1. Softening Hard Water

Introduction

Our water comes from lakes, rivers, and wells. Even if it is fit to drink, it is never chemically pure; it is a solution. Water from these sources always contains a variety of dissolved ions, including Ca^{2+}, Mg^{2+}, Fe^{3+}, HCO_3^-, and SO_4^{2-} ions. Water with relatively small concentrations of Ca^{2+} and Mg^{2+} ions is called *soft water*. If the concentrations of these ions are relatively large, the water is called *hard water*.

Hard water causes many problems. However, there are several methods for removing Ca^{2+} and Mg^{2+} ions. Any method that removes these ions is called *water softening*. One technique for softening water is *ion exchange*.

Purpose

This experiment begins with an examination of some reactions of aqueous Ca^{2+} and Mg^{2+} ions. Some of these reactions are important in our natural waters. The experiment concludes with a study of water softening by ion exchange.

The source of hard water

Calcium and magnesium ions are often found in minerals as the carbonates $CaCO_3$ and $MgCO_3$. These substances are insoluble in pure water. Hard water is a result of their solubility in the dilute solutions of carbonic acid (H_2CO_3) that occur in natural water. Atmospheric carbon dioxide (CO_2) dissolves in natural water to form this acid according to the equation

$$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$$

The carbonic acid formed in this process reacts with a carbonate mineral to give a soluble substance. For example, the acid reacts with $CaCO_3$ to form soluble calcium hydrogen carbonate:

$$CaCO_3(s) + H_2CO_3(aq) \rightarrow Ca^{2+}(aq) + 2HCO_3^-(aq)$$

The overall equation for this process is the sum of these equations:

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

A similar equation can be written for $MgCO_3$.

The effects of hard water

The reactions that are responsible for the solubilities of $CaCO_3$ and $MgCO_3$ in dilute solutions of H_2CO_3 are readily reversed when heat is applied. The reversal occurs because CO_2 is evolved from the hot solutions. As a result, the solution becomes less acidic and the insoluble carbonates return. These carbonates are partly responsible for the residues that coat the inside surfaces of tea kettles, hot-water pipes, boilers, and heat exchangers.

Another problem occurs when soap is used in hard water. The Na^+ ion in sodium stearate ($C_{17}H_{35}COO^-Na^+$), a common ingredient in soap, is replaced by Ca^{2+} and Mg^{2+} ions to form an insoluble curdy scum. This material, which consists of calcium and magnesium stearates, is responsible for the dull appearance of clothes washed in hard water and for the ring of scum that can form on a bathtub. Detergents have replaced soap to avoid these effects.

Measuring hardness

Hardness is usually measured through a titration of the water with a solution of the sodium salt of dihydrogen ethylenediaminetetraacetate ions. Figure 1.1 shows the structure of the parent anion, which is called EDTA. The doubly protonated EDTA anion that is used in the titration reacts with a Ca^{2+} ion (or almost any other metal ion) to form a complex ion (Ebbing/Gammon, Section 23.3). The equation for this reaction is

$$H_2EDTA^{2-}(aq) + Ca^{2+}(aq) \rightleftharpoons Ca(EDTA)^{2-}(aq) + 2H^+(aq)$$

A similar reaction occurs with Mg^{2+} ions.

The endpoint in the titration can be detected with an indicator such as Eriochrome Black T. This indicator, whose aqueous solutions are blue, forms rose-pink complex ions with Ca^{2+} and Mg^{2+} ions. For example, the reaction with Ca^{2+} ions can be written as

$$Ca^{2+}(aq) + \underset{\text{(blue)}}{In(aq)} \rightleftharpoons \underset{\text{(rose pink)}}{Ca(In)^{2+}(aq)}$$

where In represents the complicated formula of the indicator. When H_2EDTA^{2-} anions are added to this solution during a titration, the metal ions are removed from the indicator complex ion to form the complex ion with EDTA. The reaction with Ca^{2+} ions is

$$H_2EDTA^{2-}(aq) + \underset{\text{(rose pink)}}{Ca(In)^{2+}(aq)} \rightleftharpoons Ca(EDTA)^{2-}(aq) + \underset{\text{(blue)}}{In(aq)} + 2H^+(aq)$$

The reaction occurs because the $Ca(EDTA)^{2-}$ ion is more stable than the indicator complex ion. A similar reaction can be written for magnesium. The endpoint of the titration occurs when the blue color due to the free indicator appears.

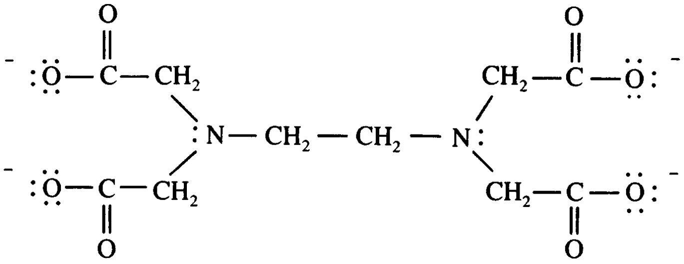


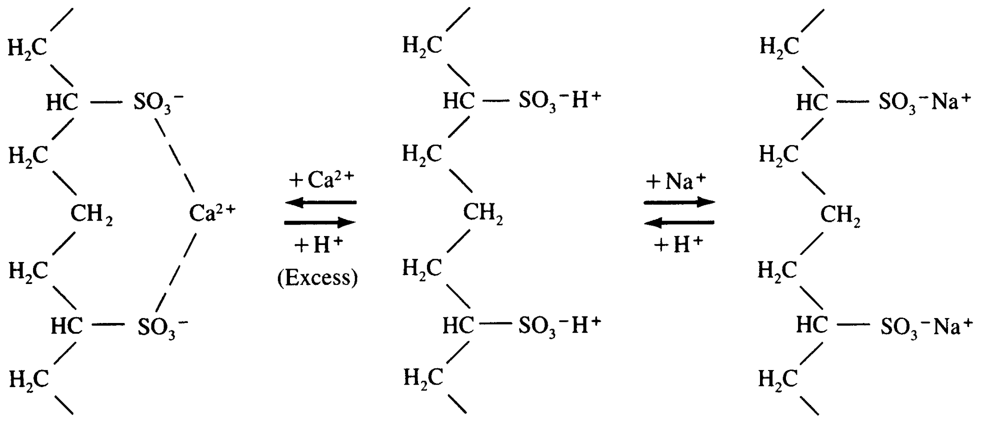
FIGURE 1.1
The structure of the ethylenediaminetetraacetate (EDTA) anion.

Ion exchange

A cation-exchange resin [Ebbing/Gammon, Chapter 12, “A Chemist Looks At: Water (A Special Substance for Planet Earth)”] will be used in this experiment. This resin is an insoluble organic substance whose molecules consist of long chains of atoms. The sulfonic acid group, $-SO_3H$, is chemically bonded to the chain in many places. Figure 1.2 shows the mechanism for cation exchange. One type of ion simply replaces an ion of another type.

FIGURE 1.2

A cation-exchange resin in the H^+ form (center), the Ca^{2+} form (left), and the Na^+ form (right).



Ions with a +2 charge, such as Ca^{2+} ions, are more strongly bound to the resin than are ions with a +1 charge, such as Na^+ or H^+ ions. As a result, a cation-exchange resin in the H^+ form will easily exchange ions with a dilute solution of Ca^{2+} and Mg^{2+} ions. After this exchange has occurred, the resin in its original H^+ form can be regenerated, but a large excess of a strong acid must be used. Ion-exchange resins are best employed in columns so that a solution can percolate through the resin.

Concept of the experiment

Because $CaCO_3$ and $MgCO_3$, along with CO_2, play important roles in the formation of hard water and in some of its effects, the first part of the experiment will focus on these substances. Read the section on the formation of gases in your textbook (Ebbing/Gammon, Section 4.4) again so that you understand some reactions that lead to the formation of CO_2. It will also be helpful if you have read the section in your textbook that deals with hard water [Ebbing/Gammon, Chapter 12, “A Chemist Looks At: Water (A Special Substance for Planet Earth)”].

Water softening by ion exchange is the subject of the second part of this experiment. Although ion-exchange resins in columns are very efficient, this experiment uses an easier technique. This method consists of stirring the resin and a water sample in a beaker. You should still achieve quantitative or near-quantitative cation exchange, because you will use a large excess of the resin.

To judge the hardness of the water sample before and after ion exchange, you will use Na_2H_2EDTA. However, you will use a semi-quantitative titration via a medicine dropper. The sample will be tap water or, if your water is very soft, an artificial sample provided by your laboratory instructor.

Procedure

Getting started

1. Obtain 4 small test tubes and 2 pieces of blue litmus paper. Additional litmus paper can be obtained if you need it.
2. Obtain about 6 g of dry cation-exchange resin or about 9 g of wet resin in a 250-mL beaker. Because this resin is very expensive, it must be returned when you have finished the experiment.
3. Your laboratory instructor will tell you whether you are to use tap water or an artificial sample for ion exchange.

Observing reactions of Ca^{2+} and Mg^{2+} ions

1. Add 10 drops of 0.1 *M* $Ca(NO_3)_2$ to each of 3 test tubes.
2. Add 10 drops of 0.1 *M* Na_2CO_3 to the first test tube, another 10 drops of this solution to the second test tube, and 10 drops of 0.1 *M* $NaHCO_3$ to the third test tube.
3. Shake each of the test tubes gently. Observe the results carefully and record them.
4. Add dry ice (solid CO_2) slowly to the first test tube. You should use a quantity about the size of 2 peas. Shake the test tube gently until no further effects can be seen. Record the result.
5. Add 2 drops of 6 *M* HCl to the second test tube. Record the result.

   CAUTION: Handle the solution of hydrochloric acid carefully. It can cause chemical burns in addition to ruining your clothing. If you spill any on you, wash the contaminated area thoroughly and report the incident to your laboratory instructor. You may require further treatment.

6. Heat the third test tube gently in the flame of your laboratory burner.

   CAUTION: Do not point the test tube toward anyone. Do not let the flame linger in any one place. Move the test tube continuously in the flame.

   Record the result.
7. Cool the third test tube in tap water. Add 2 drops of 6 *M* HCl. Record the result.
8. Add a pea-sized portion of solid $CaCO_3$ to the fourth test tube. Add several drops of 6 *M* HCl and observe. Record the result. What you have seen here also occurred in Steps 5 and 7, but it may not have been noticed.
9. Discard the solutions. Wash and rinse the test tubes.
10. Repeat Steps 1 through 7 using 0.1 *M* $Mg(NO_3)_2$ instead of 0.1 *M* $Ca(NO_3)_2$.

Preparing the resin

1. Make sure that the resin is in the H^+ form even if you obtained it in this form.

2. Add 6 M HCl to the beaker containing the resin until the resin is barely covered. Allow the mixture to stand for about 2 min.
3. Add about 200 mL of distilled water, and let the mixture stand until the resin settles to the bottom of the beaker.
4. *Carefully* decant (pour off) the solution above the resin until only a few milliliters of solution remain.
5. Wash the resin by adding 200 mL of distilled water. Let the resin settle to the bottom and then decant again.
6. Repeat Step 5 three more times.
7. Repeat Step 5 again, but test the solution with blue litmus paper before decanting. If the paper turns pink, continue washing according to Step 5 until no change occurs when you test the solution with blue litmus paper.

Softening hard water

1. Cover the resin in the beaker with a quantity of tap water or the artificial sample. Use 100 mL unless your laboratory instructor provides other directions. If you are using an artificial sample, you will need enough for water softening (100 mL) plus an additional quantity of about 50 mL.
2. Let the mixture of resin and water stand for 10 min with occasional stirring.
3. During this time, add 20 mL of unsoftened water (either tap water or your artificial sample) to a clean 125-mL Erlenmeyer flask from a clean graduated cylinder.
4. Add 5 mL of an NH_3–NH_4Cl buffer ($[OH^-] \approx 10^{-4}\ M$) to this flask.
5. Add a very small portion of a solid mixture of Eriochrome Black T and sodium chloride. This portion should not exceed 1/8 inch on the tip of a metal spatula. Hard water should provide a light rose-pink color.
6. Add 0.01 M Na_2H_2EDTA *slowly* by drops from a medicine dropper, counting the drops and swirling the solution in the flask. As the endpoint is approached, you should see a lavender color. After this point, add the solution more slowly until the first appearance of the blue color. Record the number of drops that were required.
7. If you wish, repeat Steps 3 through 6 with another 20 mL of unsoftened water. Calculate and record the mean.
8. After 10 min have elapsed, *carefully* decant the softened water into a clean beaker until only a few milliliters of the water remain with the resin.
9. Repeat Steps 3 through 5 using softened water instead of unsoftened water.
10. The blue color will appear immediately if virtually all of the Ca^{2+} and Mg^{2+} ions in the water have been removed. If so, record this result. If not, repeat Step 6.

Finishing the experiment

1. Convert the resin to the H^+ form, using the same method that you used to prepare the resin.
2. Return the resin to your laboratory instructor.

CAUTION: Before you leave the laboratory, make sure that your gas outlet and those of your neighbors are closed.

Softening Hard Water

Date:		Student name:	
Course:		Team members:	
Section:			
Instructor:			

Prelaboratory assignment

1. Provide definitions for the following terms:
   a. Hard water

   b. Soft water

   c. Water softening

   d. Ion exchange

   e. Cation-exchange resin

2. a. Give two detrimental effects that result from using hard water.

b. Write equations that describe the insoluble curdy precipitate that is formed when soap is used in hard water.

3. Write equations that describe the titration of Mg^{2+} ions with H_2EDTA^{2-} ions in the presence of the indicator.

4. What will you do with the cation-exchange resin after the experiment?

5. What safety precautions should be observed during this experiment?

Softening Hard Water

Date:		Student name:	
Course:		Team members:	
Section:			
Instructor:			

Results

1. *Reactions of Ca^{2+} and Mg^{2+} ions*

	$Ca(NO_3)_2$	**$Mg(NO_3)_2$**
Na_2CO_3		
$Na_2CO_3 + CO_2$		
$Na_2CO_3 + HCl$		
$NaHCO_3$		
$NaHCO_3$ + heat		
$NaHCO_3$ + heat + HCl		

Solid $CaCO_3 + HCl$	

2. *Softening hard water*

Drops of 0.01 *M* Na_2H_2EDTA

Before ion exchange: ....

After ion exchange: ....

Questions

1. Write an equation for every reaction that you observed with Ca^{2+} and Mg^{2+} ions in the first part of the experiment. If Mg^{2+} ions behaved somewhat differently from Ca^{2+} ions, give a reason.

2. Determine the percent efficiency of your water softening from the number of drops of the Na_2H_2EDTA solution that were required before and after you treated the water with the cation-exchange resin.

Student name: .... Course/Section: .... Date: ....

3. Describe how a cation-exchange resin and a solution of NaOH with a known concentration could be used to determine the amount of NaCl in an aqueous solution.