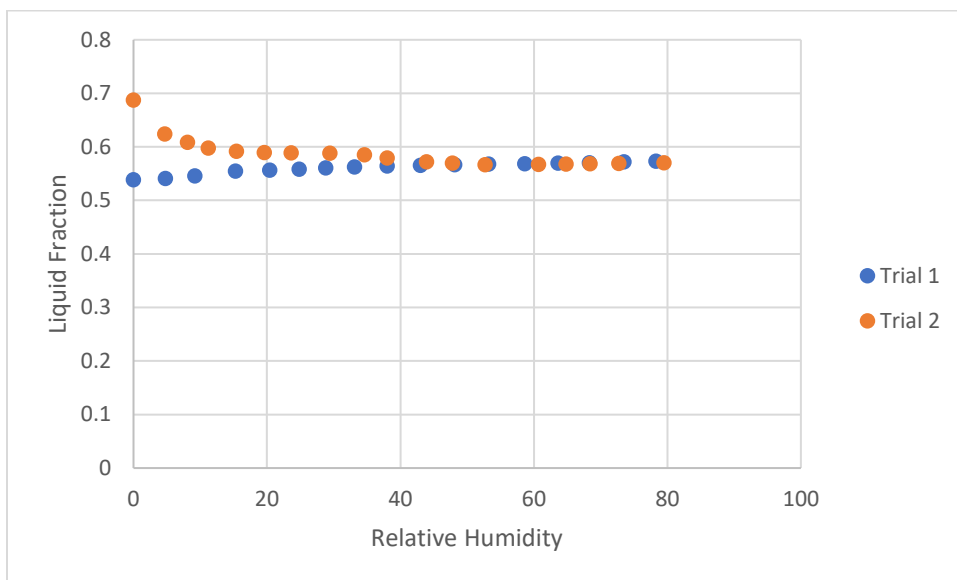


Figure 6. The plot above shows the results of the fraction of liquid-like water present on the PSPMA brush containing the ytterbium counterion for each trial as a function of relative humidity. The standard deviation between data points was found to be +/- 0.011.

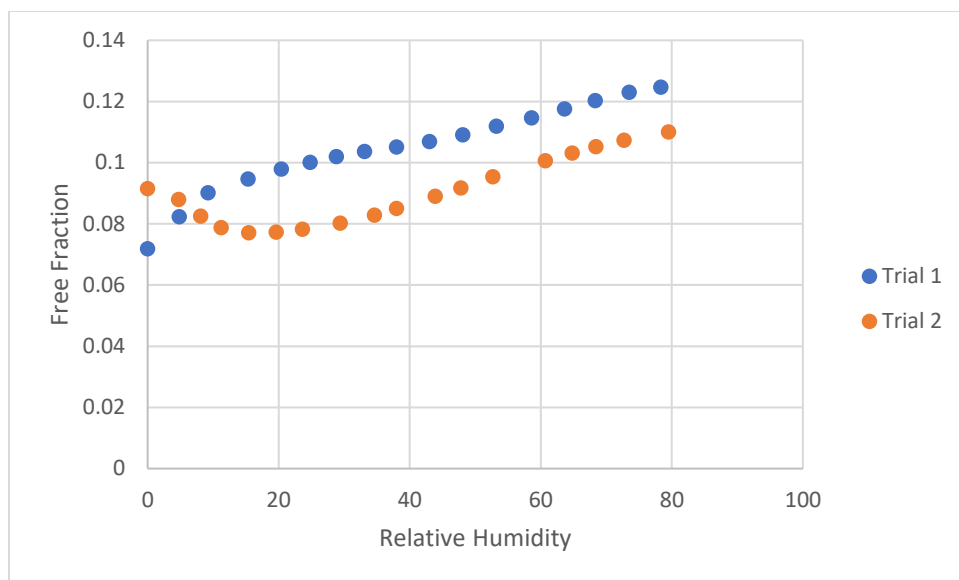


Figure 7. The plot above shows the results of the free water fraction on the PSPMA brush containing the ytterbium counterion for each trial as a function of relative humidity. The standard deviation between data points was found to be +/- 0.008.

The results of both experiments performed using ytterbium as the counterion on the PSPMA brush presented in Figure 5, Figure 6, and Figure 7 tend to diverge at a relative humidity less than 20% and agree at a relative humidity greater than 20%. Therefore, the trends in the ytterbium counterion presented in Figures 2, 3, and 4 are valid. A minimum of two trials were also conducted on magnesium and sodium to ensure the trends presented in 2, 3, and 4 are reasonably accurate for both monovalent and multivalent ions. The same analysis was then applied to the PMETAC brush. At least two trials were conducted on both chlorine and sulfate counterions; the standard deviation between measurements was calculated and reported alongside the corresponding figures.

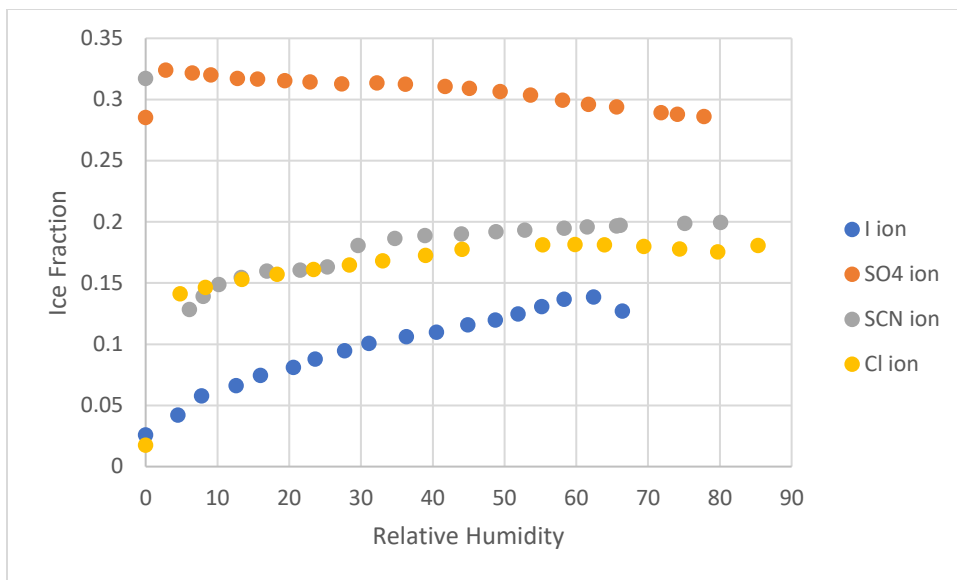


Figure 8. The plot above shows the fraction of ice-like water present on the PMETAC brush for each counterion as a function of relative humidity. The error associated with ice fraction was as follows: chlorine ± 0.050 and sulfate ± 0.096 .

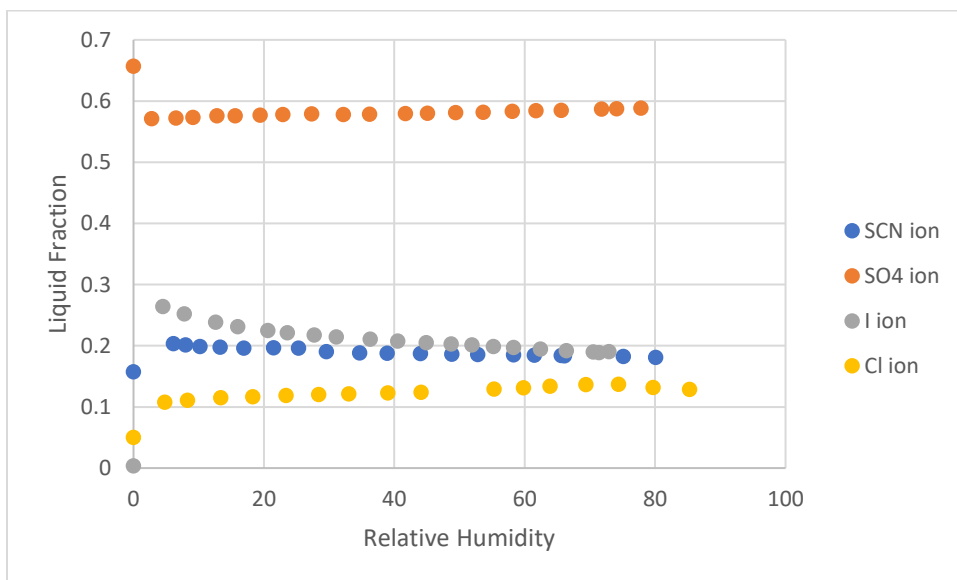


Figure 9. The plot above shows the fraction of liquid-like water present on the PSPMA brush for each counterion as a function of relative humidity. The error associated with liquid fraction was as follows: chlorine ± 0.122 and sulfate ± 0.086 .

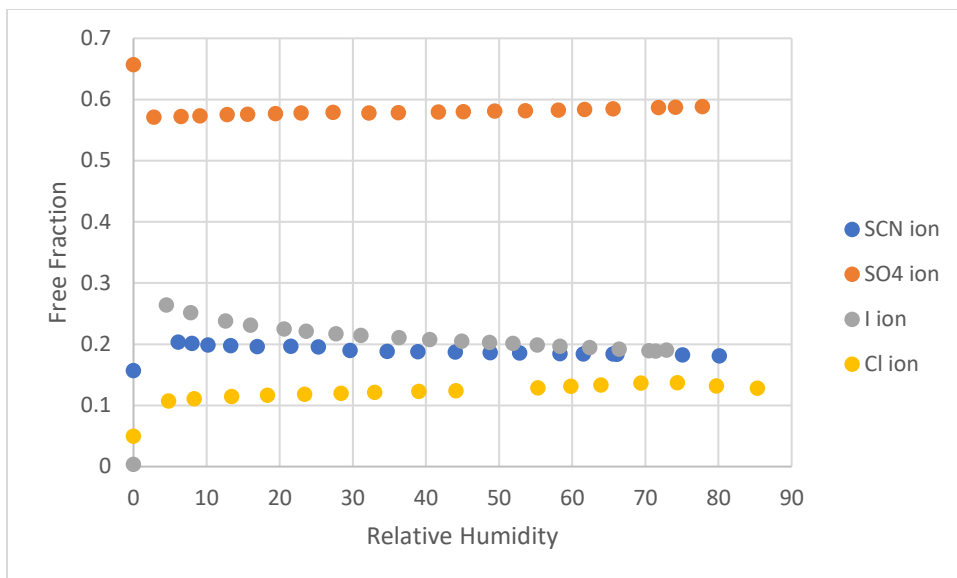


Figure 10. The plot above shows the fraction of free water present on the PMETAC brush for each counterion as a function of relative humidity. The error associated with free fraction was as follows: chlorine ± 0.073 and sulfate ± 0.011 .

Analyzing the data provided in Figure 8, Figure 9, and Figure 10, the sulfate ion produced a much larger fraction of each water type relative to the other ions studied. To ensure agreement in this trend, additional experiments were conducted with sulfate as the counterion.

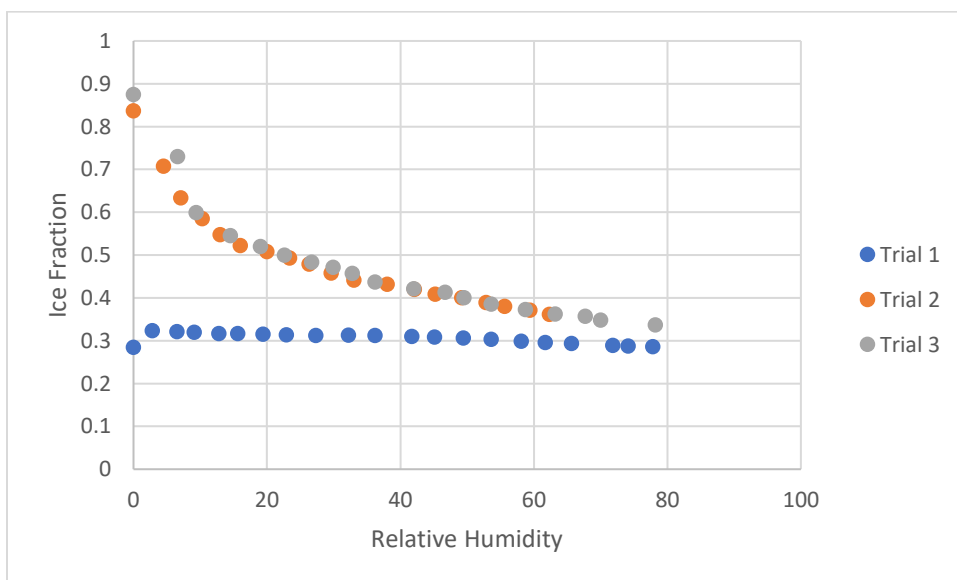


Figure 11. The plot above shows the fraction of ice-like water on a PSPMA brush as a function of relative humidity for a PSPMA brush with sulfate as the counterion for each trial conducted.

The standard deviation between ice fraction measurements was calculated to be ± 0.096 .

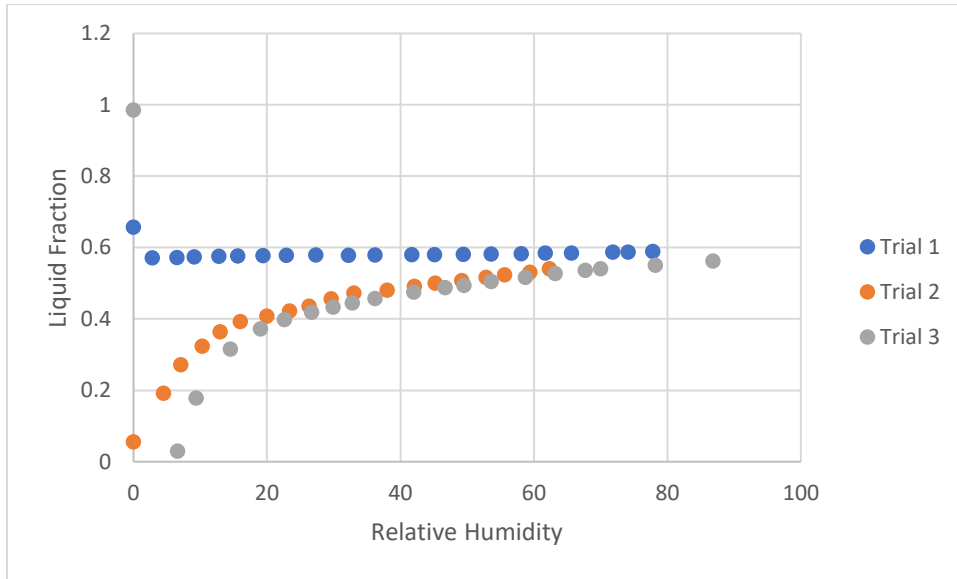


Figure 12. The plot above shows the fraction of liquid-like water as a function of relative humidity for a PSPMA brush containing sulfate as the counterion for each trial conducted. The standard deviation between liquid fraction measurements was found to be ± 0.086 .

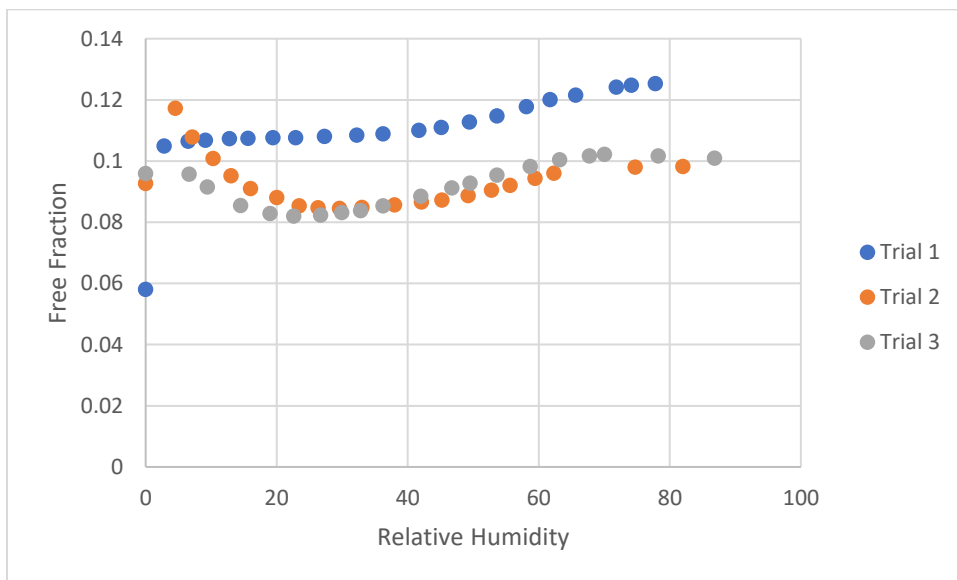


Figure 13. The plot above shows the fraction of free water as a function of relative humidity for a PSPMA brush containing sulfate as the counterion for each trial conducted. The standard deviation between free fraction measurements was found to be ± 0.011 .

As shown in Figure 11, Figure 12, and Figure 13, there is an agreement between the trends present in trials 2 and 3, but a disagreement between these trials and trial 1. The fraction of ice-like and liquid-like water decay in trials 2 and 3 asymptotically approach the fraction of water present in trial 1. The difference between measurements can be explained by differences in the polymer brushes used to collect the spectrums. Since the brushes needed to be re-synthesized to ensure a uniform brush thickness after completing six experiments, trial one was completed using one PSPMA brush, and trials 2 and 3 were collected using a different PSPMA brush. Though both brushes were synthesized on the same crystal, differences in initiator thickness and total brush thickness could result in different absorbances at the same relative humidity. Regardless of what trial is considered, the sulfate ion produces a ice-like, liquid-like, and free water fraction greater than the other monovalent ions studied.

The data collected for the sulphate ion and magnesium ion at each humidity level were compiled onto master spectra curves shown in Figure 14 and Figure 15. These ions were compared since both ions are multivalent and have a charge of ± 2 . As the humidity level increases, so does the absorbance at that wave number. As this occurs, the peak shifts to lower wavenumbers, resulting in a shift in the different water structures present on the polyelectrolyte brushes. The area of ice-like, liquid-like, and free water is smaller at low humidity levels and greater at higher humidity levels. This shift describes the strength of the hydrogen bonding network of the water molecules, where absorbance near 3200 cm^{-1} indicates a stronger bond, or ice-like water, and an absorbance near 3600 cm^{-1} indicates a weaker bond or free water.² The

peaks shown in Figures 14 and 15 support this shift towards a more ice-like water structure at high humidity.

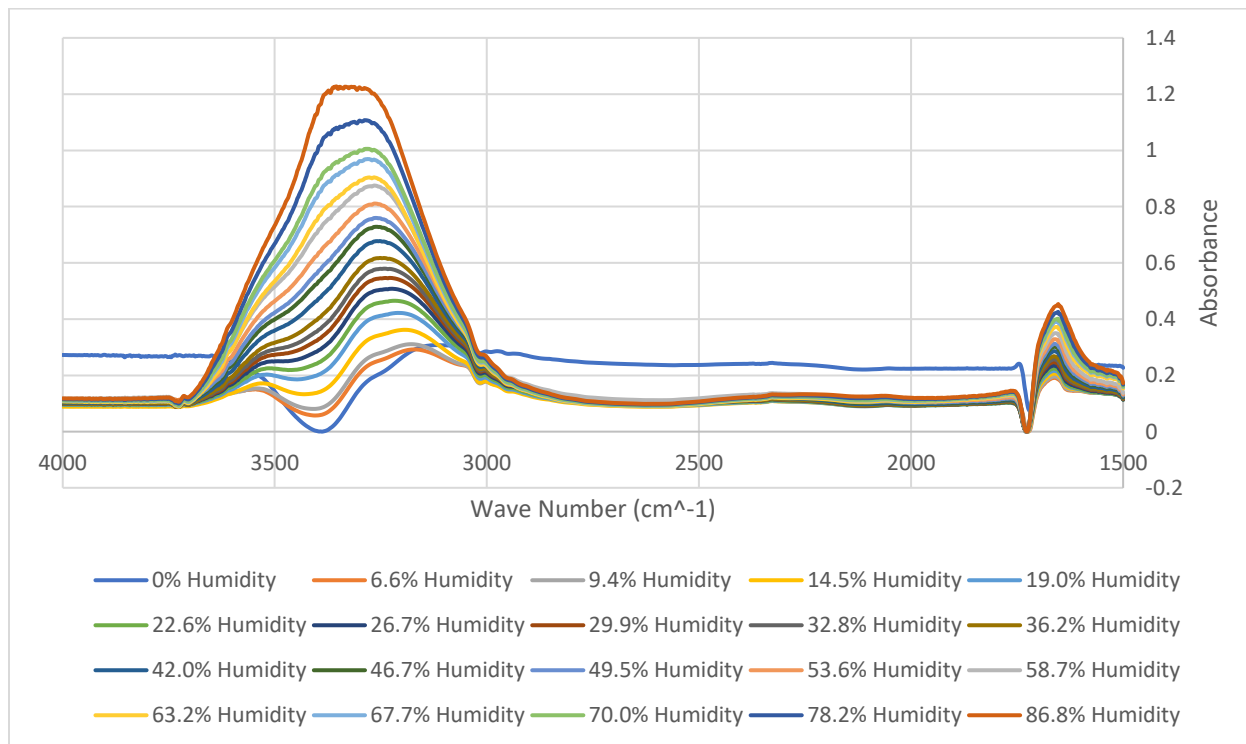


Figure 14. The plot above shows the spectra collected at different humidity levels for the sulphate ion on the same figure. As the humidity increases, the peak present at $\sim 3300 \text{ cm}^{-1}$ increases and shifts to lower wavenumbers.

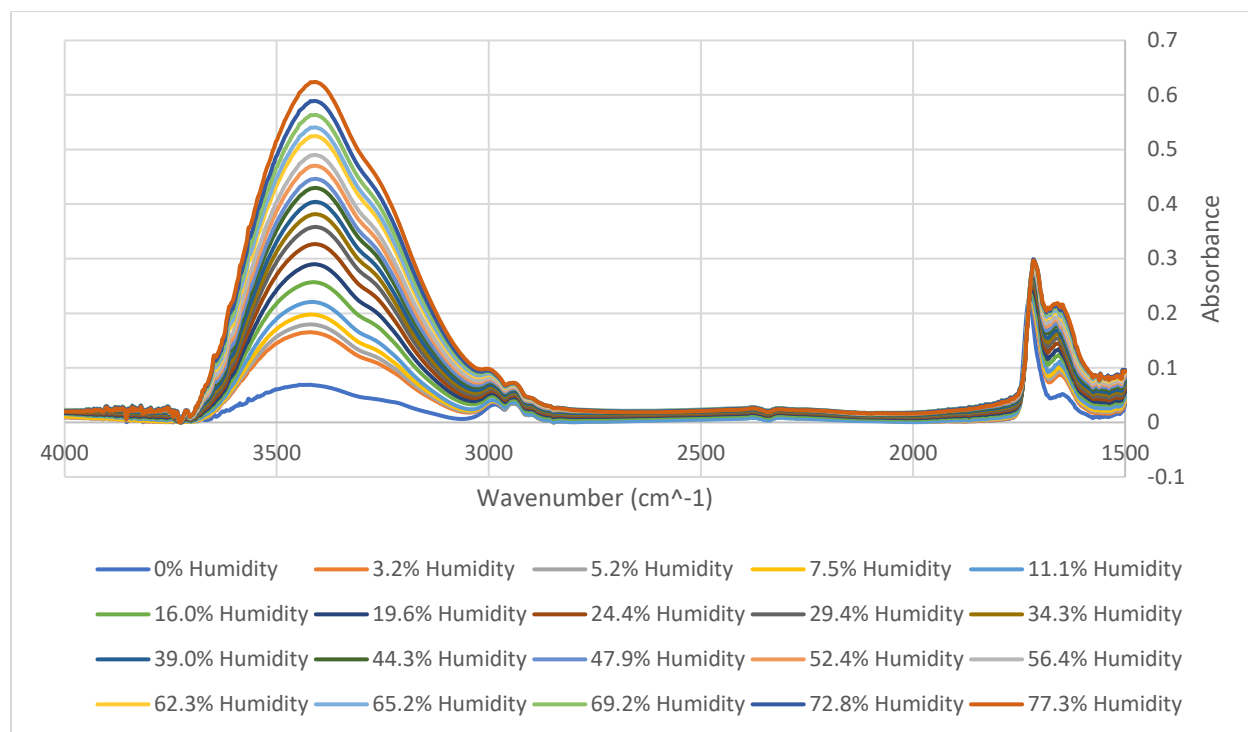


Figure 15. The plot above shows the spectra collected at different humidity levels for the magnesium ion on the same figure. As the humidity increases, the peak present at $\sim 3300 \text{ cm}^{-1}$ increases and shifts to lower wavenumbers.

Discussion/Analysis

Figures 14 and 15 support the experimental finding that both positively and negatively charged polyelectrolyte brushes absorb water and swell when exposed to humid vapor in air. ATR-IR was used to visualize the changes that occur when humidity is increased by collecting spectra at different humidity levels. As the humidity increased, the water peaks increased and shifted to lower wavenumbers. These peaks were then divided into three different regions, ice-like, liquid-like, and free water, which provided greater insight on the type of bonding occurring between water molecules and the surface of the brush. According to Xu in “Ion-Specific Effects of Divalent Ions on the Structure of Polyelectrolyte Brushes”, the valency of the ion present on the polyelectrolyte brush can affect both brush thickness and hydration properties.⁴ Looking at Figure 2, it is evident that ions with a valency greater than one, ytterbium, calcium, magnesium, and barium, generate a larger ice fraction than ions with lower valency such as sodium for a

PSPMA polyelectrolyte brush. Likewise, Figure 8 also supports this claim for the PMETAC brush since sulfate is multivalent and the rest of the ions examined are monovalent. According to Ghosh in “Understanding Mono- and Bivalent Ion Selectivities of Nanoporous Graphene Using Ionic and Bi-ionic Potentials”, multivalent ions have a “higher ability to screen surface charge than monovalent counterions”.² Figures 2 and 8 support this finding since the multivalent ions hold a higher fraction ice-like water at all relative humidities. Additional trials could be conducted using a variety of multivalent ions to better visualize the trend between ion valency and water structure on the polyelectrolyte brush.

Throughout the experiments performed, some errors in measurement must be accounted for. For example, when the relative humidity was measured at 0% on the hygrometer, the data presented in Figures 14 and 15 indicate that water exists on the brush even at 0% humidity.³ At 0% humidity, there is still a visible water peak at a wavenumber of approximately 3300 cm^{-1} for both the PSPMA and PMETAC counterions. Due to the hydrophilic nature of polyelectrolyte brushes, it is nearly impossible to remove all water molecules from the surface. Therefore, all humidities are relative to the results collected at 0% humidity throughout all experiments. Likewise, the measurements of relative humidity throughout the experiments conducted embody additional error since the relative humidity fluctuated by a few tenths of a percent over the length of each spectra scan. Additionally, the same brush was used to test all positively or negatively charged counterions. Since ion exchange occurred over 5 minutes opposed to the 60 minutes presented in *Tuning ice nucleation with counterions on polyelectrolyte brush surfaces*, the brush could have contained a combination of both the previous ion and the target ion. Soaking the crystal in the ion solution for a longer time interval may improve ion selectivity and therefore

generate a more accurate spectrum. Future experiments may explore the relationship between ion exchange time and spectra collected.

To ensure validity of results, a minimum of two experimental trials were conducted for each counterion presented. If the results from the first two trials were not in agreement, additional trials were completed to better grasp the relationship between increasing humidity and water structure on the brush's surface. Once a few trials of each counterion were completed, the data was checked against the trends presented in Figure 2 of "Humidity-Induced Glass Transition of a Polyelectrolyte Brush Creates Switchable Friction in Air" to ensure the trend of increasing water fraction over increasing humidity was correct. Future experiments might also explore how multivalent counterions affect friction measurements at different humidity levels, since Merriman's paper explores the effects of monovalent counterions on friction.

With the knowledge that different ions induce different absorbance and structure of water on the surface of the brush, polyelectrolyte brushes can be prepared to mimic any environment in which they can be applied. Monovalent counterions resulted in less water absorption and smaller fractions of ice-like and liquid-like water than multivalent ions. Additionally, increasing relative humidity increased the absorption of humid vapor by the brush regardless of the counterion used. Using these findings, polyelectrolyte brushes can be synthesized using a specific counterion to achieve desired humid vapor absorption and water structure on the surface of the brush.

Literature Cited

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- ³Merriman, S., Singla, S., & Dhinojwala, A. (n.d.). *Humidity-Induced Glass Transition of a Polyelectrolyte Brush Creates Switchable Friction in Air*.
- ⁴Xu, X., Mastropietro, D., Ruths, M., Tirrell, M., & Yu, J. (2015, August 15). *Ion-specific effects of divalent ions on the structure of polyelectrolyte brushes* / *Langmuir*. ACS Publications. <https://pubs.acs.org/doi/10.1021/acs.langmuir.9b01984>
- ⁵Zhiyuan He *et al.*, Tuning ice nucleation with counterions on polyelectrolyte brush surfaces. *Sci. Adv.* **2**, e1600345 (2016). DOI: [10.1126/sciadv.1600345](https://doi.org/10.1126/sciadv.1600345)

Appendices

The following Matlab code was used to generate a master file that provides the area for each water type (ice, liquid, and free) at the corresponding humidity level from the individual data sets collected during the experiment.

```
clear

[file,path]=uigetfile('*.csv','MultiSelect','On');

Total_Areas=[];
Ice_Areas=[];
Ice_Frac= [];
Liquid_Areas=[];
Liquid_Frac= [];
Free_Areas=[];
Free_Frac= [];

for i=1:length(file)

    data=readmatrix([path file{i}]);
    x_raw=data(:,1);
    y_raw=data(:,2);

    xbase=[1879 3692];
    low=find(x_raw>1879,1);
    high=find(x_raw>3692,1);
    ybase=[y_raw(low) y_raw(high)];
    y_baseline=interp1(xbase,ybase,x_raw,'pchip');
    y=y_raw-y_baseline;

    %Total Area
    low=find(x_raw>3061,1);
    high=find(x_raw>3742,1);
    total_area=trapz(y(low:high));

    % Ice-Like Area
    low=find(x_raw>3061,1);
    high=find(x_raw>3265,1);
    ice_area=trapz(y(low:high));
    ice_frac=ice_area/total_area;

    % liquid-Like Area
    low=find(x_raw>3265,1);
    high=find(x_raw>3520,1);
    liquid_area=trapz(y(low:high));
    liquid_frac=liquid_area/total_area;

    % Free Area
    low=find(x_raw>3520,1);
    high=find(x_raw>3742,1);
```

```

free_area=trapz(y(low:high));
free_frac=free_area/total_area;

Total_Areas=[Total_Areas total_area];
Ice_Areas=[Ice_Areas ice_area];
Ice_Frac=[Ice_Frac ice_frac];
Liquid_Areas=[Liquid_Areas liquid_area];
Liquid_Frac=[Liquid_Frac liquid_frac];
Free_Areas=[Free_Areas free_area];
Free_Frac=[Free_Frac free_frac];
end

[file2,path]=uinputfile('*.xlsx');
writecell(['' file],[path file2])
writecell(['' {'Total Area'} {'Ice Area'} {'Liquid Area'} {'Free Area'} {'Ice Frac'} {'Liquid Frac'} {'Free Frac'}],[path file2])
writematrix([Total_Areas' Ice_Areas' Liquid_Areas' Free_Areas' Ice_Frac' Liquid_Frac' Free_Frac'],[path file2],'Range','B2')

```

The following Matlab program calculates the water content as a ratio of the OH bending peak to the carbonyl peak. A baseline is calculated from the left and right of each peak to ensure an accurate calculation. The carbonyl baseline is calculated between the 1700 and 1746 wavenumber. The OH baseline is calculated between a wavenumber of 1610 and 1655. The program accepts all data files from each humidity level collected during the experiment, and the peaks and ratios are calculated for each humidity level on the same file.

```

clear

% read a file and save the data as x_raw and y_raw
[file,path]=uigetfile('*.csv','MultiSelect','On');

OH_Peaks=[];
CO_Peaks=[];
OH_peak_locations=[];
CO_peak_locations=[];
Ratios=[];

for i=1:length(file)

data=readmatrix([path file{i}]);
x_raw=data(:,1);
y_raw=data(:,2);

%linear baseline subtraction
% xbase=[1530 1800]; %wavenumber points for the baseline
% low=find(x_raw>1530,1); % find the index corresponding to each wavenumber point
% high=find(x_raw>1800,1);
xbase=[1535 1860]; %wavenumber points for the baseline
low=find(x_raw>1535,1); % find the index corresponding to each wavenumber point
high=find(x_raw>1860,1);

ybase=[y_raw(low) y_raw(high)]; %find the absorbance corresponding to each wavenumber

```

```

y_baseline=interp1(xbase,ybase,x_raw,'pchip'); %do a linear fit
y=y_raw-y_baseline; %do the actual baseline subtraction

% OH peak
low=find(x_raw>1600,1);
high=find(x_raw>1680,1);
[OH_peak, index]=max(y(low:high));
OH_peak_location=x_raw(index+low);

%area between 1530 and 1683
% low=find(x_raw>1530,1);
% high=find(x_raw>1683,1);
% OH_area=trapz(y(low:high));

% CO peak
low=find(x_raw>1680,1);
high=find(x_raw>1760,1);
[CO_peak,index]=max(y(low:high));
CO_peak_location=x_raw(index+low);

ratio = OH_peak/ CO_peak;

OH_Peaks=[OH_Peaks OH_peak];
% OH_Peaks=[OH_Peaks OH_area];
CO_Peaks=[CO_Peaks CO_peak];
Ratios=[Ratios ratio];

OH_peak_locations=[OH_peak_locations; OH_peak_location];
CO_peak_locations=[CO_peak_locations; CO_peak_location];

end

[file2,path2]=uiputfile('*.xlsx','Select where to save the output file: ');
writecell([' ' file'],[path2 file2])
writecell([' ' {'OH Peak'} {'CO Peak'} {'Ratios'} {'OH location'} {'CO location'}],[path2 file2])
writematrix([OH_Peaks' CO_Peaks' Ratios' OH_peak_locations CO_peak_locations],[path2 file2],'Range','B2')

```

The following Matlab program was used to combine all the spectra collected at each relative humidity for a single ion and combine them onto a single dataset.

```

clear,clc

% Program prompts user for a group selection of files .csv format and puts
% them all into a single file assuming first column is the same for all
% files (like for an IR spectrum).

%% Read files
[file,path]=uigetfile('*.csv','MultiSelect','on');

spectra=[];
names={' '};

```

```
for i=1:length(file)
    data=readmatrix([path file{i}]);
    wavenumbers=data(:,1);
    Intensities=data(:,2);
    name=file{i};

    spectra=[spectra, Intensities];
    names=[names, name];
end

%% Output new file

[file2,path]=uinputfile('*.xlsx');

writecell(names,[path file2])

writematrix(wavenumbers,[path file2],'Range','A2')
writematrix(spectra,[path file2],'Range','B2')
```