Experiment 20

DETERMINATION OF THE SOLUBILITY OF CaSO₄ BY ION-EXCHANGE AND BY COMPLEXOMETRIC TITRATION

MATERIALS: 13-14 mL of cation-exchange resin in a 50 mL buret, saturated CaSO₄ (aq), 1 M HCl, standardized NaOH, 50 mL buret, 25 mL pipet, 10 mL graduated cylinder, 250 mL Erlenmeyer flask, 250 mL beaker, phenolphthalein indicator solution, blue litmus paper, 0.0250 M Na₂EDTA, HNB indicator, 0.0100 M Ca(CH₃COO)₂, 6.0 M NaOH, stirring rod.

PURPOSE: The purpose of this experiment is to determine the solubility of calcium sulfate, CaSO₄.

LEARNING OBJECTIVES: By the end of this experiment, the student should be able to demonstrate the following proficiencies:

1. Explain the principle of ion exchange.
2. Use proper experimental techniques with a column containing an ion-exchange resin.
3. Use stoichiometry to relate the data from an acid-base titration to the amount of a metal ion removed by a cation-exchange column.
4. Define a back-titration.
5. Use stoichiometry to relate the data from a complexometric titration to the amount of metal ion in a solution.

DISCUSSION:

There are several methods to determine solubility. Some methods are direct (e.g., by determining the mass of the dry residue produced by evaporation of a known volume of a saturated solution) while others are indirect. In this experiment, two indirect methods will be used to determine the amount of calcium in a saturated solution of calcium sulfate.

A. Ion exchange

In the first part of this experiment, an ion-exchange resin will be used. An ion-exchange resin consists of beads of an organic polymer. On the surface of the beads, there are functional groups capable of removing ions from solution and replacing them with ions of like charge from the resin. If the resin exchanges cations with the solution, it is a cation-exchange resin; if it exchanges anions, it is an anion-exchange resin.

Some examples of the reactive groups of ion-exchange resins are:

a. The carboxylic acid group: cation exchanger

\[
\text{Uncharged form} \quad \text{R-COOH} \quad \text{Charged (active) form} \quad \text{R-COO}^- + \text{H}^+
\]

b. The sulfonic acid group: cation exchanger

\[
\text{Uncharged form} \quad \text{R-SOH} \quad \text{Charged (active) form} \quad \text{R-SO}^- + \text{H}^+
\]

c. The amine group: anion exchanger

\[
\text{Uncharged form} \quad \text{R-NH}_2 \quad \text{Charged (active) form} \quad \text{R-NH}^+ + \text{A}^-
\]

---

The acidic hydrogen atoms of a cation-exchange resin can dissociate as H⁺ ions. The amine groups of anion-exchange resin can accept protons to form charged groups, RNH₃⁺. These ammonium ions then bind anions via electrostatic attraction. (Note that the anion exchanger amine group does not bind the acid HA. The acid is necessary to protonate the amine group to make the ammonium cation; this cation is then available to bind and exchange any anions in solution.)

If a cation-exchange resin is immersed in a solution containing cations (such as Na⁺) some of the hydrogen ions associated with the resin will be exchanged for the sodium ions in solution. The exchange process between a solution of sodium ions and a sulfonic acid resin is represented below. Cations with +2 or +3 charges liberate two or three protons, displacing the protons from two or three sulfonic acid groups, respectively.

\[
\begin{align*}
\text{C} & \text{SO}_3^- \quad \text{H}^+ \\
\text{C} & \text{C} \quad + \quad 2 \text{Na}^+ \\
\text{C} & \text{SO}_3^- \quad \text{H}^+ \\
\text{C} & \text{C} \\
\text{C} & \text{SO}_3^- \quad \text{Na}^+ \\
\text{C} & \text{C} \quad + \quad 2 \text{H}^+
\end{align*}
\]

Unreacted resin

Spent resin

The negative charges of the reactive groups on the resin are always balanced by the positive charges of the small mobile cations. These cations are free to move from one reactive site to another and may be further exchanged with cations in the solution surrounding the resin. Since the resin as a whole is electrically neutral, the exchange of cations in the solution for cations in the resin is stoichiometric.

As indicated by the arrows in the figure, the ion-exchange reaction is reversible. If particles of the original resin are stirred with a solution containing sodium ions, an equilibrium is eventually established. Thus, if one repeatedly separated the “spent” resin from the sodium ion-containing solution and added the solution to unreacted resin, one could remove nearly all of the sodium ions from the solution. Of course the solution is still electrically neutral because it gained hydrogen ions through the exchange.

Repeating a stir-decant procedure many times would be laborious. Fortunately, there is a more efficient way to attain the same ion-exchange result. The resin can be packed into a vertical glass tube, forming an ion-exchange column. The solution containing the sodium ions is then added to the top of the resin in the column and slowly passed through the resin. As the solution proceeds through the column, it exchanges more and more of its cations with the hydrogen ions of the resin. The replacement of cations in the solution by hydrogen ions from the resin will be essentially complete if the rate of flow is slow enough to allow the exchange equilibrium to establish itself all along the column, and if all portions of the solution have been in contact with fresh resin before leaving the column. The resin can be regenerated by passing acid through the column and reversing the entire process.

In this experiment, a saturated solution of calcium sulfate will be passed through a cation-exchange resin. The calcium ions in the solution will exchange with a stoichiometric amount of hydrogen ions on the resin. The amount of hydrogen ions in the effluent, the solution flowing off the column, will be determined by titration with a solution of standard sodium hydroxide. From the stoichiometry of the exchange reaction, the total amount of calcium in the saturated solution can be calculated and the solubility of calcium sulfate can then be determined.
B. Complexometric Titration

In the second part of this experiment, the calcium concentration will be determined by an entirely different method. Calcium ions react with ethylenediaminetetraacetic acid (EDTA), a chelating agent, to form a complex ion. EDTA is an organic polyprotic acid with the structure:

\[
\text{HOOC-CH}_2\text{N-CH}_2\text{HOOC} \quad \text{H}_2\text{C-COOH}
\]

The EDTA anion (EDTA\(^{4-}\)) is a powerful cation-complexing agent. Both nitrogen atoms and one oxygen atom of each carboxylate (-COO\(^{-}\)) group bond to a metal cation to form a complex ion in which the atoms bonded to the metal ion are oriented octahedrally. These complexes are extremely stable and contain EDTA and the metal cation in a 1:1 molar ratio.

In a direct titration to establish the concentration of a metal cation, EDTA is added to the solution with an unknown metal cation concentration. Under the experimental conditions, the EDTA combines quantitatively with the metal cation to form the complex ion. The end point occurs when all the metal cation is bound by EDTA.

One requirement of this procedure is that a suitable indicator be available to detect the end-point of the reaction. In the case of calcium ions, hydroxynaphthol blue (HNB) indicator is purple in the complexed form and blue in the uncomplexed form and so it is a suitable indicator.

\[
\begin{align*}
\text{Ca}^{2+} + \text{HNB} & \rightarrow \text{W}_{\text{HNB@Ca}^{2+}} \\
\text{blue} & \quad \text{purple}
\end{align*}
\]

The use of HNB as an indicator introduces a new problem. For the color change to occur, the solution must be quite basic. When the solution is basic, the calcium may react with the available hydroxide ions to form calcium hydroxide precipitate, Ca(OH)_2(s). Since the goal of the experiment is to determine the solubility of calcium sulfate, CaSO_4, any precipitation of calcium compounds complicates the analysis. One way around the problem is to perform the measurement as a “back-titration”, in which the saturated calcium sulfate solution is combined with an excess of EDTA (i.e., a known amount of EDTA which is greater than the amount required by the 1:1 stoichiometry). The excess amount of EDTA insures that all of the dissolved calcium is complexed and the precipitation reaction is prevented. Once the calcium is completely complexed, the solution can be made basic and the left over EDTA is titrated with a different Ca\(^{2+}\) solution of known concentration - a standard calcium acetate solution, Ca(CH_3COO)_2 (aq). Since the total amount of EDTA added is known, and the amount of Ca(CH_3COO)_2 required to react with the excess EDTA is measured (by titration), then the unknown amount of calcium in the original saturated solution can be determined by difference (i.e. moles Ca\(^{2+}\) = total moles EDTA added – moles EDTA left over).

In this experiment, the reactions occurring are:

\[
\begin{align*}
\text{CaSO}_4 \text{(aq)} + \text{EDTA}^{4-} \text{(aq)} & \rightarrow \text{CaEDTA}^{2+} \text{(aq)} + \text{SO}_4^{2-} \text{(aq)} \quad (1) \\
\text{Ca(CH}_3\text{COO})_2 \text{(aq)} + \text{EDTA}^{4-} \text{(aq)} & \rightarrow \text{CaEDTA}^{2+} \text{(aq)} + 2 \text{CH}_3\text{COO} \text{(aq)} \quad (2)
\end{align*}
\]

<table>
<thead>
<tr>
<th>The Complexometric Titration of CaSO(_4) Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount of EDTA initially added (25.00 mL of 0.0250 M EDTA)</td>
</tr>
<tr>
<td>Pipet this</td>
</tr>
<tr>
<td>Titrate this</td>
</tr>
<tr>
<td>Calculate this</td>
</tr>
</tbody>
</table>

E20-3
PROCEDURE:

Part A. Ion Exchange

TO ENSURE THAT THE ION EXCHANGE RESIN WORKS PROPERLY, NEVER ALLOW THE LIQUID IN THE COLUMN TO FALL BELOW THE LEVEL OF THE RESIN.

1. If there is any liquid above the resin in the column, open the stopcock and drain the solution through the resin until the top of the solution is just level with the top of the resin bed.

2. Place about 10 mL of 1 M HCl in the column and drain to the level of the resin, catching the effluent in a 250 mL beaker. Then add about 10 mL of distilled water to the column and drain to the level of the resin. Repeat the rinsing with 10 mL portions of distilled water until a drop of the effluent from the column has no effect on blue litmus paper, and then repeat the rinsing with an additional 10 mL of distilled water. Note, test the drops emerging from the column, not the liquid collected in the beaker. Drain your final water rinse to the level of the resin.

3. Pipet a 25.00 mL sample of the saturated CaSO4 solution onto the resin. Drain the liquid to the level of the resin, collecting the acidic solution in a clean 250 mL Erlenmeyer flask. Add three 10 mL portions of distilled water to the top of the column, draining to the level of the resin each time. Collect all of the effluent in the same 250 mL Erlenmeyer flask. Test a drop of the last effluent with litmus paper. If the solution is still acidic, rinse the column with another 10 mL of distilled water.

4. The concentration of hydronium ions in the effluent can now be determined by titrating the acidic solution in the flask with a standard NaOH solution. Add three drops of phenolphthalein indicator to the acidic solution in the 250 mL flask and titrate with the standard sodium hydroxide solution provided. Record the buret readings in the DATA SECTION.

5. Record the exact molarity of the standard NaOH solution used.

6. Record the temperature of the room.

Part B. Complexometric Titration

1. Pipet 25.00 mL of saturated CaSO4 solution into a clean 250 mL Erlenmeyer flask. Add approximately 50 mL of distilled water.

2. Pipet 25.00 mL of 0.0250 M EDTA solution into the flask. Swirl to mix.

3. With a graduated cylinder, add 2 mL of 6.0 M sodium hydroxide.

4. Using the preset dispenser cap, add 0.1 g HNB indicator (one portion) to the flask. Mix well until the solid dissolves. Titrate with 0.0100 M Ca(CH3COO)2 until the blue solution turns purple. Record the buret readings in the DATA SECTION.

5. Repeat Steps 1-4 with a second sample of saturated CaSO4 solution.

Clean up:

1. All solutions may be disposed of in the sink.

2. Make sure there is distilled water above the level of the resin in the column.

3. Return all equipment to their proper locations.
DATA SECTION
Experiment 20

**Part A. Ion Exchange**

Molarity of standard NaOH solution  
Initial buret reading  
Final buret reading  
Volume of standard NaOH added  
Room Temperature

**Part B. Complexometric Titration**

Concentration of standard Ca(CH₃COO)₂ solution

<table>
<thead>
<tr>
<th>Trial 1</th>
<th>Trial 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial buret reading</td>
<td></td>
</tr>
<tr>
<td>Final buret reading</td>
<td></td>
</tr>
<tr>
<td>Volume of standard Ca(CH₃COO)₂ added</td>
<td></td>
</tr>
</tbody>
</table>
DATA TREATMENT
Experiment 20

Show all work and be sure to include the proper number of significant figures and units.

Part A. Ion Exchange

(A.1) From the volume and molarity of the sodium hydroxide used in the titration, calculate the number of moles of H\(^+\) present in the effluent.

\[
\text{moles of H}^+ \text{ present} = \quad \text{______________}
\]

(A.2) Calculate the number of moles of calcium ions in the original saturated calcium sulfate sample.

\[
\text{moles of Ca}^{2+} \text{ in original sample} = \quad \text{______________}
\]

(A.3) Calculate the molarity of calcium in the saturated CaSO\(_4\) solution (i.e., the molar solubility of calcium sulfate in water at room temperature).

\[
\text{molarity of Ca}^{2+} \text{ in CaSO}_4 \text{ solution} = \text{solubility of CaSO}_4 = \quad \text{______________}
\]

at temperature = \quad __________ °C
Part B. Complexometric Titration

(B.1) Calculate the total number of moles of EDTA initially added to each sample of saturated calcium sulfate.

moles of EDTA added = __________________

(B.2) Calculate the number of moles of Ca(CH₃COO)₂ added during each titration. Note that this is equal to the number of moles of excess EDTA in the solution.

Trial 1: __________________           Trial 2:__________________

(B.3) Calculate the number of moles of calcium in each of the original saturated calcium sulfate solutions. Show your work. Review page E20-3 if you are having problems.

Trial 1: __________________           Trial 2:__________________

(B.4) Calculate the molarity of calcium in the saturated solution of CaSO₄ (i.e., the molar solubility of calcium sulfate in water at room temperature).

Trial 1: __________________           Trial 2:__________________

(B.5) Calculate the average molar solubility by this method and specify the temperature.

Average solubility of CaSO₄ = __________________ at ___________ °C
QUESTIONS
Experiment 20

1. Calculate the average molar solubility of calcium sulfate from the values determined in Parts A and B.

2. Calculate the molar solubility of CaSO₄, using the value $K_{sp} (\text{CaSO}_4) = 2.4 \times 10^{-5}$

3. Calculate the percent deviation between the theoretical molar solubility (Question 2) and the average experimentally determined molar solubility (Question 1). Use the experimentally determined molar solubility as the denominator (see Appendix J, “Kinds of Measurement and their Reliability”, available on the lab manual webpage, a review of percent deviation).

4. You just determined that the molar solubility calculated from the $K_{sp}$ value (Question 2) and the experimentally determined molar solubility (Question 1) are not identical. This is not due solely to experimental error. The reason for the large deviation is that not all of the calcium sulfate in the solution is present as dissociated ions. Significant ion-pairing occurs between Ca²⁺ and SO₄²⁻ ions as shown in the equations and figure below. This effect is similar to the ion pairing that you observed in the Deicers Experiment, where a small amount of NaCl “stuck together” in solution briefly rather than dissociating fully to ions.

\[
\begin{align*}
\text{Dissolution:} & \quad \text{CaSO}_4 (s) \rightleftharpoons \text{Ca}^{2+} (aq) + \text{SO}_4^{2-} (aq) \quad K_{sp} = [\text{Ca}^{2+}] [\text{SO}_4^{2-}] \\
\text{Association:} & \quad \text{Ca}^{2+} (aq) + \text{SO}_4^{2-} (aq) \rightleftharpoons \text{CaSO}_4 (aq) \quad K_{assoc} = \frac{[\text{CaSO}_4 (aq)]}{[\text{Ca}^{2+}] [\text{SO}_4^{2-}]} 
\end{align*}
\]
a. Given that ion pairing occurs in solution, list all aqueous species present in a CaSO₄ solution.

b. Both experimental methods utilized in this lab give the total calcium concentration in solution, without regard to its aqueous form (i.e., both Ca²⁺ (aq) and CaSO₄ (aq)). The Kₚ value gives just the amount of soluble calcium in ionic form, Ca²⁺ (aq).

From your average experimental molar solubility and the theoretical molar solubility determined from Kₚ, calculate the concentration of CaSO₄ (aq).

5. a. Calculate the value of Kₐssoc, the association constant for the Ca²⁺ and SO₄²⁻ ions in solution.

\[ K_{assoc} = \] 

b. Calculate the percent of soluble calcium in the form of ion pairs.

\[ \% \text{ as ion pairs} = \] 

6. Compare the percent of soluble calcium in the form of ion pairs with the percent deviation between the Kₚ solubility and the experimentally determined molar solubility. Explain what this indicates about the primary source of the large percent deviation.