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An Alkalinity Experiment for Nonscience Majors

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Abstract: his article describes a simple experiment that is designed to illustrate the concepts of buffer capacity and alkalinity, while also focusing on the geological factors that influence the susceptibility of a body of water to the effects of acid rain. The students perform a semiquantitative titration of four different water samples with a dilute solution of sulfuric acid. The titrations are monitored with a pH meter. Streams flowing through regions rich in limestone have naturally high alkalinities due to the formation of bicarbonate ions from the dissolution of calcium carbonate. The focus of the experiment is to compare the buffer capacities of water samples taken from a stream that flows through a limestone-rich region with those obtained from a stream near its source at a limestone-deficient location. Students plot the pH vs. the number of drops of dilute acid added to each of the samples. The relative buffer capacities are determined from the number of drops required to reach a pH of about 4.4. Tap water and water taken from a major river that flows through central Pennsylvania were found to have fairly large buffer capacities, while deionized water and water taken from a smaller stream near its source were found to have very low buffer capacities. The results show that different bodies of water can have vastly different susceptibilities to the effects of acid rain, depending on the concentration of the bicarbonate ion. The examination of the titration curves enable students to appreciate the sudden drop in pH that occurs once all of the bicarbonate ions have been consumed.

Introduction

Last fall I taught an issue-based chemistry course for nonscience majors at Dickinson College. This course was modeled after a similar course developed by Trumbore at the University of Delaware [1]. A topic that is covered in detail is acid rain, and its origin and consequences. Performing the traditional alkalinity experiment [2] and calculating alkalinities can be cumbersome and counterproductive for nonscience majors. Gran plots, in conjunction with computer programs, have been used to calculate alkalinities of steams and lakes [3]. This approach, however, is still quite complex for nonscience majors. Halstead used test strips available at swimming-pool supply stores to monitor the alkalinity of rain, lakes, and rivers [4]. While this approach is simple and easy, the students do not gain an appreciation for how the pH changes during the course of the titration. I have opted for an approach that falls somewhere between these two extremes. The students perform a semiquantitative titration of water samples with a dilute solution of sulfuric acid. Instead of using an acid–base indicator, a pH meter is used to follow the titrations, enabling the students to obtain a graphical illustration of the concept of buffer capacity. Samples are selected carefully to show large differences in buffer capacity. These include samples from a major river that flows through a region rich in limestone and from a small creek that flows through state game lands at a site fairly close to its source and absent of limestone. Students are able to determine relative buffer capacities of the samples by examining plots of pH vs. the number of drops of dilute acid added for each titration. This approach succeeds in illustrating the concept of buffer capacity. It also focuses on the geological factors that influence susceptibility of a body of water to the effects of acid rain, rather than the mathematical and stoichiometric relationships involved in calculating alkalinities.

Background

Alkalinity is a measure of the concentration of basic species present in water that are capable of neutralizing strong acids. The alkalinity of natural waters is dominated by the carbonate buffer system. The pK_{a1} and pK_{a2} of carbonic acid are 6.35 and 10.33, respectively, and at pH values below 8.0, the dominant ion contributing to the alkalinity is the bicarbonate ion. Thus, the alkalinity of most rivers and lakes is simply equal to the concentration of the bicarbonate ion. An acid titration of sample containing bicarbonate ions yields an equivalence point at a pH of about 4.4. At this point, all of the bicarbonate ion has been converted to carbonic acid, which subsequently dissociates to give water and carbon dioxide, and the buffer capacity of the water has been destroyed. The amount of acid required to reach the equivalence points depends on the alkalinity of the sample. Samples containing low levels of the bicarbonate ion do not require much acid to cause a sharp drop in pH.

The bicarbonate ion concentration of a natural water system is mostly dependent on the geology of the surrounding environment. Some of the bicarbonate ions present in the water originate from the equilibrium that is established with dissolved carbon dioxide. In regions that are rich in limestone, however, the vast majority of bicarbonate ions are produced through the dissolution of calcium carbonate.

$$CaCO_3(s)+CO_2+H_2O \rightarrow 2HCO_3^-+Ca^{2+}$$

Thus, bodies of water that are in contact with limestone tend to have high alkalinities and are well buffered against large changes in pH. However, streams and lakes in regions deficient in limestone can be especially susceptible to the effects of acid rain. Under these conditions, the pH of the water can fall to potentially dangerous levels. At pH values of

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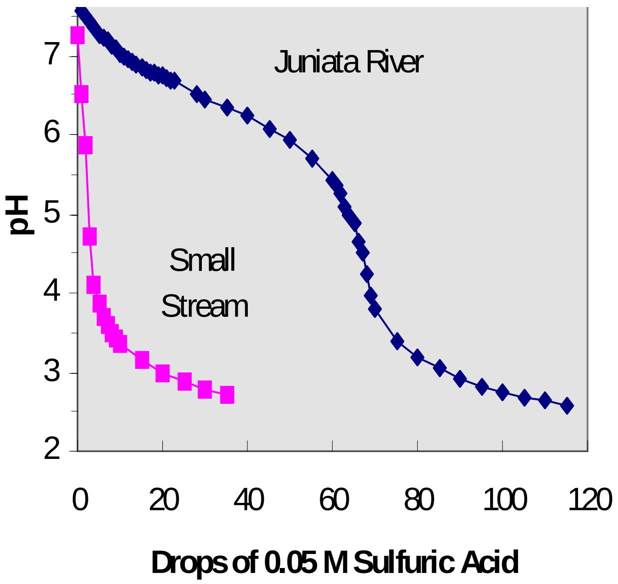

Figure 1. The alkalinity plots for 100-mL samples of the Juniata River and the small stream, titrated with 0.05 M sulfuric acid.

3 to 4.5, toxic metals are considerably more soluble, which can result in devastating fish kills.

Experimental Procedure

The students perform a semiquantitative titration of four different water samples with 0.05 M sulfuric acid. The four samples include water from the Juniata River, water from a small creek that originates on state game lands, tap water, and deionized water. The water samples from the Juniata River and the small creek were obtained in large jugs by the laboratory coordinator using proper sampling techniques. Students work in pairs, and each pair analyzes two of the four samples. The students acquire 100 mL of a sample, and a reading of the initial pH is taken. While the solution is stirred, the 0.05 M sulfuric acid is dispensed dropwise from a dropper bottle. The number of drops added is recorded at intervals of 0.2 pH units. The students are instructed to carry out the titration until the pH is about 2.5. In this experiment I was mainly concerned with the concept of relative buffer capacity; to keep the experiment as simple as possible, a dropper bottle was used instead of a buret.

In the second half of the laboratory period, the students are escorted to a computer laboratory in the chemistry building and are asked to use a standard graphing program to plot the pH vs. the number of drops added for each titration. Under instructor supervision, my students had very little difficulty using the software. They are asked to determine from the plots the number of drops that were required to reach a pH of 4.4 (i.e., to destroy the buffer capacity of the water). This provides a relative measure of the alkalinities of the four water samples. The data are pooled and analyzed. Students are asked to rank the four water samples in order of decreasing alkalinity, and to explain the differences in alkalinity among the four samples.

Results and Discussion

Figure 1 shows the titration plots for 100-mL samples of the Juniata River and the small stream. The Juniata River was found to have a fairly high alkalinity. This is mainly due to the large limestone deposits located in Central Pennsylvania. The bicarbonate ion concentration of the river increases from the dissolution of calcium carbonate as it carves its way through these regions rich in limestone. Agricultural runoff may also contribute to the alkalinity of the river.

Water from the small stream on the state game land had a considerably lower alkalinity. Since the sample was taken not far from its source, the stream had not come into contact with any limestone deposits and was well removed from any sources of agricultural runoff. This stream is clearly much more susceptible to the effects of acid rain than is the Juniata River.

Tap water generally has a very high alkalinity. Our data indicated that the local tap water had a higher alkalinity than the Juniata River, which led to a classroom discussion of water-treatment plants. At some water-treatment plants, sodium carbonate or lime is added to the water in an effort to raise the pH. This removes some of the metal ions through the formation of insoluble carbonates or hydroxides. The addition of sodium carbonate at the water treatment plant is useful in forcing the equilibrium between the lead ion and lead carbonate toward lead carbonate, decreasing the solubility of lead. (The lead plumbing in many older houses can cause dangerous levels of soluble lead in drinking water.) The water-treatment plant at Carlisle, however, does not add any carbonate or lime because the alkalinity of the incoming water from the Letort River is great enough to counteract the potential problems with lead pipes and other metals. Thus, the difference in alkalinity between the tap water and the Juniata River is a consequence of the Letort River having a greater alkalinity than that of the Juniata.

Deionized water has a very limited buffer capacity. Most of the bicarbonate ions are removed through the ion-exchange process, which was discussed briefly the next week in lecture.

For samples that are very low in alkalinity, changes in the dissolved carbon dioxide concentration can effect the results of this experiment. For samples that contain very little bicarbonate, such as the small stream or deionized water, an increase in the concentration of dissolved carbon dioxide in the water forces the equilibrium between carbonic acid and the bicarbonate ion toward the formation of more bicarbonate ions, increasing the alkalinity of the water. This phenomenon can be readily explained through a straightforward application of Le Chatelier's principle.

$$CO_2\ (g) + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+$$

Proper sampling procedures require that samples be taken toward the middle of the stream at a depth of several feet. Such samples are rarely saturated with dissolved carbon dioxide. Therefore, when samples are collected, the container must be filled to the very top, sealed, and refrigerated so that the concentration of carbon dioxide in the sample does not change before analysis. In the lab, students should analyze their 100-mL samples as soon as they are taken from the container, and they must put the cap back on the common samples immediately. If they allow their sample to sit on the counter for 20 minutes before performing the titration, they may observe slightly higher alkalinities due to an increase in the dissolved carbon dioxide concentration.

Conclusion

This laboratory experiment is appropriate for a chemistry course designed for nonscience majors. It takes between two and three hours to complete. The concepts of buffer capacity

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and alkalinity using real samples are demonstrated graphically, while avoiding confusing mathematical and stoichiometric relationships. In general, the students enjoyed the experiment because we were analyzing real samples. The use of pH meters and the construction of the titration plots are essential to the success of this experiment. Although alkalinity tests are most often performed with acid–base indicators instead of a pH meter, the titration curve provides a visual image that enables the students to gain an appreciation for the sudden drop in pH that occurs once all of the bicarbonate has been consumed. In addition, the contrast between the alkalinities of the Juniata River and the small stream clearly illustrated the influence that geological environments have on the chemistry that occurs in natural bodies of water.

Technical Notes

The contrast between two samples from nearby streams is a very effective aspect of this experiment from a pedagogical standpoint. However, I realize that not all communities are blessed with the geological diversity of Central Pennsylvania. As a guideline, I have provided the actual values for the alkalinities of the samples discussed in this paper. The alkalinity of the Juniata River, the small stream, and the tap water were about 60, 2, and 85 mg $CaCO_3$ per liter, respectively.

This experiment was designed for nonscience majors. However, it can be modified so that it is appropriate for chemistry majors course or an environmental chemistry course. In the spring of 1999 I had my Environmental Chemistry students perform a similar experiment. Students in this course were junior and senior environmental science majors. They used burets to accurately measure the volume of a 0.05 M sulfuric acid required to reach the equivalence point. They were instructed to first standardize the sulfuric acid to accurately and precisely determine its concentration. They also were required to perform the titration three times and to calculate an average alkalinity in terms of equivalent mg/L of calcium carbonate. The stoichiometry used for this calculation is based on the equation for the dissolution of calcium carbonate given above.

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