THE EFFECT OF pH ON THE ABSORPTION CAPACITY OF SODIUM POLYACRYLATE POLYMER

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Introduction

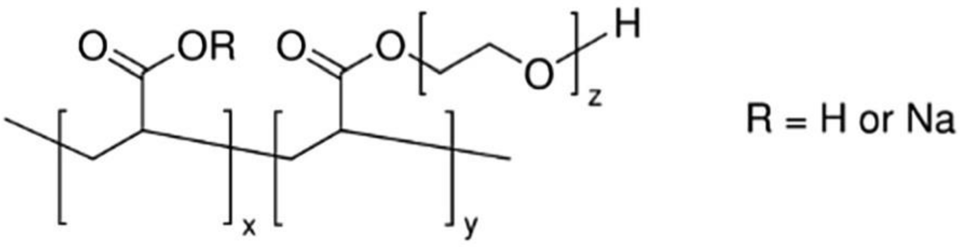
Sodium Polyacrylate

This paper investigates the research question: **How does the change in pH (0–14) affect the absorption capacity of sodium polyacrylate as measured by the mass of solution absorbed per gram of polymer?**

Sodium polyacrylate (SPA) is a cross-linked polymer with repeating acrylic acid monomer units (IUPAC: propenoic acid). Acrylic acid is an organic carboxylic acid with a double bond on its ending carbons, enabling it to undergo a free-radical polymerization reaction (Halyal, 2021). The free-radical reaction has a degree of randomness in the monomer bonding, causing branching and an atactic form. Branching and less order weaken the intermolecular forces between polymer chains, resulting in low-density and flexible properties. Figure 1 below shows possible repeating units of SPA.

Figure 1

Condensed Structural of Sodium Polyacrylate



Note. Figure 1 is taken from Mahon et al. (2019).

The mechanism for absorption occurs in the carboxyl functional group. The hydrogen attached to the single-bonded oxygen can be acidic as the double-bond connected to the same carbon creates resonance stability. Hence, the bond between the O^- and R-placeholder can have ionic characteristics, and the Na^+ may be displaced by another electropositive moment. H_2O water is a polar molecule exhibiting a permanent dipole between the electronegative oxygen and the electropositive hydrogens. SPA absorbs water through an osmotic process, as the Na^+ tends to disperse its concentration equally between the water and the polymer (Jacobson et al., 2009). The H_2O molecules that replace the Na^+ ions form hydrogen bonds with the O^-. Water absorption causes the polymer to uncoil from a curly pigtail shape into a straightened chain, resulting in swelling and increased viscosity (Halyal, 2021).

Previous literature suggests that SPA can absorb anywhere between 200 to 1000 times its weight, with differences strongly influenced by solvent ion concentrations and polymer cross-links (Mahon et al., 2019). Absorption is calculated according to Equation 1 below:

$$\text{Absorption} = \frac{m_f - m_{\text{SPA}}}{m_{\text{SPA}}} \tag{1}$$

Where:

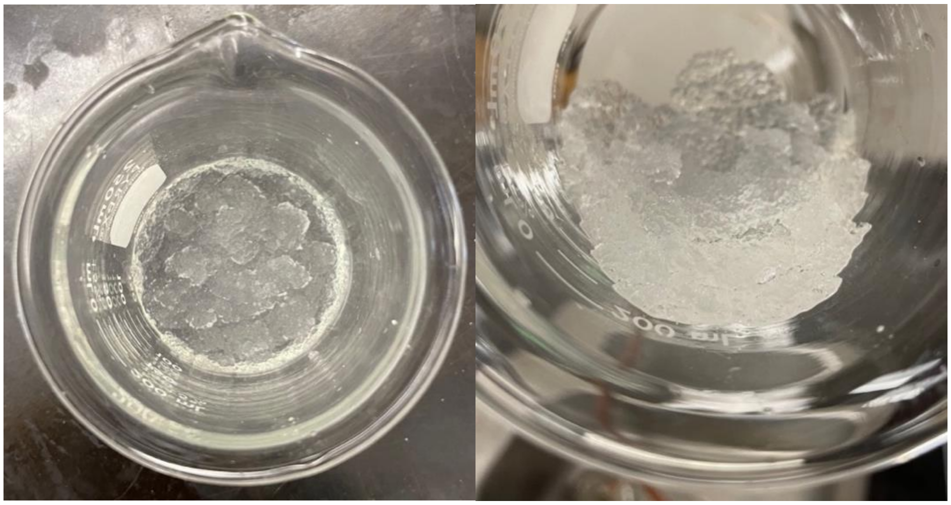
m_f = Final mass of solution added and SPA

m_{SPA} = Initial mass of SPA

The absorption capacity is the saturation point of the polymer: the state at which no more water can be absorbed. This experiment will determine SPA's absorption capacity through qualitative observation. The polymer forms ~4 cm clumps at the absorption capacity with a thin, barely noticeable layer of non-absorbed water on top of the polymer, as shown in Figure 2.

Figure 2

Photo of Experiment SPA at Absorption Capacity



The Effect of pH

This experiment uses the strong acid $HCl_{(aq)}$ and strong base $NaOH_{(aq)}$ to change pH. These reagents were chosen because they completely dissociate in water, allowing for more control over pH. When an acidic solution is added to SPA, the dissociated H^+ ions prompt the polymer chains to protonate, meaning the carboxyl group $-COO^-$ is more likely to pick up an H^+ than the molecule of H_2O that causes swelling. Moreover, the anionic Cl^- causes more of the positive dipoles of H_2O to be attracted to the Cl^- rather than to the carboxyl group. A similar process occurs when SPA is in a basic environment. While the dissociated OH^- encourages the SPA to deprotonate, the increased Na^+ cations balance out the effect. As the Na^+ concentration increases in the water, the osmotic process that the Na^+ from SPA undergoes becomes less significant as there is more of an equilibrium between polymer and solution. Applications of SPA where the pH of the environment may fluctuate include its use as a thickening agent for foods, sewage, and construction materials; water retention for agriculture; biomass fuel suspensions; and diapers.

Hypothesis

As pH decreases from 7 to 0, the increase in acidity and [H^+] prevents H_2O molecules from displacing the Na^+ of SPA. This means that a solution at pH 7 would be absorbed by SPA the most, while low pH will decrease absorption capacities. Similarly, as pH increases from 7 to 14, the increase in [Na^+] erodes the osmotic process, thus reducing water absorption. Hence, high pH also decreases absorption capacities. The overall trend across pH 0–14 would look like a parabolic curve, peaking at pH 7 as the ideal pH for absorption.

Apparatus and Variables

Table 1

Measurement Apparatus with Uncertainties

Quantity	Apparatus	Uncertainty
1x	Electronic Balance	± 0.01 g
1x	pH Probe	± 0.05
1x	10.0 mL Graduated Cylinder	± 0.5 mL
1x	100.0 mL Graduated Cylinder	± 0.5 mL
5x	80 mL Beaker	–
14x	250 mL Beaker	–

Table 2

Experiment Variables with Descriptions

Variables	Type of Variable	Description
pH	Independent	The pH of each solution (0–14) was prepared by diluting 1.0 M stock solutions with a 5% uncertainty. Then, the pH was measured with a pH probe to confirm the value. Each variation reflects a 10-fold change in H^+ concentration. The $\log_{10}$ pH scale is used because it simplifies plotting small concentrations and is the accepted scale for acids and bases.
Mass of solution absorbed	Dependent	The maximum mass of the solution that can be absorbed depends on the pH of the solution. This mass value calculates the absorption capacity by dividing it by the mass of sodium polyacrylate.
Absorption time	Control	The amount of time after adding each solution to the SPA before measuring the weight difference. Absorption time was kept to 3 minutes to ensure that all SPA trials had the same opportunity to undergo an osmotic process.
Initial 1.0 M $HCl_{(aq)}$ and 1.0 M $NaOH_{(aq)}$	Control	$HCl_{(aq)}$ and $NaOH_{(aq)}$ stock solutions are assumed to be accurate with a 5% uncertainty. All subsequent prepared pH solutions are dilutions of these two initial solutions.
Reaction container	Control	An 80 mL beaker in which the SPA and solution are mixed. Keeping the container where the reaction occurs consistent limits any potential influence that container shape and volume have on absorption.
Sodium polyacrylate	Control	All SPA samples were of the same bottle manufactured by ProlabScientific. How the polymer is synthesized affects its cross-links and absorption capacity. Using the same source of SPA is essential because it keeps SPA qualities constant.
Mass of sodium polyacrylate	Control	0.50 g of SPA, as measured by an electronic balance, is used for every trial to ensure identical starting amounts of the absorbing polymer. 0.50 g was chosen because of beta-testing results where the maximum swelled SPA fit inside the 80 mL beakers. Additionally, using conservative amounts of reagents decreases environmental impact when disposing.
Solution temperature	Control	All solutions were prepared in advance and set aside in the lab to acclimate to room temperature of 21.1 ± 0.5°C. On the days of the experiment, this temperature was confirmed again with a thermometer across all solutions. The solution temperature is critical to consider as it affects the equilibrium constant of water and, thus, the concentrations of H^+ and OH^-.
Use of tap water	Control	Tap water is used in the dilution process and as calibration for pH 7. Tap water may contain minerals such as calcium, copper, magnesium, or sodium, which alter the initial ionic concentration. Although these confounding ions may influence the absorption of SPA, the effect is assumed to be negligible when compared to the concentrations of $HCl_{(aq)}$or $NaOH_{(aq)}$ added.

Methodology

The experiment is divided into two data sets combined into one: dilutions of $HCl_{(aq)}$ and dilutions of $NaOH_{(aq)}$. There is no titration process. The separate dissociation of the acid and base yields two data sets that are then graphed into one continuous pH range. Refer to Tables 1 and 2 for a list of apparatus and materials used in the following procedures:

Preparation

1. Dilute 1.0 M stock solution of $HCl_{(aq)}$ by measuring 10.0 mL with a 10.0 mL graduated cylinder and adding it to 90.0 mL of tap water in a 100.0 mL graduated cylinder. Then, take the newly made concentration and repeat the dilution process until pH 0 to 6 solutions are prepared.
2. Calibrate the pH probe to pH 4.01 with an acidic buffer pill in tap water. Use the probe to record the experimental pH of each prepared acidic solution (pH 0–6).
3. Repeat steps 1 and 2 for $NaOH_{(aq)}$. Prepare pH 8 to 14 solutions. Calibrate the pH probe to 10.01 with a basic buffer pill in tap water.
4. Allow for the solutions to acclimate to room temperature.

Experiment

1. Using an electronic balance, measure 0.50 g of sodium polyacrylate into an 80 mL beaker.
2. Slowly add the pH solution to the 80 mL beaker until it reaches saturation point; refer to **Background Theory** for qualitative observation details.
3. Record the mass of the solution added and follow Steps 1–2 for repeated trials.
4. Then, repeat for each prepared pH 0–6 and pH 8–14 solution. For pH 7, use only room temperature tap water, calibrate to 7.01 using a pH probe, and then follow Steps 1–2.

Safety, Environmental, and Ethical Considerations

Wear protective eye goggles and wash hands after contact when handling strong acids and bases. Exercise care with glassware, appropriately disposing of faulty or broken ones in broken glass bins. SPA is classified as an eye and respiratory irritant; wearing goggles and a mask can prevent polymer dust from entering the eye or being breathed in. SPA must be neutralized before safe disposal in the organics bin; each trial was neutralized by adding the corresponding acid or base concentration (i.e., the pH 2 trial was neutralized by adding an equal amount of pH 12 solution). Do not rinse SPA down drains; absorbent properties may clog the drains and impact sewage.

Results and Calculations

Table 3

Results of Adding $HCl_{(aq)}$ *Solutions*

Concentration of $HCl_{(aq)}$		pH		Mass of $HCl_{(aq)}$ Absorbed (g) (± 0.02)						Absorption Capacity
(mol/dm^3)	(± %)	Calculated	Measured (± 0.05)	t_1	t_2	t_3	t_4	t_5	$\bar{t}$	(g/g)
1.0	5%	0.00	0.04	4.28	4.32	3.87	3.81	3.43	3.94	7.9 ± 0.2
1.0×10^{-1}	10.5%	1.00	1.04	15.08	15.00	14.78	14.87	14.81	14.92	29.8 ± 0.6
1.0×10^{-2}	16.0%	2.00	2.05	44.13	44.71	44.42	44.21	43.99	44.29	88 ± 2
1.0×10^{-3}	21.5%	3.00	3.08	71.31	72.25	70.12	70.92	71.84	71.29	143 ± 3
1.0×10^{-4}	27.0%	4.00	4.12	82.26	84.16	82.52	84.49	83.74	83.43	167 ± 3
1.0×10^{-5}	32.5%	5.00	5.15	90.01	89.20	86.32	89.31	88.42	88.65	177 ± 4
1.0×10^{-6}	38.0%	6.00	6.19	~~87.21~~	92.56	91.11	91.64	92.44	91.94	184 ± 4
1.0×10^{-7}	–	7.00	7.01	93.24	94.31	92.64	93.04	93.88	93.42	187 ± 4

Note. Trial 1 of pH 6 is excluded from subsequent calculations as it is a visible outlier in Figure 3. Reasons for discrepancies are discussed in the **Evaluation**.

Table 4

Results of Adding $NaOH_{(aq)}$ *Solutions*

Concentration of $NaOH_{(aq)}$		pH		Mass of $NaOH_{(aq)}$ Absorbed (g) (± 0.02)						Absorption Capacity
(mol/dm^3)	(± %)	Calculated	Measured (± 0.05)	t_1	t_2	t_3	t_4	t_5	$\bar{t}$	(g/g)
1.0×10^{-6}	38.0%	8.00	8.13	95.52	97.16	96.43	92.49	94.35	95.19	191 ± 4
1.0×10^{-5}	32.5%	9.00	9.09	92.02	93.02	91.88	92.16	94.02	92.62	185 ± 4
1.0×10^{-4}	27.0%	10.00	10.08	90.24	89.28	88.72	88.67	90.38	89.46	179 ± 4
1.0×10^{-3}	21.5%	11.00	11.08	83.14	84.16	84.76	82.38	81.24	83.14	166 ± 3
1.0×10^{-2}	16.0%	12.00	12.06	71.36	73.74	75.61	74.14	72.39	73.45	147 ± 3
1.0×10^{-1}	10.5%	13.00	13.04	39.50	41.63	39.23	38.79	38.12	39.45	79 ± 2
1.0	5%	14.00	13.94	9.18	9.19	10.31	10.21	9.87	9.75	19.5 ± 0.4

Table 5

Sample Calculations and Uncertainty Propagation of Data

Data	Formulae	Sample Calculations and Uncertainty Propagation
Dilution of Concentrations	$M_1V_1 = M_2V_2$	Preparation of 1.0×10^{-1} $HCl_{(aq)}$: $(1.0\text{ M} \pm 5\%)(10.0 \pm 0.5\text{ mL}) = M_2(100.0 \pm 0.5\text{ mL})$ $M_2 = \frac{(1.0\text{ M} \pm 5\%)(10.0\text{ mL} \pm 5\%)}{(100.0\text{ mL} \pm 0.5\%)}$ $M_2 = 0.10\text{ M} \pm 10.5\%$ $M_2 = 1.0 \times 10^{-1}\text{ M} \pm 10.5\%$

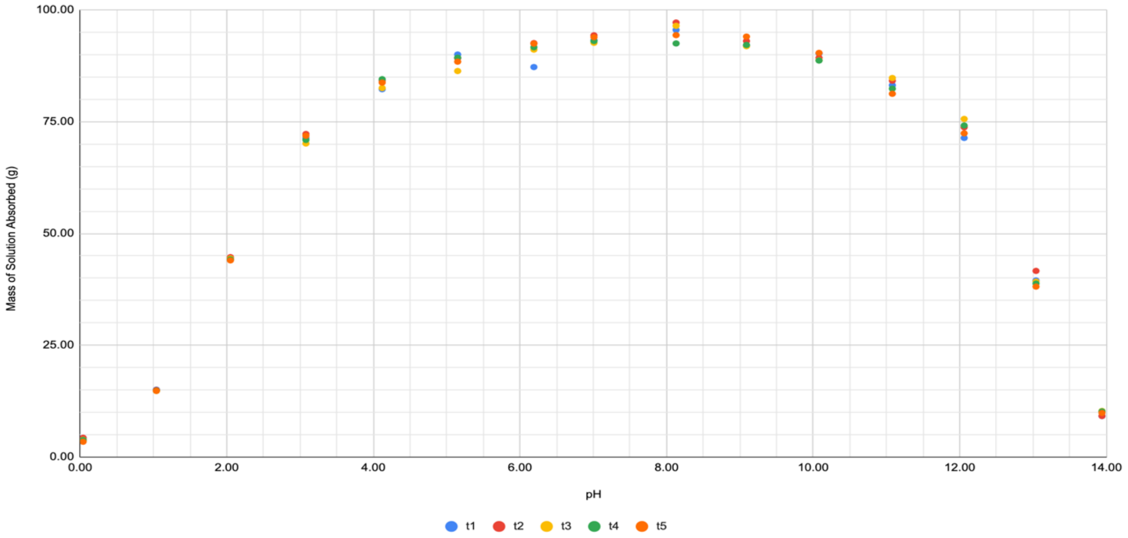
Determination of pH from $[H^+]$	$pH = -\log([H^+])$ $\pm pH = \frac{\lvert pH_{upper} - pH_{lower}\rvert}{2}$	Calculation of pH from 1.0×10^{-1} $HCl_{(aq)}$: $HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$ $[HCl] = [H^+] = 1.0 \times 10^{-1}\ M$ $pH = -\log(1.0 \times 10^{-1}\ M \pm 10.5\%)$ $pH = 1.00 \pm \frac{\lvert -\log(0.10\ M - 10.5\%) - -\log(0.10\ M + 10.5\%)\rvert}{2}$ $pH = 1.00 \pm 0.05$
Mass Absorbed	Mass Absorbed (g) = [total mass (g)] – [mass of SPA (g)]	Calculation of Amount Absorbed for 1.0×10^{-1} $HCl_{(aq)}$ Trial 1 Sample: $t_1 = (15.58 \pm 0.01\ g) - (0.50 \pm 0.01\ g)$ $t_1 = 15.08 \pm 0.02\ g$
Average Mass Absorbed ($\bar{t}$)	$\bar{t} = \frac{t_1 + t_2 \ldots + t_n}{n}$	Calculation of Average Amount Absorbed for 1.0×10^{-1} $HCl_{(aq)}$: $\bar{t} = \frac{15.08 + 15.00 + 14.78 + 14.87 + 14.81 + 14.91}{5} \pm 0.02\ g$ $\bar{t} = 14.92 \pm 0.02\ g$
Absorption Capacity	Absorption Capacity $= \frac{\bar{t}}{0.50 \pm 0.01\ g}$	Calculation of Absorption for 1.0×10^{-1} $HCl_{(aq)}$: $A = \frac{14.92 \pm 0.02\ g}{0.50 \pm 0.01\ g}$ $A = 29.84\ g/g \pm \left(\frac{0.02\ g}{14.92\ g} + \frac{0.01\ g}{0.50\ g}\right)\%$ $A = 29.84\ g/g \pm \left(\frac{0.02\ g}{14.92\ g} + \frac{0.01\ g}{0.50\ g}\right)\%$ $A = 29.84\ g/g \pm 2.13\%$ $A = 29.8 \pm 0.6\ g/g$

Analysis

Figure 3 was plotted first to visualize raw data dispersion and combine Table 3 and Table 4. It also provides visuals for outliers.

Figure 3

Graph of Raw Data from Tables 3 and 4 of Mass of $HCl_{(aq)}$ *and* $NaOH_{(aq)}$ *Solutions Absorbed*



From Figure 3, the pH 4–13 data seems to be the most dispersed trials. This is likely because the absorption capacity becomes more challenging to determine qualitatively as more solution is added. Additionally, trial 1 of pH 6 looks to be an outlier compared to the other trials.

Figure 4 is plotted to visualize the trend of absorption capacity across pH by combining the data from Table 3 and Table 4. The error bars for the absorption capacity were propagated, as shown in Table 5.

Figure 4

Graph of Absorption Capacity Against pH

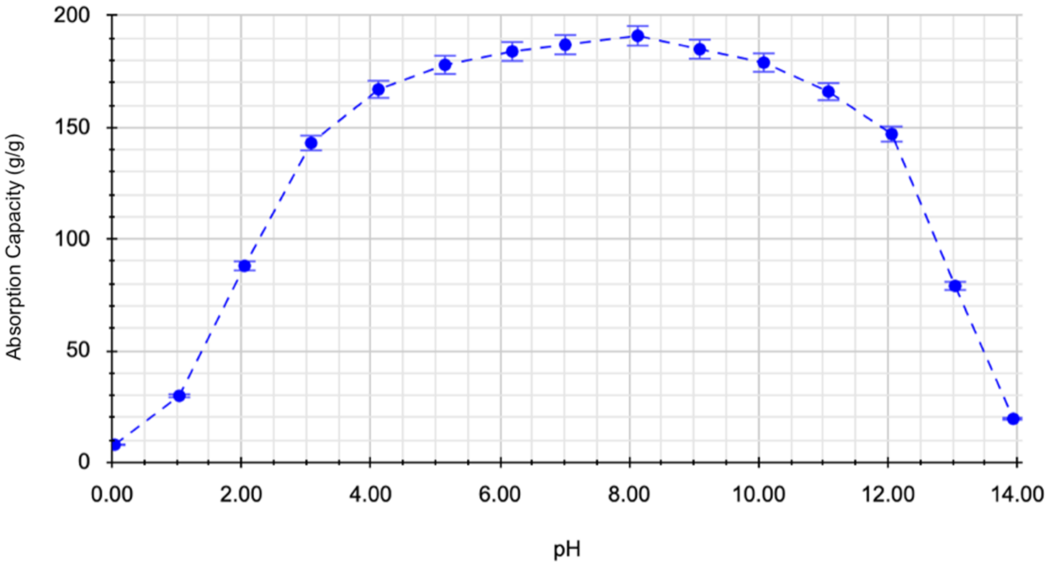


Figure 4 reveals a bell-curve-shaped trend. From pH 0–7, the absorption capacity follows a logistical growth pattern, suggesting that as the pH of the solution becomes more neutral, the absorption capacity approaches a carrying capacity. Likewise, from pH 7–14, the absorption capacity decreases at a negative inverse exponential rate. Figure 4 also reveals what looks like an inflection at pH 1, indicating that a minimum amount of solution SPA can hold between itself regardless of the strength of the acid. This inflection is not seen on the base side within the data.

The carrying capacity, also known as the maximum absorption capacity, is determined by finding the vertex of a parabola from the data between pH 3–12. This range was selected instead of the entire data set because the absorption capacities are greater than 140 g/g at these pH values. Another reason was that the absorption capacity difference between sequential pH values began converging at a more standard rate; this pattern can be observed in Figure 4.

Figure 5

Graph of Absorption Capacity Against pH 3–12

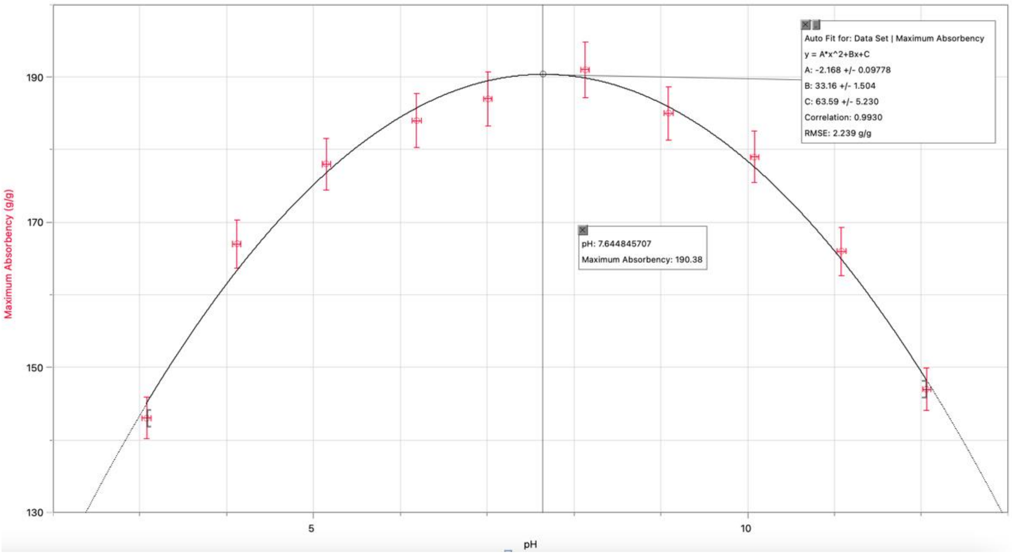


Figure 5 shows that the vertex of the parabola is (7.64, 190.38), interpolating that the maximum absorption capacity is 190.38 g/g by adding a pH 7.64 solution. This value is less than the experimental data point at pH 8.13 ± 0.05, where the absorption measured 191 g/g ± 4. The discrepancy suggests that the ideal maximum absorption capacity and pH may be higher and more basic.

Interestingly, the data reveals a ‘shift’ towards basicity; the curves in Figure 4 and Figure 5 are slightly offset from neutral point pH 7 to pH > 7. For example, the parabola’s vertex in Figure 5, representing the maximum absorption capacity, is 190.38 g/g at pH 7.64. This “basic shift” phenomenon is also found in existing literature. Mahon et al. (2019) conducted a similar experiment on the effect of pH on the absorbency of SPA, finding the highest swelling performance to be at pH 9 after two hours. The shift may explain why no symmetrical inflection point is noticed on the pH > 7 side of Figure 4; if there were one, it would lie beyond pH 14.

I came to two possible explanations for this phenomenon. Firstly, I thought that the solution temperature caused the shift. All solution temperatures were measured to be 21.1°C (Table 2). This temperature is close to 20°C, which, according to the IB Chemistry booklet, has a K_w ionization constant of 0.684×10^{-14}. Therefore, the neutral pH point at this temperature would be greater than pH 7 at approximately pH 7.08. However, this explanation does not encompass the extent of the shift towards basicity that the experiment and literature entail, and hence, it cannot be a primary influence.

The second explanation I considered was the nature of acrylic acid as a monomer. As seen in Figure 1, the R-placeholder was assumed to be Na^+ while, in reality, it could have been a hydrogen ion. Hence, the SPA used may have had a substantial amount of hydrogen atoms still in its carboxyl groups that dissociated when the solutions were added. These extra hydrogens mop up and neutralize small amounts of the hydroxide concentrations, which explains why adding a slightly basic solution causes optimal absorption capacity and there is an overall shift towards basicity.

Mahon et al. (2019) explain the phenomenon using the osmotic pressure ion theory. Though that theory is out of the scope of this investigation, Mahon et al. also mention that more possible factors can contribute to the shift, implying the multifaceted nature of the cause.

Conclusion

The absorption capacity follows a bell-curve trend as the pH of the solution added changes from pH 0–14. From pH 0–7, the trend follows a logistical growth curve. From pH 14–7, the trend seems to follow a negative inverse exponential curve; however, the trend may also be a logistical decay curve, as it was speculated that an inflection point may exist beyond pH 14. This experiment found that the pH range of 6.19 to 9.09 provided the highest absorption capacity values, with 191 ± 4 g/g at pH 8.13 being the greatest. A quadratic relation was found by interpolating the data from pH 3–12, showing that the maximum absorption capacity is 190.38 g/g at pH 7.64. These values fall within the range established by previous studies, where optimal pH absorption was between pH 6.5 and 9 (Mahon et al., 2019).

While the general pattern of absorbency across pH agrees with my hypothesis, pH 7 was not the ideal pH where maximum absorbency occurred. The whole curve revealed a “basic shift.” While numerous explanations and causes for this shift may exist, two ideas I distilled are the effect of the solution temperature on the neutral pH point and the acidic character of polyacrylate. Other studies, such as Mahon et al. (2019), also share this “basic shift.”

In conclusion, pH significantly affects the absorption capacity of SPA, especially when $[H^+] > 1.0 \times 10^{-3}$ and $[OH^-] > 1.0 \times 10^{-2}$. SPA has an optimal absorption pH slightly above 7, making its application in mildly basic environments the most effective. This means, however, that SPA’s applicability in systems affected by acid deposition, extreme acidity, and extreme basicity is severely limited.

Evaluation

Strengths

When preparing the solutions for each pH variation, this experiment's use of a pH probe to confirm and provide a measured value helped ensure accuracy in the results. If only left to the dilution calculations, the subsequently prepared solutions would have large error rates such as 38.0% for pH 6 and 8 (Table 3 & Table 4); the probe helped determine that the solutions had a pH of 6.19 and 8.13, which were values off from the dilution calculation but within its error percentage.

Another strength of this experiment was the wide range of data and repeated trials. Firstly, the variation of pH 0–14 allowed for analysis of the effect of extreme acidity (pH 0–3) and basicity (pH 12–14) on absorption, a topic underexplored in existing literature. Additionally, the range allowed for a quadratic trend to be interpreted from pH 3–12 (Figure 5). This quantifies the trend and enables the x optimal absorption peaking at pH 7.64 to be determined. By averaging the data of multiple trials, differences due to qualitative subjectivity could be minimized. Additionally, the repeated trials allowed a spread to be visualized and enabled outliers to be identified and excluded from calculations (Figure 3).

Limitations and Improvements

The materials and procedures can be refined to make this experiment stronger. Notably, the use of tap water was a systematic oversight that significantly influenced the absorption values. Although set as a control, the use of tap water and the effect of mineral contamination impacted the accuracy of the absorbency. Though the trends and effects of pH would remain the same, the measured maximum absorption capacity value of 191 ± 4 g/g is lower than the reported potential range of 200 g/g to 1000 g/g absorption value (Mahon et al., 2019). Compared to Jacobson et al. (2009), who reported that SPA could absorb up to 300 times its weight with tap water, the experimental value determined is $\frac{|\,300\text{ g/g} - 191\text{ g/g}|}{300\text{ g/g}} \times 100\% = 36.3\%$ off from the literature. This suggests that the tap water used in this experiment likely contained more minerals and ions than expected, making it a variable that cannot be overlooked and assumed negligible. In future experiments, distilled water should be used instead, ensuring that no other ion concentration except for pH changes would affect the absorption.

Another area of systematic limitation would be the qualitative nature of determining absorbency. Although the absorption capacity was defined with photo evidence in the **Background Theory**, the degree of subjectivity in deciding when the SPA has reached its absorption capacity can create room for discrepancies. Such was the case in trial 1 of pH 6, where only when compared to the other data did the trial seem to be an outlier. For future experiments, using a quantitative approach to characterize absorbency may be more reliable, such as measuring the viscosity of the polymer after swelling or the light transmitted through the polymer after swelling.

Extension

When conducting beta tests, I initially examined the effect of temperature on absorption capacity. In these non-repeated and non-rigorous experiments, I found that the solution temperatures between 0°C and 80°C did not directly affect the absorption capacity. Upon further research, I discovered that the given time for absorption greatly influences the effect of temperature. Specifically, increasing the absorption time allows the polymer to swell more because the water molecules would have more opportunity to permeate the polymer cross-links (Mahon et al., 2019). Hence, greater temperatures have higher average kinetic energy and can permeate the polymer faster, increasing the rate of absorption. I recorded in my beta-testing that the time it took for 160 mL of 77.3°C water to reach a visual absorption capacity point by 1.00 g of SPA was 2.64 seconds, while 160 mL of 1.5°C water took 4.68 seconds. Although this data is not rigorous evidence for the relationship, it still suggests that these variables have potential for further exploration. This paper arbitrarily kept the absorption time to 3 minutes due to personal time constraints. However, research by Mahon et al. (2019) has found that 2, 4, and 6 hours of absorption time significantly changes what pH solution yields the maximum absorption capacity. These results lead me to wonder how temperature oscillations may affect SPA's absorbency. As SPA may be used in environments with sharp temperature changes (i.e. day-night cycles and seasonal changes), future research into this effect would contribute to understanding SPA’s strengths, weaknesses, and applications.

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