Experiment 21. Determination of the Sodium Hypochlorite Concentration of Commercial Bleach

PURPOSE

In this experiment, you will determine the concentration of household bleach by means of an oxidation-reduction titration involving iodine. This is an example of a classic "wet bench" qualitative analysis.

BACKGROUND

Nature and Production of Bleach.

Liquid household bleaches usually contain approximately 3-8% sodium hypochlorite (NaOCl) by weight; it is the oxidizing power of the hypochlorite ion that is responsible for the beneficial action of bleach. Hypochlorite performs its bleaching function by oxidizing stains (or dyes) to produce colorless, soluble, or gaseous species. Many at laundry novices discover the hard way that bleach splashed on clothes leads to white spots.

Liquid laundry bleach is prepared commercially by electrolysis of a cold, stirred solution of sodium chloride. Chlorine gas is produced at the anode:

$$2\ Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^- \qquad \textit{Oxidation}$$

and hydroxide ion is formed at the cathode:

$$2\ H_2O_{(l)} + 2e^- \rightarrow 2\ OH^-_{(aq)} + H_{2(g)} \qquad \textit{Reduction}$$

In solution, the chlorine gas and hydroxide ion react to give **hypochlorite ion**:

$$Cl_{2(g)} + 2\ OH^-_{(aq)} \rightarrow \mathbf{OCl^-}_{(aq)} + H_2O_{(l)} + Cl^-_{(aq)}$$

Preparation of a Sodium Thiosulfate Solution.

In this experiment, you will prepare 500 mL of 0.1 M sodium thiosulfate solution. You will use this solution for the final titration of I_3^- ion. Its concentration should be close to 0.1 *M* but will not be precisely that concentration. Among the reasons that a sodium thiosulfate solution cannot be prepared accurately by weight is that the solid sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) effloresces (forms gaseous products) easily and, as a consequence, its composition is not exact. In addition, fresh solutions of sodium thiosulfate tend to undergo a slight change in concentration because of the presence of sulfur-consuming bacteria in distilled water or plastic storage bottles; this decomposition can be suppressed if the water is boiled before the solution is prepared and if a tiny amount of sodium bicarbonate is added to the solution.

Accordingly, you must standardize the sodium thiosulfate solution. We will use primary-standard-grade potassium iodate (KIO_3) to standardize the solution of sodium thiosulfate. However, before considering the standardization procedure, you should be aware of some additional facts concerning thiosulfate. First, when a solution of thiosulfate is acidified, the resulting unstable thiosulfuric acid ($H_2S_2O_3$) slowly decomposes to yield elemental sulfur, sulfur dioxide, and water:

$$H_2S_2O_{3(aq)} \rightarrow S_{(s)} + SO_{2(g)} + H_2O_{(l)}$$

In spite of this decomposition, thiosulfate can be used successfully to titrate triiodide in an acid solution *if* ***the solution is so thoroughly mixed during a titration that no excess of thiosulfate is present at any time***. Second, thiosulfate solutions can be oxidized by dissolved atmospheric oxygen; for this reason, solutions being titrated (and the water used to prepare the sodium thiosulfate solution) are often boiled to remove the dissolved oxygen.

Part A. Standardization of a Sodium Thiosulfate Solution.

In the procedure for the standardization of sodium thiosulfate, the species actually being titrated is the triiodide ion (I_3^-), which is formed stoichiometrically from the reaction between a known (weighed) amount of potassium iodate and an excess of iodide ion:

$KIO_{3(s)} + 8\ KI_{(s)} + 6\ HCl_{(aq)} \rightarrow 3\ I_3^-{}_{(aq)} + 3\ H_2O_{(l)} + 6\ KCl_{(aq)} + 3\ K^+{}_{(aq)}$ (Reaction 1)

The triiodide ion produced in the above reaction is then titrated with the solution of the sodium thiosulfate (the same reaction that will be used to titrate the I_3^- formed by the sodium hypochlorite reaction). The $I_3^-{}_{(aq)}$ ion is yellow in dilute solution, and dark red-brown when concentrated.

$I_3^-{}_{(aq)} + 2\ Na_2S_2O_{3(aq)} \rightarrow 3\ I^-{}_{(aq)} + Na_2S_4O_{6(aq)} + 2\ Na^+{}_{(aq)}$ (Reaction 2)

The concentration of the thiosulfate can then be calculated through the stoichiometry of the 2-step process.

Potassium iodate is advantageous for this standardization over other standard oxidants (such as potassium dichromate) because it forms a colorless reduction product (I^- ion) and because it reacts almost instantly in a solution which is only slightly acidic. But it can decompose to KI and O_2, we will want to work with a fresh bottle. This latter fact is significant because iodide ion is rapidly oxidized by atmospheric oxygen in a strongly acidic solution.

Part B. Determination of Hypochlorite (OCl^-) Concentration.

Because hypochlorite is an oxidizing agent, its quantity or concentration in solution can be determined by means of a paired set of oxidation-reduction reactions. First, hypochlorite is reduced quantitatively and rapidly to chloride ion in an acidic aqueous medium by excess iodide ion, which is simultaneously converted to triiodide ion (in the presence of the excess iodide):

$NaOCl_{(aq)} + 3\ KI_{(s)} + 2HCl_{(aq)} \rightarrow I_3^-{}_{(aq)} + 3\ KCl_{(aq)} + H_2O_{(l)} + Na^+{}_{(aq)}$ (Reaction 1)

Second, the triiodide ion (which is stoichiometrically equivalent to the original amount of hypochlorite) is determined titrimetrically with a standard solution of sodium thiosulfate, the thiosulfate ion being converted to tetrathionate ion:

$I_3^-{}_{(aq)} + 2\ Na_2S_2O_{3(aq)} \rightarrow 3\ I^-{}_{(aq)} + Na_2S_4O_{6(aq)} + 2\ Na^+{}_{(aq)}$ (Reaction 2)

The endpoint of the titration is detected with the aid of starch, which forms an intensely colored purple complex with triiodide ion that disappears at the endpoint. We use this two-step quantitative reaction to obtain a good color change at the endpoint. Otherwise, we could not identify when the reaction was complete.

Use of Starch as an Indicator for Titrations Involving Iodine.

In titrations involving iodine or triiodide ion, the appearance or disappearance of yellowish-brown iodine or triiodide ion can be detected visually with considerable sensitivity, if the solution is not otherwise colored or turbid. However, much greater sensitivity in the detection of endpoints is gained if starch is used as an indicator for the appearance or disappearance of iodine or triiodide ion; in the presence of starch, a concentration of iodine or triiodide ion as low as 10^{-7} *M* can be detected in an otherwise colorless solution.

Certain precautions are necessary in the use of the starch indicator. First, the starch solution must be freshly prepared or properly preserved. Second, starch must not be added to the solution being titrated as long as an appreciable concentration of iodine (triiodide) is present; otherwise, some iodine tends to remain adsorbed onto the dispersed starch even at the endpoint. Third, starch cannot be used in a strongly acidic solution because the starch hydrolyzes to form other products. For the best results throughout this experiment, you should use the same quantity of starch for the standardization of the thiosulfate solution that you later use for the determination of hypochlorite in bleach.

PROCEDURE

A. Preparation and Standardization of a Sodium Thiosulfate Solution

Boil approximately 500 mL of deionized water on a hot plate. Allow the solution to cool to room temperature. In the prelab questions, you are asked to calculate the mass of sodium thiosulfate pentahydrate needed to prepare 500 mL of an approximately 0.10 *M* solution. Dissolve that amount of sodium thiosulfate pentahydrate in enough water to make 500 mL of solution. Add a "pinch" of sodium bicarbonate. ***Note: You may begin the preparation of KIO_3 samples while you wait for the water to boil, but do not add the acid until you are ready to titrate***.

Your instructor will provide primary standard grade KIO_3 dried and ready for use. Mass precisely (± 0.0001g) three samples, each with an approximate mass of 0.15g. Put each sample into a separate 250-mL Erlenmeyer flask. From this point on, titrate the three potassium iodate samples one at a time.

Add to the flask approximately **25 mL of distilled water** to dissolve the **potassium iodate**. Then add approximately **2 g of solid potassium iodide (KI)** to the solution; after the potassium iodide has dissolved. Just before titrating, add **10 mL of 1 M hydrochloric acid (HCl).** Titrate the resulting I_3^- with the sodium thiosulfate solution to be standardized. Near the endpoint, when the color due to I_3^- ion has become light orange to yel1ow, add 2 mL of the starch indicator solution and continue the titration until the violet-blue color of the starch- I_3^- complex just disappears.

Repeat the standardization procedure with the second and third weighed samples of potassium iodate. From the results of the three titrations, calculate the average molar concentration of the sodium thiosulfate solution. You need to have at least two trials with relative range on the molarity less than **2%** to move on.

B. Determination of Hypochlorite in Bleach

You will be assigned to work with fresh bottles of bleach, with concentrations from 2.75% to 8.25%. Pipet **2.00 mL** of the assigned household bleach into a 250-mL Erlenmeyer flask. Add 50 mL of deionized water and approximately 3 g of solid potassium iodide (KI) to the flask. When the potassium iodide has dissolved, (and just before you are ready to titrate) add 10 mL of 1 *M* hydrochloric acid (HCl), and immediately titrate the resulting solution with the standardized solution of sodium thiosulfate. Near the endpoint of the titration, when the solution is only light yellow, add 2 mL of starch indicator solution and continue to add the sodium thiosulfate solution in drops and then fractions of drops until the violet-blue color of the starch-I_3^- complex just disappears.

Repeat the procedure with two more **2.00 mL** aliquots of the bleach. From the results of the three titrations, determine the average molarity of hypochlorite in the bleach. You need to have at least two trials with a relative range less than **5%** to be done. The densities of bleach solutions are as follows: 1.050 g/mL for 2.75 to 3%, 1.070 g/mL for 5.25%, 1.090 g/mL for 6% and 1.100 g/mL for 8.25% bleach. Calculate the average % NaOCl by mass in the bleach.

LAB REPORT:

Please provide a FULL lab report in the style of other experiments in this course (by this point you shold know how).

DATA / CALCULATIONS / RESULTS

Provide the data, carry out the calculations, and report the results as described in the procedure.

DISCUSSION QUESTIONS

1. Why is NaOCl first reacted with iodide ions to form triiodide ions for titration with $S_2O_3^{2-}$ ions, instead of titrating the hypochlorite directly?
2. Write the balanced chemical equations for the 2 reactions in the standardization process.
3. Write the balanced chemical equations for the 2 reactions in the titration of the bleach solution.
4. Calculate relative ranges for your [$Na_2S_2O_3$] and [NaOCl]. Discuss your precision for each part.
5. Calculate your percent difference for the mass % NaOCl bleach you determined and that reported by the manufacturer. Discuss sources of any discrepancy.
6. Error Analysis Questions for Bleach Titration:

    a. A student rinsed a pipet with distilled water immediately before being used to measure the commercial bleach solution sample. Would this error affect the percent of NaOCl (too high, too low, or no change)?
    b. 3 grams of KI were used instead of two grams. Would this error affect the percent of NaOCl (too high, too low, or no change)?
    c. Discuss any additional sources of error.

CONCLUSIONS

A. Average molarity of the sodium thiosulfate solution.

B. Average molarity of hypochlorite in bleach.

C. Mass percentage of NaOCl in the bleach solution.

Bleach Titration Experiment

PRELAB QUESTIONS Name: _____

1. Calculate the mass of sodium thiosulfate pentahydrate ($Na_2S_2O_3 \bullet 5\ H_2O$) needed to prepare 500 mL of an approximately 0.10 *M* solution. ***Answer this question in the PRELAB in your lab notebook.***

2. When should the starch indicator be added in the titration and why is it added then?

3. A 3.00-mL bleach (NaOCl is the active ingredient) sample is mixed with potassium iodide and acid to completely form triiodide (I_3^-) ions. You then titrate the I_3^- ions with a thiosulfate ($S_2O_3^{2-}$) solution you have previously determined to be 0.1306 *M*. The endpoint is reached when 31.52 mL of the thiosulfate solution is added. What is the molar concentration of the bleach solution? What is its mass percent? *Note: This question is very similar to part B of the lab. See previous page for the densities of commercial bleach.*