Experiment 20B

DETERMINATION OF THE SOLUBILITY OF CaSO$_4$ BY ION-EXCHANGE AND BY COMPLEXOMETRIC TITRATION[1]

MATERIALS: 13-14 mL of cation-exchange resin in a 50 mL buret, saturated CaSO$_4$ (aq), 1 M HCl, standardized NaOH (~ 0.0250 M), 50 mL buret (2), 25 mL pipet (2), 10 mL graduated cylinder, 250 mL Erlenmeyer flask (2), 250 mL beaker, 50 mL beaker (2); phenolphthalein indicator solution, blue litmus paper, 0.0250 M Na$_2$EDTA, HNB indicator, 0.0100 M Ca(CH$_3$COO)$_2$, 6.0 M NaOH, stirring rod.

PURPOSE: The purpose of this experiment is to determine the solubility of calcium sulfate, CaSO$_4$.

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.
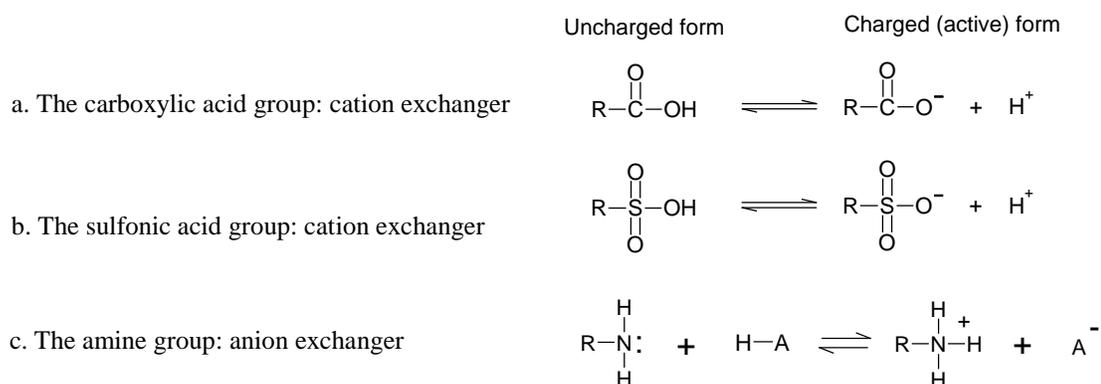

Figure 1: Some examples of the reactive groups of ion-exchange resins.

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, RNH$_3^+$. These ammonium ions then bind anions *via*

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[1]Koubek, E., *Journal of Chemical Education*, **53**, 254 (1976) and Haight, G. P., *Journal of Chemical Education*, **55**, 452 (1978).

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.

Unreacted resin   Spent resin
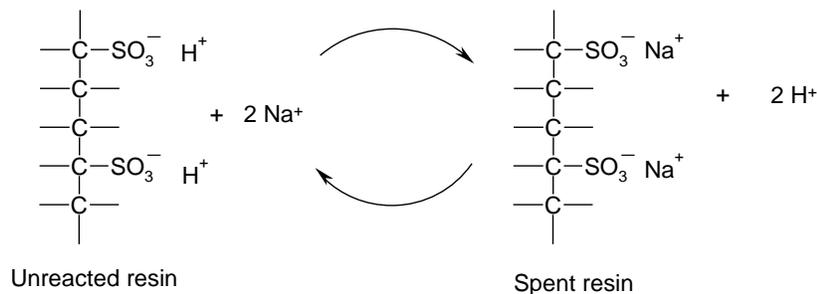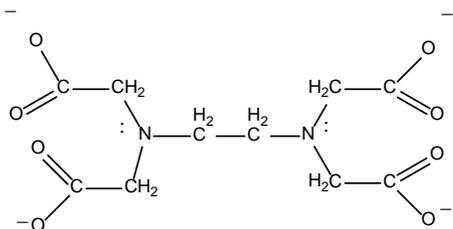
Figure 2: Ion Exchange Equilibrium

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 standardized sodium hydroxide. From the stoichiometry of the exchange reaction, the total amount of calcium ions 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 ion concentration will be determined by an entirely different method. Calcium ions react with the tetra-anion of ethylenediaminetetraacetic acid (EDTA, Figure 3), a chelating agent, to form a complex ion (Figure 4).

**Figure 3:** Deprotonated tetra-anion form of ethylenediaminetetraacetic acid (EDTA^{-4}).
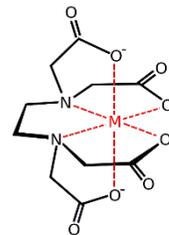
Figure 4: Metal complexed (wrapped around or "chelated") by EDTA^{-4}. Note: The resulting complex is charged,

The EDTA anion is a powerful cation-complexing agent, which contain EDTA and the metal cation in a 1:1 molar
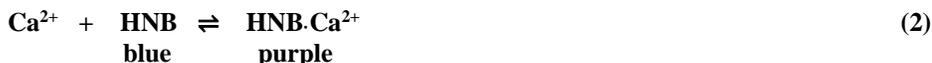
ratio. Both nitrogen atoms and one oxygen atom of each carboxylate (-COO⁻) group of the $EDTA^{4-}$ bond to a metal cation. The 2 N's and 4 O's are oriented octahedrally around the metal, in our case calcium, ion.

Under the necessary reaction conditions (very basic pH), it is more reliable to titrate in Ca^{2+}(aq) to a solution with un-complexed $EDTA^{4-}$ than vice versa. However, our analysis sample, $CaSO_4$ (aq), has an unknown amount of Ca^{2+}(aq). How do we deal with this dilemma? We add more than enough $EDTA^{4-}$, **a) in Figure 5**, to bind up all of Ca^{2+}(aq) in $CaSO_4$ (aq), **b) in Figure 5**. The remaining $EDTA^{4-}$ is reacted with Ca^{2+}(aq) in the titrant, $Ca(CH_3COO)_2$ (aq), **c) in Figure 5**.
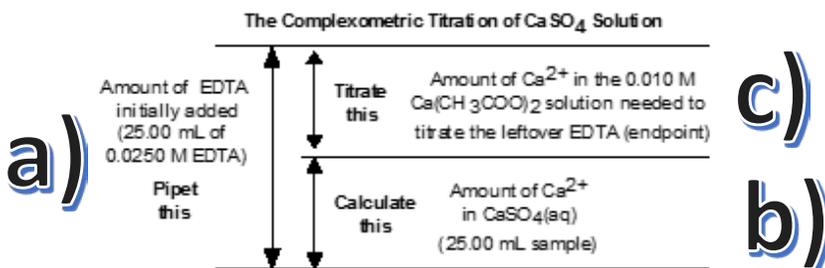
Figure 5: Illustration of the stoichiometry of the a) pipetting of $EDTA^{4-}$, b) the Ca^{2+} in $CaSO_4$ (aq) and c) the Ca^{2+} in the $Ca(CH_3COO)_2$ (aq) titrant.

The calculation of the moles in **a)** is a simple conversion problem using volume pipeted and concentration of the solution (Problem B1, p. E20B-8). The endpoint (color change) of the titration of excess $EDTA^{4-}$ with $Ca(CH_3COO)_2$ (aq) is a challenge. The Ca^{2+} in $Ca(CH_3COO)_2$ (aq) reacts more with quickly $EDTA^{4-}$ (Equation (**1**)) than with the calcium ion indicator hydroxynapthol blue (HNB, Equation (**2**)).

$$\textbf{Ca(CH}_3\textbf{COO)}_2 \textbf{ (aq) } + \textbf{ EDTA}^{4-} \textbf{(aq) } \rightarrow \textbf{ CaEDTA}^{2-} \textbf{(aq) } + \textbf{ 2 CH}_3\textbf{COO}^- \textbf{(aq)} \qquad \textbf{(1)}$$

$$\textbf{Ca}^{2+} \textbf{ + } \textbf{HNB} \rightleftharpoons \textbf{HNB·Ca}^{2+} \qquad\qquad\qquad\qquad\qquad\qquad \textbf{(2)}$$
$$\qquad\qquad \textbf{blue} \qquad\quad \textbf{purple}$$

Therefore, until all of the excess $EDTA^{4-}$ is complexed, the HNB does not sense the calcium ions, and therefore we do not visually sense the changing the solution from blue to purple. Once the last of the $EDTA^{4-}$ is complexed, the next drop of $Ca(CH_3COO)_2$ (aq) causes the HNB to react with the Ca^{2+}, and ***then*** we sense the solution color change to purple. Now, a blue-to-purple color change might not be the most dramatic, but once it is observed, we obtain the volume of the $Ca(CH_3COO)_2$ (aq) titrant. Then, once again, it is a simple conversion problem to determine the number of moles of Ca^{2+} in the titration (value **(c)**, Problem B2, p. E20B-8). Referring to Figure 5, once we have a) and c), it is a mere subtraction to get to b) Problem B3, p. E20B-8). **Summarizing**:

1. Excess $EDTA^{4-}$ (aq) is added is added to a $CaSO_4$ (aq) solution. (Problem B1, p. E20B-8).
2. $Ca(CH_3COO)_2$ (aq) is titrated to react with the $EDTA^{4-}$ (aq) that did not already react with Ca^{2+} from $CaSO_4$ (aq). **(**Problem B2, p. E20B-8)
3. The difference between the two values above is the amount of Ca^{2+} from $CaSO_4$ (aq). **(**Problem B3, p. E20B-8)

Applications of the Technology

Ion exchange columns are widely used in residential, industrial and military applications. The most common residential use is in home water softeners. "Hard" water is water containing Ca^{2+} and Mg^{2+} ions; these can form hard precipitates ("scale" deposits) that can damage plumbing. They also decrease the effectiveness of soap, forming precipitates (soap scum) rather than lather. In residential use, two Na^+ are exchanged for each Ca^{2+}; the column is regenerated with concentrated NaCl solution, rather than acid. In the Navy, ion exchange columns are used to demineralize feedwater for boiler systems, removing Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-} with a mixed bed of anion- and cation-exchange resins. Brominated resins are also used aboard most surface ships to provide safe drinking water at sea, where the use of chlorinating agents carry unacceptable fire risks.

EDTA is added to many food products – fruits, vegetables, canned goods, grain-and fat-based products – to preserve

color and flavor and prevent spoilage from air oxidation.   It is a main treatment for heavy metal poisoning, where it sequesters the metal ions and makes them water-soluble and suitable for excretion. The Navy also uses EDTA in its chelation process of boiler feedwater purification, and is a dandy product to remove calcium deposits from the walls of showers.

PROCEDURE:

Part A. Ion-Exchange

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

Loading the column resin with H^+:

1.   Locate the ion-exchange resin column, NOT the buret. The dark material in the bottom third of the column is the cation-exchange resin. If there is any liquid above the resin in the column, open the stopcock and drain the solution through the resin into a waste beaker until the top of the solution is just level with the top of the resin bed. DO NOT let any part of the resin become dry.

Ion-Exchange
Resin Column

Buret
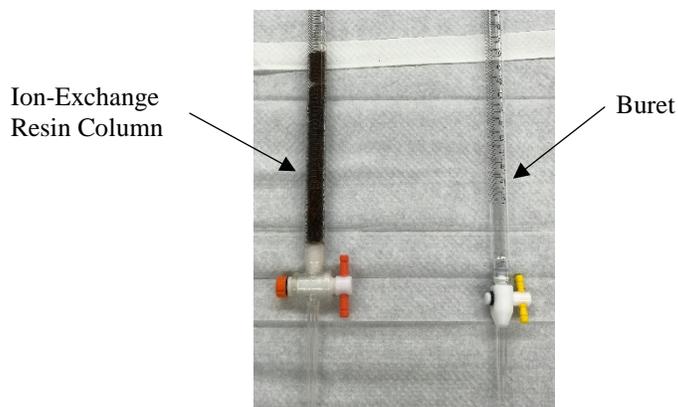
2.   Using a graduated cylinder, place about 10 mL of 1 M HCl in the ion-exchange resin column and drain to the level of the resin, catching the effluent in a 250 mL beaker.

3.   Add about 10 mL of distilled water to the ion-exchange resin column and drain to the level of the resin.

4.   Repeat the rinsing with 10 mL portions of distilled water until a drop of the effluent from the ion-exchange resin 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.

5.   Discard the contents of the beaker in the sink.

Adding the sample to the prepared column:

6.   Use the 50 mL beaker to obtain a sample of the saturated CaSO$_4$ solution.

7.   *Rinse* a 25 mL pipet with the saturated CaSO$_4$ solution, and discard the rinse.

8.   Use the rinsed pipet to deliver a 25.00 mL sample of the saturated CaSO$_4$ solution onto the ion-exchange resin in the column.

9.   Drain the liquid to the level of the resin, collecting the acidic solution in a *clean* 250 mL Erlenmeyer flask.

10.   Add three 10 mL portions of distilled water to the top of the ion-exchange resin column, draining to the level

of the resin each time. Collect all of the effluent in the same 250 mL Erlenmeyer flask.

11.   Test a drop of the last effluent with litmus paper. If the solution is still acidic, rinse the resin column with another 10 mL of distilled water.

Analyzing the column effluent by titration: The concentration of hydronium ions in the effluent can now be determined by titrating the acidic solution in the flask with a standardized NaOH solution.

12.   Add three drops of phenolphthalein indicator to the effluent collected in the 250 mL Erlenmeyer flask.

13.   *Rinse* and then fill a clean buret (NOT the ion exchange column!) with standardized NaOH solution (approx. 0.025 M, NOT 6 M!).

14.   Titrate the effluent obtained from the ion-exchange column to a pale pink endpoint. Record the buret readings in the DATA SECTION.

15.   Record the exact molarity of the standardized NaOH solution used.   Record the temperature of the room.

Part B. Complexometric Titration

1.   Use the 50 mL beaker to obtain a sample of the saturated $CaSO_4$ solution.

2.   *Rinse* a 25 mL pipet with the saturated $CaSO_4$ solution, and discard the rinse.

3.   Now use the rinsed pipet to deliver a 25.00 mL sample of the saturated $CaSO_4$ solution into a clean 250 mL Erlenmeyer flask. Add approximately 50 mL of distilled water.

4.   Use a clean 50 mL beaker to obtain a sample of the 0.0250 M EDTA solution. *Rinse* a 25 mL pipet with the EDTA solution, and discard the rinse. Now use the rinsed pipet to deliver a 25.00 mL sample of 0.0250 M EDTA solution into the same flask that already contains the saturated $CaSO_4$ sample. Swirl to mix.

5.   With a graduated cylinder, add 2 mL of 6.0 M sodium hydroxide to the flask.

6.   Add ~0.1 g HNB indicator to the flask. Mix well until the solid dissolves. *Rinse* and fill a clean buret with 0.0100 M $Ca(CH_3COO)_2$ solution (NOT $CaSO_4$!) and titrate until the blue solution turns purple. Record the exact concentration of the standardized $Ca(CH_3COO)_2$ solution. Record the buret readings in the DATA SECTION.

7.   Repeat Steps 1-4 with a second sample of saturated $CaSO_4$ 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 ion-exchange column.

3.   Return all equipment to their proper locations.

Name _____   Section _____

Partner _____   Date_____

DATA SECTION
Experiment 20B

Part A. Ion Exchange

Initial buret reading   _____

Final buret reading   _____

Volume of standard NaOH added   _____

Molarity of standard NaOH solution   _____

Room Temperature   _____

Part B. Complexometric Titration

Concentration of standard $Ca(CH_3COO)_2$ solution   _____

	Trial 1	Trial 2
Initial buret reading	_____	_____
Final buret reading	_____	_____
Volume of standard $Ca(CH_3COO)_2$ added	_____	_____

DATA TREATMENT
Experiment 20B

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.

moles of H^+ present = _____

(A.2) Based on the number of moles of H^+ titrated and the ion exchange stoichiometry, calculate the number of moles of calcium ions in the original saturated calcium sulfate sample.

moles of Ca^{2+} in original sample = _____

(A.3) From the moles of calcium ions and the volume of the $CaSO_4$ sample, calculate the molarity of calcium ions in the saturated $CaSO_4$ solution (*i.e.*, the molar solubility of calcium sulfate in water at room temperature).

molarity of Ca^{2+} in $CaSO_4$ solution = solubility of $CaSO_4$ = _____

at temperature = _____ °C

Part B. Complexometric Titration:
Refer to Discussion of these calculations in E20B-8.

(B.1) Calculate the total number of moles of EDTA pipetted into each sample of saturated calcium sulfate.

moles of EDTA added = _____

(B.2) Calculate the number of moles of $Ca(CH_3COO)_2$ added during each titration. (Note: 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 ions in each of the original saturated calcium sulfate solutions. Show your work.

Trial 1: _____   Trial 2:_____

(B.4) From the moles of calcium ions and the volume pipetted of the $CaSO_4$ sample, calculate the molarity of calcium ions in the saturated solution of $CaSO_4$ (*i.e.*, the molar solubility of calcium sulfate in water at room temperature).

Trial 1: _____   Trial 2:_____

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

Average solubility of $CaSO_4$ = _____at _____ °C

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

_____ M

2. The solubility of $CaSO_4$ at 22°C is reported to be 0.2030 g per 100.0 g H_2O.

      a. What is the **mass percent** $CaSO_4$ in this solution?

_____ %

      b. What is the **molality** of $CaSO_4$ in this solution?

_____ mol/kg

3. Using the mass percent $CaSO_4$ in a saturated solution at 22°C just determined, calculate the **molarity** (molar solubility) of the solution at this temperature. The density of the solution is 1.003 g/mL.

_____ mol/L

4. Compare your average experimental value of the molar solubility (question 1) to the accepted value just determined by calculating the percent difference.

_____ %

5. It turns out that of all of the $CaSO_4$ that dissolves, only about 29% of all the $CaSO_4$ that dissolves also fully dissociates to make isolated ("free") Ca^{2+}(aq) and isolated SO_4^{2-}(aq) ions, the remainder exist in the form of "ion pairs" – Ca^{2+} ions strongly associated with SO_4^{2-} ions. Based on that fact and your data, what is the molar concentration of free Ca^{2+}(aq) in a saturated solution of $CaSO_4$?

_____ mol/L

Name _____   Section _____
                                                          Date _____

PRE-LAB EXERCISES
Experiment 20B

1. The sample to be analyzed in this experiment is a **saturated solution** of calcium sulfate. What does that mean?

a. The mole fraction of calcium sulfate in the solution is equal to one.
b. The molarity of calcium sulfate in the solution is equal to one.
c. The molality of calcium sulfate in the solution is equal to one.
d. The concentration of calcium sulfate is as high as possible for a stable solution at its temperature.

2. The cation-exchange resin used in part A will release hydrogen ions in proportion to the calcium ions from the sample that attach to it. These hydrogen ions are collected for the analysis. The total number of moles of hydrogen ions collected will be

a. one-half the number of moles of calcium ions attached.
b. equal to the number of moles of calcium ions attached.
c. two times the number of moles of calcium ions attached.
d. four times the number of moles of calcium ions attached.

3. In part B, the calcium ions from the sample solution react with ethylenediaminetetraacetate (EDTA) ions to form "complex ions", where each N atom and four O atoms bond to the metal ion in an octahedral arrangement.
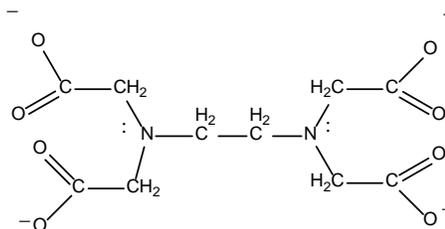
What mole ratio is expected for the complex ion product?

a. one calcium to two EDTA
b. one calcium to one EDTA
c. two calcium to one EDTA
d. three calcium to one EDTA

4. As a result of the analysis, a 25.00 mL sample of saturated calcium sulfate solution is found to contain 0.0525 g of solute. What is the molar concentration of calcium sulfate in the sample?

_____ M