

Applications of Solubility Product Principles

There are many instances in which a knowledge of solubility equilibria and solubility product values is important to a chemist. You were introduced to the study of qualitative analysis in Chapter 16 in a rather simple way. More detailed schemes for identifying a large number of different ions depend on a knowledge of K_{sp} values, and the common ion effect is often used to control the concentration of the reagents in order to exceed the K_{sp} for one ion and not another, thus effecting a separation.

One aspect of solubility equilibria with which you may already be familiar is the topic of water hardness. Essentially, hard water is water that does not allow soap to lather well because Ca^{2+} and Mg^{2+} ions are present in the water, though some other metal ions can also be involved. The Ca^{2+} and Mg^{2+} ions get into the water from the geological formations over which the water flows. Water found in limestone areas is more likely to be hard than water which contacts mainly granite. Thus, how much of a problem water hardness is depends greatly on where you live.

The reason why hard water does not allow soap to form suds very well is that the Ca^{2+} and Mg^{2+} ions react with the stearate ion, $\text{C}_{17}\text{H}_{35}\text{COO}^-$ (soap consists mostly of sodium or potassium stearates), forming an insoluble curd or scum. Thus, a lot of soap gets wasted, precipitating Ca^{2+} and Mg^{2+} before it can start to lather and help remove dirt.

There are two main types of hard water. *Temporarily hard water* contains $\text{Ca}(\text{HCO}_3)_2$ or $\text{Mg}(\text{HCO}_3)_2$, which can be removed by boiling. *Permanently hard water* contains mainly sulfates and chlorides of Ca^{2+} and Mg^{2+} , which cannot be removed by boiling; other means must be used. In Parts I and II of this experiment you will investigate temporarily and permanently hard water respectively, and investigate ways of removing the hardness.

One other important application of solubility equilibria and K_{sp} values is in analytical chemistry, in situations where the quantity of a dissolved ion needs to be determined. This is often done by precipitation, and in Part III of this experiment you will determine the $[\text{Cl}^-]$ in a sample of water (tap water, river water, lake water, or an unknown chloride solution) by titrating with a standard solution of silver nitrate. Sodium (or potassium) chromate can be used as an indicator. Since AgCl is less soluble than Ag_2CrO_4 , it will be precipitated first. When all the chloride has been precipitated, Ag_2CrO_4 will be formed. It has a brick-red color (as opposed to white for the AgCl), so the first appearance of a brick-red color indicates that all the chloride has been precipitated.

OBJECTIVES

1. to demonstrate the formation of temporarily hard water, as well as how the hardness can be eliminated
2. to demonstrate the effect of permanently hard water, as well as how the hardness can be eliminated
3. to determine the concentration of Cl^- in a water sample by titrating with standard AgNO_3

MATERIALS

Apparatus

Erlenmeyer flask (250 mL)
Bunsen burner
ring stand
clamp
wire gauze
test-tube rack
8 test tubes (13 mm × 100 mm)
buret (50 mL)
stopper
pipet (25 mL) *or*
graduated cylinder (25 mL)
2 beakers (250 mL)
filter funnel
lab apron
safety goggles

Reagents

saturated limewater
(calcium hydroxide, $\text{Ca}(\text{OH})_2$)
 CO_2 supply
powdered pure soap *or*
liquid soap
0.4M MgSO_4
0.4M CaCl_2
2M Na_2CO_3
0.100M AgNO_3
sample of water containing
chloride ions
0.10M Na_2CrO_4

PROCEDURE

Part I Temporarily Hard Water

1. Put on your lab apron and safety goggles.
2. Obtain 25 mL of saturated limewater solution and record its appearance in your copy of Table 1 in your notebook.
3. Bubble CO_2 gas into the solution from the cylinder provided or from the CO_2 gas generating flask and record the appearance of the solution in Table 1. Keep bubbling until the precipitate which forms at first dissolves again, and record the appearance of the solution.
4. Pour off about 5 mL of this solution into a 13 mm × 100 mm test tube (A).
5. Set up the flask on the stand, and heat with the Bunsen burner until the solution has boiled for 5 min. Observe the result.
6. Pour 5 mL of the flask's contents into a second test tube in the rack (B). Discard the remaining contents.
7. Place 5 mL of distilled water into a third test tube (C).
8. To each test tube add enough powdered pure soap to cover the surface of the liquid, or 1 drop of liquid soap.
9. Shake each test tube. Note the relative amount of lathering in each test tube, and record your observations in your copy of Table 2.

Part II Permanently Hard Water

1. Set up five 13 mm × 100 mm test tubes in a rack. Label them A to E, and add the following to each:
A: distilled water
B: 4 mL of 0.4M MgSO_4
C: 4 mL of 0.4M CaCl_2
D: 4 mL of 0.4M MgSO_4 + 1 mL of 2M Na_2CO_3
E: 4 mL of 0.4M CaCl_2 + 1 mL of 2M Na_2CO_3

- To each add enough pure soap powder to cover the surface of the liquid, or 1 drop of liquid soap. Note the appearance of each in your copy of Table 3.
- Shake each test tube. In Table 3, record the relative amount of lathering in each test tube.

Part III Determination of Chloride Ion Concentration in a Water Sample

- Obtain approximately 100 mL of 0.100M silver nitrate solution, AgNO_3 , in a 250 mL beaker. (Your teacher may suggest more or less of this, depending on the amount of chloride in your samples to be tested and how many measurements you are to make.)
- Set up the buret with its clamp and stand, and pour about 10 mL of AgNO_3 into it, using a filter funnel. Rinse back and forth (use a stopper, not your finger!), and discard the rinsings through the tip into a 250 mL beaker. Use this beaker for all your silver wastes.
- Refill the buret to the top, and drain enough into your silver wastes beaker that the tip is filled and free from air bubbles.
- Your teacher will recommend using a 25 mL, 50 mL, or 100 mL sample of water, depending on the amount of chloride content in it. Transfer the specified amount to your Erlenmeyer flask, using either a 25 mL pipet or a graduated cylinder. Record the volume of the sample in your copy of Table 4.
- Add 2 mL of 0.10M Na_2CrO_4 to the water sample.
- Record the initial volume reading on the buret in Table 4, and run the AgNO_3 solution into the flask, swirling all the time. You should notice that, although a white precipitate is produced, the solution stays yellow because of the chromate ions.
- As the titration continues you will notice a reddish color begin to form which disappears as the swirling continues. Slow down the rate at which you are adding the AgNO_3 at this point, until you are adding it drop by drop. Stop at the point where the contents of the flask show the first sign of a reddish color that remains.
- Read the final volume in the buret, and calculate the volume used to precipitate all the Cl^- ions. Record both figures in Table 4.
- Empty the contents of the flask into your beaker containing silver wastes.
- Repeat Steps 3 to 9 once or twice more, with either the same water sample or a different one, as directed by your teacher.
- Wash your hands thoroughly with soap and water before leaving the laboratory, using a fingernail brush to clean under your fingernails.



CAUTION: Silver nitrate is poisonous, and is corrosive to skin and eyes. It will result in brown stains on your skin if you spill any on yourself. If this occurs, wash with sodium thiosulfate solution, then with plenty of water. Call your teacher.

CAUTION: Sodium chromate is poisonous, and is an irritant to skin and eyes. Do not get any on your skin. If you do, wash it off with plenty of water.

REAGENT DISPOSAL

All the solutions from Parts I and II may be safely disposed of by being rinsed down the sink with copious amounts of water. Empty your beaker of silver wastes from Part III into the designated waste container. Return any unused silver nitrate solution to the container provided. Clean all glassware carefully.