CHEM 3281

Experiment Eight
Atomic Absorption Spectrophotometric Study Of The Partitioning Of Cupric Ion Across The Methyl Isobutyl Ketone - Water Interface

Objective:

The objectives of this experiment are:
1. to measure the concentration of copper in both aqueous and nonaqueous samples using the atomic absorption spectrometer.
2. to evaluate the efficiency of the extraction of copper from aqueous solutions into nonaqueous solutions using 8-hydroxyquinoline as the chelating extractant.
3. to determine the pH dependence of the distribution ratio of the copper-oxime complex between methyl-isobutyl ketone and water.

Text Reference:


Introduction:

The partitioning of mixture components between two immiscible phases is one of the most often used methods for isolation of the component(s) of interest. The procedure usually provides rapid isolation of the component(s) of interest and is easily scaled to meet the needs of the experimenter. The theory behind the practice is straightforward. The ratio of the concentration of the species of interest, X, in each phase is defined as the *partition coefficient*, $K_p$.

$$K_p = \frac{[X]_{\text{organic}}}{[X]_{\text{aqueous}}}$$

When species X exists in more than one form in either phase, the term *distribution ratio*, D, is used to quantitate the total concentration of X in each phase.

$$D = \frac{C_X_{\text{organic}}}{C_X_{\text{aqueous}}}$$

For example, if X is a weak acid, then it exists in the aqueous phase in both the associated and dissociated forms HX and X, respectively.
\[ D = \frac{C_X \text{organic}}{C_X \text{aqueous}} = \frac{[HX] \text{organic}}{([HX] \text{aqueous} + [X^-] \text{aqueous})} \]

The distribution ratio is then dependent upon pH and the pK\(_a\) of the weak acid.

\[ D = K_p [H_3O^+] / (K_a + [H_3O^+]) \]

In this experiment, 8-hydroxyquinoline will be used as a chelating extractant for cupric ion. This material is a diprotic acid.

\[
\begin{align*}
C_9H_6NOH_2^+ + H_2O & \rightleftharpoons C_9H_6NOH + H_3O^+ \\
K_{a1} &= [H_3O^+][HOx]/[H_2Ox^+] = 1.23 \times 10^{-5} \\
C_9H_6NOH + H_2O & \rightleftharpoons C_9H_6NO^- + H_3O^+ \\
K_{a2} &= [H_3O^+][Ox^-]/[HOx] = 1.55 \times 10^{-10}
\end{align*}
\]

The value of \(K_p\) for HOx is \(\sim 200\) (MIBK and H\(_2\)O). The stoichiometry of the extraction is:

\[
\text{Cu}^{2+} \text{aqueous} + 2 \text{HOx}_{\text{mibk}} \rightleftharpoons \text{Cu(Ox)}_2 + 2 \text{H}^+ \text{aqueous}
\]

An equilibrium constant \(K_{\text{eq}}\) can be written as:

\[
K_{\text{eq}} = [\text{Cu(Ox)}_2][H_3O^+]^2/[\text{Cu}^{2+}][\text{HOx}]^2_{\text{organic}}
\]

This straightforward equilibrium constant involves several speciation steps and phase transfers as per your classnotes. If (a) no metal hydroxy species are present in the aqueous phase; (b) only one complex is formed in the aqueous phase; (c) the partition coefficient of the metal complex is large (literature value is 3020); (d) no other complexing agents are present; and (e) the metal chelate exists in only one form in the organic phase, then the distribution ratio for copper is defined as:

\[
D_{\text{copper}} = [\text{Cu(Ox)}_2]_{\text{organic}} /[\text{Cu}^{2+}]_{\text{aqueous}}
\]

Substituting \(D_{\text{copper}}\) into \(K_{\text{eq}}\) (above) yields:

\[
\begin{align*}
K_{\text{eq}} &= D_{\text{copper}} [H_3O^+]^2/[\text{HOx}]^2_{\text{organic}} \\
\text{or} & \\
D_{\text{copper}} &= K_{\text{eq}} [\text{HOx}]^2_{\text{organic}}/[H_3O^+]^2
\end{align*}
\]

From your classnotes:

\[
K_{\text{extraction}} = (K_{\text{pmx}} K_1 K_a)/K_{\text{phx}} = K_{\text{eq}}
\]

If the concentration of \([\text{HOx}]_{\text{organic}}\) is large and approximately constant, we can define

\[
K' = K_{\text{extraction}} [\text{HOx}]^2_{\text{organic}} = K_{\text{eq}} [\text{HOx}]^2_{\text{organic}}
\]
and the distribution ratio $D$ becomes

$$D_{\text{copper}} \sim K'[\text{H}_3\text{O}^+]^2$$

for this extraction.

Thus, a plot of the log $D$ versus pH might be linear at certain pH’s. The atomic absorption spectrometer will be used to determine the total concentration of copper in each phase.

**Experimental:**

**Part I. - Preparation**

1. Obtain and clean the following items:
   - 16 10 mL vials
   - 4 100.0 mL volumetric flasks
   - 2 10.0 mL volumetric flasks
   - 1 60 mL separator funnel
   - assorted pipets

2. Obtain the following materials:
   - pipet bulb
   - copper sulfate reagent
   - 8-hydroxyquinoline reagent
   - 1.0 M hydrochloric acid solution

3. Weigh to the nearest 0.1 mg approximately 0.01 g of copper sulfate. Transfer this sample to an appropriately labeled 100.0 mL volumetric flask and dilute to the mark with distilled, deionized water. Weigh to the nearest 0.1 mg approximately 0.58 g of 8-hydroxyquinoline. Transfer this sample to an appropriately labeled 100.0 mL volumetric flask and dilute to the mark with methyl isobutyl ketone.

**Part II. – Determining the Effect of pH on Extraction of Copper from Aqueous Solution**

Using the stock solutions prepared in part 1, prepare the following solutions by pipetting into appropriately labeled vials the following volumes:

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<td>0.0</td>
<td>4.0</td>
<td>Aq. Blank</td>
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<tr>
<td>2</td>
<td>2.0</td>
<td>0.0</td>
<td>2.0</td>
<td>0.0</td>
<td>High Aq. std.</td>
</tr>
<tr>
<td>3</td>
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<td>2.0</td>
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<tr>
<td>4</td>
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<td>4.0</td>
<td>2.0</td>
<td>0.0</td>
<td>pH study</td>
</tr>
<tr>
<td>5</td>
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<td>1.0</td>
<td>pH study</td>
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<tr>
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<td>1.5</td>
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<tr>
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</tr>
<tr>
<td>8</td>
<td>2.0</td>
<td>4.0</td>
<td>0.5*</td>
<td>1.0</td>
<td>pH study</td>
</tr>
<tr>
<td>9</td>
<td>2.0</td>
<td>4.0</td>
<td>2.0**</td>
<td>0.0</td>
<td>pH study</td>
</tr>
<tr>
<td>10</td>
<td>2.0</td>
<td>4.0</td>
<td>2.0**</td>
<td>1.0</td>
<td>High Org. std.</td>
</tr>
<tr>
<td>11</td>
<td>2.0</td>
<td>4.0</td>
<td>1.0**</td>
<td>1.0</td>
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</tbody>
</table>
* prepare a 1:9 dilution of the stock HCl solution (i.e., use 0.10 M HCl)
** prepare a 1:99 dilution of the stock HCl solution (i.e., use 0.010 M HCl)

Vigorously mix each solution. Note any emulsion created at the interface. While one student in the team is mixing each solution, the other should become familiar with the Varian Spectraa10 Atomic Absorption Spectrometer (see appendix to this experiment for details). When you run an instrument you should record all operating conditions such as 1) type of line source used 2) wavelength used 3) slit width 4) background correction?—type of correction?

Part III. – Single vs. Multiple Extractions

Single: Transfer into the separatory funnel the following volumes:
- Copper stock solution: 5.0 mL
- Oxime stock solution: 30.0 mL
- 1.0 M hydrochloric acid solution: 5.0 mL
Mix the two phases and then separate into vials. Retain the phases for analysis.

Multiple: Transfer into the separatory funnel the following volumes:
- Copper stock solution: 5.0 mL
- Oxime stock solution: 10.0 mL
- 1.0 M hydrochloric acid solution: 5.0 mL
Mix the two phases and then separate. Drain the aqueous phase (lower layer) into a vessel. Remove the methyl isobutyl ketone phase (upper layer) and retain for analysis. Transfer the aqueous phase back into the separatory funnel and add an additional 10.0 mL of the oxime stock solution to the separatory funnel and repeat the extraction. After separation of the two phases, follow the procedure given above and again retain the MIBK phase for analysis. Extract the aqueous phase with a third portion of fresh oxime solution. Retain each of the MIBK extracts as well as that of the aqueous phase that remains for analysis.

Part IV. - Measuring Aqueous Phase Copper Concentrations

Transport the vials to the bench adjacent to the spectrophotometer. Make sure that the capillary uptake tube is in the LOWER, aqueous phase prior to initiating aspiration! Use the aqueous phase of vial #1 to zero the absorbance reading and serve as the low calibration standard for the aqueous samples. The aqueous phase of vial #2 will serve as the high calibration standard for the aqueous samples. Measure the absorption of the aqueous phase for vials #4 through #10 (lower phase) and the aqueous phase of the liquid-liquid extractions from parts 3. Aspirate the sample for 5 seconds before taking a reading.

Part V. - Measuring Organic Phase Copper Concentrations

Adjust the acetylene flow to 1.0. Make sure that the capillary uptake tube is in the UPPER, organic phase prior to initiating aspiration! Now, reset the low calibration standard setting for the organic phase (upper phase) by measuring the absorbance of the organic phase of vial #3. Reset the high calibration standard setting by measuring the absorbance of the contents of the organic phase of vial #11. Measure the absorption of the organic phase for vials #4
through #10 and the organic phases of the liquid-liquid extractions from part 3. Be sure to aspirate water for at least 10 sec between organic samples to clear the nebulizer! **Ignore 'out of calibration range' errors.** You have to calculate the real concentrations from absorbances using a calibration curve anyway.

When finished, return the acetylene flow to 1.5 and aspirate at least 200 ml of water to clear the nebulizer. Turn off the acetylene supply at the cylinder. After the gas has been drained from the line, turn off the compressed air supply. After the gas has been drained from the line, turn off the valves on the spectrometer for both acetylene and air. After ensuring that you have a printout of all results, turn off the spectrometer.

**Calculations:**

1. **Draw two calibration curves on one graph**- Absorbance vs. REAL concentration: one for aqueous phase, one for organic phase. Note that you only have one standard and one blank to create each line. Vial #1 is your aqueous blank and vial #2 is your one point high standard for aqueous copper. The AA instrumental method gives you a “fake” or normalized concentration unit for each absorbance measured. (0.000 for the blank and 0.999 for the high standard). This is used just as a consequence of the software which will write any new concentrations to disk and alter the method permanently. (Instrument expecting only one user-not 12!) So you must calculate the real concentrations of the standards to make your calibration curve. (from what you weighed out and taken aliquot for standards vials) Force a straight line through these two points.

   Plot the absorbances of the “unknowns” vial # 4-10 aqueous layer onto the aqueous line. Do likewise for the organic phase using vial #3 as your organic blank and organic phase of vial #11 as your high “standard”. Use the linear calibration curve generated in step 1 to tell you how much copper was partitioned across the water/organic interface in vials #4-10. Be sure to include this final plot. Include error bars for any replicate measurements!

2. **Plot log D vs. pH.** Connect the points to make a smooth curve. Comment on the real shape of the curve. Over what pH range is log D linear? Why does it flatten out at either end? What is the slope of the “linear” portion of the curve? Is it close to 2?

3. **For each “unknown” extraction (vials #4-10) sum the real copper concentrations determined in each phase by AA and compare the sums to the expected value (from what you weighed out and taken aliquot).** Can you account for any deviations from expectation?

**Reporting the Results:**

The report should consist of a brief description of atomic absorption spectroscopy, labeled diagram of your instrument, instrumental parameters used, raw data-labeled, calculated data-in tables, please), sample calculations for anything calculated, all plots and a short discussion of the results. In addition to an assessment of the precision in the measurements and an analysis of sources of error in this experiment, the discussion section should contain answers to the following questions:

1. Based on your results, what is the preferred procedure for extracting copper from
aqueous solutions: repeated extractions with an equal volume of organic phase or a
single extraction with a larger volume of organic phase?

2. At what pH value will exactly one-half of the copper present in the aqueous phase be
extracted into an equal volume of organic phase with the chelator and solvent used in
this experiment? (based on your experimental data?)

3. Derive an equation which describes the distribution ratio of the copper oxime complex
in terms of the partition coefficient, acid ionization constant, $K_a$, and the formation
constant, $K_f$, for the complex.

What is the "theoretical value" for the pH at which exactly one-half of the copper
present in the aqueous phase be extracted into an equal volume of organic phase with
the conditions used in this experiment? How does it compare to the value you
determined? Account for any discrepancy.

4. Consult the AA manual (or well informed T.A.!) for a description of the optical
components and their layout. Is it single beam or double beam?

5. Why is it that the absorbances measured for the aqueous phases were so different from
those measured for the methyl isobutyl ketone extracts?

6. a. Comment on your analytical method which only uses a 2-point calibration curve. Is
this a good idea or not?

   b. Comment on how you made the high standard for water and organic phase. Is the
method you used for making the high organic standard a valid one? What pH did you
use to do this extraction.—from your plot of log D vs. pH can you assume 100%
transfer into the organic layer??

   c. Did you replicate any measurements to get an estimate of your instrumental and
operator errors?