Experiment 7
The Determination of Hypochlorite in Bleach

Reading assignment: Chang, Chemistry 9th edition, pp. 131-142.

Goals

We will study an example of a redox titration in order to determine the concentration of sodium hypochlorite, the active ingredient in commercial bleach.

Safety Note: Safety glasses are required when performing this experiment

Equipment and Materials

50.00 mL buret, 100 mL volumetric flask, 10 mL volumetric pipette, 25.00 mL volumetric pipette, pipette pump, 300 mL Erlenmeyer flask, 10 mL graduated cylinder, several beakers, commercial bleach solution, 10% potassium iodide solution, 2M hydrochloric acid solution, ~0.26M sodium thiosulfate solution, starch solution.

Discussion

An aqueous solution of sodium hypochlorite (NaOCl) is a clear, slightly yellow liquid, and is commonly known as bleach. Aside from its uses as a bleaching agent, sodium hypochlorite solutions are also used as sterilizing agents and in water treatment. Industrial uses include agriculture, food, paper production, and textiles. Sodium hypochlorite is also added to waste water to reduce odors.

The concentration of sodium hypochlorite in bleach solutions can be determined by titration. A desirable method would be to find a titrant that reacts with NaOCl to form a colored product. But there are no known titrant-indicator systems that work well. Therefore, we must use a two-step method to titrate sodium hypochlorite.

In the first step sodium hypochlorite, hydrochloric acid, iodide ion, and starch are combined to form a starch–triiodide complex. In this step there are three reactions that take place:

Hydrochloric acid reacts with sodium hypochlorite to form hypochlorous acid:

(1) $NaOCl(aq) + HCl(aq) \longrightarrow \underset{\text{hypochlorous acid}}{HOCl(aq)} + NaCl(aq)$

Hypochlorous acid reacts with iodide when the solution is acidic:

(2) $HOCl\,(aq) + HCl\;\;(aq) + 3I^{-}(aq) \longrightarrow \underset{\text{triiodide}}{I_3^{-}(aq)} + 2Cl^{-}(aq) + H_2O(l)$

Tridiodide, I_3^-, is a dark red complex. A dark blue complex is formed when triiodide is combined with starch.

(3) $\underset{\substack{\text{triiodide}\\ \text{ion}}}{I_3^{-}} + \text{starch} \rightarrow \underset{\substack{\text{triiodide starch}\\ \text{complex (dark blue)}}}{[I_3^{-}][\text{starch}]}$

The result of these three reactions is that when sodium hypochlorite is present the starch-triiodide complex is produced. This is useful because the result of these three reactions is the formation of a dark blue complex that has a concentration that is proportional to the amount of sodium hypochlorite in the solution.

In the second step the starch-triiodide product is titrated by sodium thiosulfate to form a colorless solution of iodide, dithionate, and uncomplexed starch:

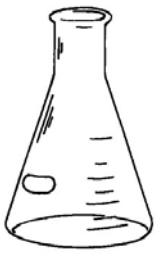
(4) $\underset{\substack{\text{triiodide starch}\\ \text{complex (dark blue)}}}{[I_3^{-}][\text{starch}]} + \underset{\text{thiosulfate}}{2S_2O_3^{2-}} \longrightarrow \underset{\substack{\text{iodide ion}\\ \text{colorless}}}{3I^{-}} + \underset{\text{dithionate}}{S_4O_6^{2-}} + \text{starch}$

If iodide is added in excess to the hypochlorous acid then all of the hypochlorous acid will be reacted, forming the dark blue starch-triiodide complex. The hypochlorite acts as a limiting reagent, determining how much triiodide is produced. We can then titrate the triiodide-starch complex with the thiosulfate to

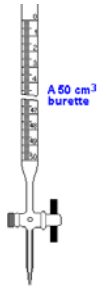
determine the concentration of the complex formed. This can then be used to calculate the initial concentration of hypochlorite.

Procedure

SAFETY PRECAUTIONS
Safety glasses or goggles must be worn throughout this experiment. Bleach is a strong oxidizer and should be washed from skin. Bleach can also damage clothing. For that reason, take care not to splash any of the bleach solution on clothing.

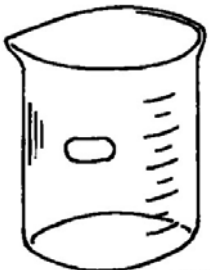


300 mL Erlenmeyer Flask

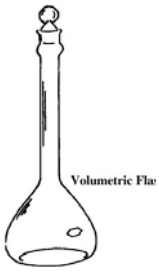


50 mL buret

25 mL pipet



beaker



250 mL volumetric flask

Students perform titrations individually. Dilution of the bleach (Step 3) can be done in pairs.

1. Rinse a 50 mL buret with tap water and then distilled or deionized water. Rinse the buret with a few milliliters of the sodium thiosulfate solution. Fill the buret to just above the 0 mL mark with sodium thiosulfate solution. Allow a few milliliters to pour through the buret tip so that any trapped air can be flushed through. Read and record the initial buret level to the nearest 0.05 mL. Record the concentration of the sodium thiosulfate solution.

2. Obtain the following reagents in the containers listed. Label the containers with the names of the reagents they contain.

Reagent	**amount**	**container**
Sodium thiosulfate (~0.26 M)	70 mL	beaker
Potassium iodide (10%)	60 mL	beaker or flask
Hydrochloric acid (2 M)	60 mL	beaker or flask
Bleach	30 mL	beaker or flask
Distilled or distilled or deionized water	60 mL	100 mL beaker or flask
Starch solution	2 mL	10 mL graduated cylinder

3. The concentration of sodium hypochlorite in bleach is high enough that it is necessary to dilute the bleach by a factor of ten. Using a 250 mL volumetric flask, a 25.00 mL volumetric pipette, and distilled or deionized water perform a dilution of the bleach solution. Carefully pipet 25.00 mL of the bleach solution into the 250 mL volumetric flask. Dilute to the 250 mL mark with distilled or deionized water,

and then mix well. The diluted bleach solution must be mixed to ensure that the concentration of bleach is homogeneous.

4. The titration takes place in a 300 mL Erlenmeyer flask. Using the 100 mL graduated cylinder add 10-20 mL of distilled or deionized water and 20 mL of 10% KI solution to the 300 mL Erlenmeyer reaction flask. This 10% KI solution should be clear, and not yellow. If the solution is yellow then it is likely contaminated.

5. Carefully pipet 25.00 mL of the diluted bleach solution into the 300 mL Erlenmeyer flask with the KI solution using the 25 mL volumetric pipette.

6. Using a 100 mL graduated cylinder add 20 mL of hydrochloric acid solution to the 300 mL Erlenmeyer flask. The hydrochloric acid solution should be added just before beginning the titration.

Before you start the titration the 300 mL Erlenmeyer flask should have: water (10-20 mL), potassium iodide (20 mL), diluted bleach (25.00 mL), and hydrochloric acid (20 mL). The buret should be filled with sodium thiosulfate. You should have 2 mL of starch in a 10 mL graduated cylinder next to the titration apparatus. The solution in the 300 mL Erlenmeyer flask should have a dark color.

7. Start the titration and allow about 4–5 mL of the sodium thiosulfate solution to run into the reaction flask and close the stopcock. Don't write the volume down at this point. You'll be adding more thiosulfate in a few moments. There may be a dark precipitate of crystals of solid iodine if you are slow in getting to this stage. It should dissolve and react with the thiosulfate solution by mixing the solution.

8. Add 2 mL of starch solution from the graduated cylinder to the 300 mL Erlenmeyer flask. The color of the solution should now be dark blue.

9. Continue the titration dropwise with constant swirling until the solution becomes clear. This clear solution signals the endpoint of the titration. Record the buret volume level in the data sheet to the nearest 0.05 mL.

10. Perform two more titrations. You will also need to obtain 2 mL of starch for each titration.

11. After completing your final titration pour any unused bleach solution into the container in one of the hoods marked "waste bleach". Other reagents can be poured down the drain. The buret should be rinsed with distilled or deionized water. All glassware should be returned to the appropriate location.

Calculations

To calculate the molarity of the sodium hypochlorite solution we use the titration volume, molarity of the thiosulfate titrant, stoichiometry of the reactions, and volume of the sample of diluted bleach solution.

1. Calculate the number of moles of titrant (sodium thiosulfate) for each titration:

$$\text{moles } S_2O_3^{2-} = \left(\text{molarity of } S_2O_3^{2-} \text{ solution}\right) \text{ x } \left(\text{volume of } S_2O_3^{2-} \text{ solution}\right)$$

2. The moles of hypochlorite are found from the stoichiometry of the reaction with thiosulfate. The stoichiometry of the equation shows that there are two moles of thiosulfate ion per mole of hypochlorous acid. Note that the moles of HOCl are equal to the moles of NaOCl and OCl^-.

$$H^+(aq) + HOCl(aq) + 2S_2O_3^{2-}(aq) \longrightarrow S_4O_6^{2-}(aq) + Cl^-(aq) + H_2O(aq)$$

$$\text{moles HOCl} = \text{moles } S_2O_3^{2-} \text{ x } \left(\frac{1 \text{ mol HOCl}}{2 \text{ mol } S_2O_3^{2-}} \right)$$

3. The bleach solution that we titrated was diluted by a factor of 10. Multiply the moles of the hypochlorous acid by 10 to take this factor into account. This will give the number of moles of HOCl in 25.00 mL of undiluted bleach.

4. Sodium hypochlorite (NaOCl) is the form of the hypochlorite that is reported on bleach bottles, not hypochlorous acid. The sodium hypochlorite mass percent is found from the mass of sodium hypochlorite in 25.00 mL and the mass of the 25.00 bleach solution:

$$\text{mass \%} = \left(\frac{\text{mass of NaOCl}}{\text{mass of bleach solution}} \right) \text{ x } 100$$

5. The mass of the NaOCl is found from the moles of NaOCl and the molar mass of NaOCl:

$$\text{mass of NaOCl} = (\text{moles of NaOCl}) \text{ x } (\text{molar mass of NaOCl})$$

6. The mass of 25.00 mL of bleach solution is found from its density and the volume (25.00 mL):

$$\text{mass of bleach solution} = (\text{density of bleach}) \text{ x } (\text{volume of solution})$$

Questions

1. Calculate the volume of the reagent thiosulfate solution which would be required if you titrated a 25 mL sample of the **original** commercial bleach instead of 25 mL of the **diluted** solution.

2. Why would we choose a graduated cylinder to measure the HCl and KI solutions instead of a volumetric pipette? When would we use a volumetric pipette?

3. You calculated the mass percent of sodium hypochlorite in the bleach (dilute and undiluted). Now calculate the molarity of the sodium hypochlorite in the dilute and undiluted solutions.

4. Use oxidation states to show that equations 2 and 4 in the introduction are redox reactions and that equation 1 is not a redox reaction.

5. Combine equations 1–3 from the discussion section to show the overall reaction for the products of the starch–triiodide complex.

6. What standard was used in this experiment?

7. Describe the naming of NaClO and HClO. What are the names of the following compounds?
$NaClO_2$ $NaClO_3$ $NaClO_4$ $HClO_2$ $HClO_3$ $HClO_4$

8. Submit a one-paged (typed) report that discusses the following topics:
   a. What were the goals or objectives of the experiment
   b. What were your results as they relate to the goals and objectives.
   c. Discuss the quality of your results.

Observations and Notes
Experiment 7: The Determination of Hypochlorite in Bleach

Date _____

Data Sheet
Experiment 7: The Determination of Hypochlorite in Bleach

Name_____

Table 1: Reagent Data

Brand name of bleach _____

Density of bleach (g/mL) _____

Volume of bleach used in each titration _____

Concentration of sodium thiosulfate _____

Titration Data

	Trial 1	**Trial 2**	**Trial 3**
Initial buret volume			
Final buret volume			
Volume delivered			

Calculations

Moles of $Na_2S_2O_3$ in titration			
Moles of NaOCl			
Average moles of diluted NaOCl			
Average moles of undiluted NaOCl			
Mass of 25.00 mL of NaOCl			
Mass of 25.00 mL bleach solution			
Mass % of NaOCl from experiment			
Mass % of NaOCl from label			