Liquid-Liquid Extraction

Objectives for LLE
The main purpose of this lab is to find a relationship of the mass transfer coefficients with respect to the flow rates of water and butyl acetate streams, and to develop a prediction of steady-state liquid-liquid extraction column operations.

1. Study the operation and performance of liquid-liquid extraction columns with different packings.
2. Determine the overall mass-transfer coefficient of the columns with different packings using number of transfer unit (NTU) method.
3. Compare the effectiveness of the extraction columns with different packing.
4. Estimate the distribution ratio of acetone in water to acetone in butyl acetate.
5. Analyze the error between experimentally determined mass-transfer coefficient and actual mass-transfer coefficient.
6. Employ dimensionless analysis and experimentally determined mass-transfer coefficient to predict the mass-transfer coefficient of a scaled-up column.

Proposed Goals
First week: Run column packed with Pall rings. Vary the flow rates of both continuous and dispersed streams to determine the $K_{xa}$ by both NTU method and empirical method ($K_{xa} = C_1 V^{C_2} L^{C_3}$).

Second week: Run the same experiments using the column packed with Rasching rings or the scaled-up Pall ring system.

Third week: By choosing a set of water and acetone-butyl acetate flow rates and use the $K_{xa}$ obtained in the previous runs to predict the outlet concentrations of product streams and compare against the experimental data with the predicted values.
Theory
In an industrial setting this is very significant in determining the end value of a crude feed, or to tell if the column is operating correctly and efficiently. Usually there are several ways of determine the performance of a column. The most traditional way is to find the overall mass-transfer coefficient (K_a) by number of transfer units (NTU) method.

\[
H_{OL} = \frac{h}{N_{OL}} \quad \text{and} \quad K_a = \frac{L}{H_{OL}A_{cross}} \tag{1}
\]

where \(H_{OL}\) is the height of transfer unit for liquid phase, \(h\) is the height of the packing column and \(N_{OL}\) is the number of transfer units, \(L\) is mass flow rate of butyl acetate and \(A_{cross}\) is the cross sectional area of the packing bed column. Under steady-state condition, number of transfer units, \(N_{OL}\), can be calculated from the equation shown as follow,

\[
N_{OL} = \frac{1}{1 - A} \ln \left( \frac{mx_s - y_R}{mx_s - y_F} \right) \tag{2}
\]

where \(x_s\) is the acetone weight concentration in the water, and \(y_F\) is the acetone weight concentration in the feed of water phase, and \(y_R\) is the acetone weight concentration in raffinate and \(m\) is the distribution coefficient, the ratio of acetone in water phase to butyl acetate phase

\[
m = K = \frac{\text{acetone in water}}{\text{acetone in butyl acetate}} \tag{3}
\]

and \(A\) is the absorption factor

\[
A = \frac{L}{mV} \tag{4}
\]

where \(V\) is the mass flow rate of butyl acetate, \(L\) is the water mass flow rate.
To determine number of transfer units ($N_{OL}$) and $K_xa$, develop a table as follows.

<table>
<thead>
<tr>
<th>Run</th>
<th>$V_1$ (kg/s)</th>
<th>$L_2$ (kg/s)</th>
<th>$A$ (-)</th>
<th>$y_F$ (-)</th>
<th>$y_R$ (-)</th>
<th>$K_xa$ (kg/s·m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$V_1$</td>
<td>$L_1$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>$V_1$</td>
<td>$L_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>$V_1$</td>
<td>$L_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>$V_2$</td>
<td>$L_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>$V_3$</td>
<td>$L_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Please make sure that the volumetric flow rate of butyl acetate is kept in the range of 0.04 to 0.08 gal/min and water volumetric flow rate from 0.25 to 0.5 gal/min.

**Correlation for Overall Mass Transfer Coefficient**

Based on the NTU determined $K_xa$, the parameter $C_1$, $C_2$ and $C_3$ in the following correlation can be determined,
\[ K_s a = C_1 V^C_2 L^{C_3} \quad (7) \]

Take natural logarithm,
\[ \ln(K_s a) = \ln C_1 + C_2 \ln(V_1) + C_3 \ln(L_2) \quad (8) \]

Take data from Run 1, Run 2 and Run 3, then plot \( \ln(K_s a) \) versus \( \ln(L) \), \( C_3 \) can be obtained from the slope of this regression line.

![Figure 2. Example of log plot of \( K_s a \) versus inlet water flow rate with constant inlet BA flow rate.](image)

For the same reason, take data from Run 2, Run 4 and Run 5, then plot \( \ln(K_s a) \) versus \( \ln(V_1) \), \( C_2 \) can be obtained from the slope of this regression line. \( C_1 \) can be obtained from the average intercept of these two lines.

**Titration**

Titration of samples will occur in a solution of hydroxylamine hydrochloride (HONH\(_2\)-HCl) with a 0.1 N sodium hydroxide (NaOH) titrant.

According to the oxime mechanism shown in Figure 3., we can find that 1 mole acetone in the solution will make 1 mole hydrochloride (HCl) release from hydroxylamine hydrochloride (HONH\(_2\)-HCl). The released hydrochloride can be further neutralized by 1 the mole of the sodium hydroxide (NaOH), which means the moles of acetone is equal to the mole of sodium hydrochloride (NaOH).
Figure 3. Mechanism of oxime.

Thus, from the following data, the volume percent of acetone in samples can be calculated:

1. Initial pH of hydroxylamine HCl solution.
2. Initial level of 0.1 N NaOH in the burette.
3. pH of solution with sample.
4. Final level of 0.1 N NaOH in the burette.
5. Final pH of the titrated solution (as a check that you stopped the titration at the end point).

**Error Analysis**

Error between predicted $y_R$ and experimental $y_R$ can be calculated by the following equation:
The errors might be caused for reasons listed as follows:

1. The BA feed is not well mixed before experiment or is mixed to different extend on different experiment day. This might cause a large fluctuation of the acetone concentration in the BA feed, therefore bringing a nonlinear change in $y_R$ and $x_E$.
2. The acetone concentration is too low in BA feed. This might cause a difficulty in the titration, because the pH value would not change evidently even when using a large amount of NaOH.
3. The readings on the pH meter. Fluctuation of readings on the pH meter would give wrong data of the percentage volume of acetone, which may also be a source of the error.
4. The water feed is too high. Higher water flow rate might cause less contact time with BA feed, so the acetone would not have enough time to dissolve in water.

Operating Procedures

**General Operations**

**Preparation of Water/acetone Waste Collection Drum**

**WARNING:** DO NOT JUMP OFF THE LOADING DOCK TO ACCESS ACETONE COLLECTION DRUMS—USE THE STAIRS.

1. Remove the drum wrench, the red float assembly, hazardous waste labels, and a pen from the center drawer on the right side of the desk in front of the titration area and take them outside.
2. Locate the 55-gallon drums outside on the containment pad for waste waster/acetone. At least two students should lift the plastic drum cover straight up until it clears the drum tops and then move it to a position on the ground near the drums.
3. Try to shake the drums one at a time to identify ones that are not full. Try to fill up drums to within 2 inches of the top.
4. Using the drum wrench, remove the large and the small plugs from the drum.

**WARNING:** UNSCREW THE PLUGS SLOWLY TO BLEED THE PRESSURE FROM THE DRUM. KEEP YOUR FACE AWAY FROM THE PLUGS.

5. Screw the red float level indicator into the small plug hole, and place the metal hose into the large plug hole and open the waste valve (V15) by the building.
NOTE: The float will begin to rise when the drum is nearly full. THIS HAPPENS SUDDENLY. Periodically (every 5 minutes) check the liquid level in the drum.

6. When a drum is full, open another drum and move the waste hose and indicator into it.

7. Label all the used drums with a yellow sticker with date on it.

8. **IMPORTANT ---- WHEN A DRUM OVERFLOWS THE ENTIRE CLASS MUST CONTACT THE LAB SUPERVISOR AND THEN CLEAN UP THE SPILL WITH ABSORBANT. THIS PROCEDURE TAKES ABOUT 1 ½ HOUR AND MUST BE DONE BEFORE ANYONE CAN LEAVE THE UNIT OPS AREA. ONE STUDENT NEED TO WATCH THE DRUMS CONSTANTLY TO AVOID SPILLS. IF SPILL HAPPENED, YOU WOULD RECEIVE ONE GRADE LESS FOR THIS LAB.**

**Start Up**
1. Turn on the water feed by opening the water feed valve (V1) on the 3rd floor.
2. Make sure the mixing pump for BA is turned off. Close the valve (V2) and open the BA feed valves (V3, V4) for turning on the BA feed on the 3rd floor.

**Shut Down**
1. Shut off BA feed by closing BA rotameter (R_{BA}) and BA inlet valve (V7).
2. Close the drain valve (V14) to fill the column with water to push the BA at the top of the column into the raffinate tank on the 1st floor.
3. When the BA/water interface is about to the raffinate exit pipe, shut off the water inlet valve (V5) and close the water rotameter (R_w) immediately.
4. Open the drain valve (V14) as much as possible to drain out the extract into the waste drum.
5. Close water inlet valve (V6) and the BA inlet valve (V8).
6. Close the BA inlet valves (V3, V4) and water inlet valve (V1) on the 3rd floor.
7. After completely drain out the extract, close extract outlet valve (V13), drain valve (V14) and BA outlet valve (V10, V11).
8. Close waste valve (V15) outside, remove the hose, cap all plug holes with the correct plug, and attach yellow labels to the drums used.

**Cleaning**
1. Empty beakers containing hydroxylamine hydrochloride solution into the appropriate waste container to the left of the fume hood and close the container.
2. Empty samples into the appropriate waste container to the left of the fume hood.
3. Make sure waste container to the left of the fume hood is labeled properly.
4. Used sample vials should be thrown into a container. They do not need to be emptied or have labels removed.
   **NOTE**: A yellow label should be on the container labeled “used sample vials containing Water, Butyl Acetate, and Acetone.
5. Throw used Kimwipes and pipette tips in the trash.
6. Turn off the pH meter.
7. Turn off the light to the fume hood and close the hood window.

**Experimental Procedures**

**Preparing the Column**

1. Select a column for the run. Check that the valves to and from the other columns are closed.
2. Set up the column by opening the outlet valves for raffinate (V10, V11) and outlet valve for extract (V13) first, then open the inlet valves for water (V5, V6) and inlet valves for BA (V7, V8).
   **NOTE 1**: The drain valve (V14) for water/acetone exit stream should be fully closed before introducing the water feed into the column.
   **NOTE 2**: At this time, no water and BA are introduced to the system, unless changing the flow rates from water rotameters (R_w) and BA rotameter (R_{BA}).
3. Introduce water by rotameter (R_w) and fill the column with water as continuous phase.
4. When the water level is about to reach the top edge of the rings, decrease the water flow rate to the value for Run 1, and open the water/acetone drain valve (V14) and control it to make sure the water does not rise to the small outlet pipe for raffinate at the top of the column.
5. Stabilize the water level somewhere in between the rings and the raffinate exit pipe near the top. This is done by setting a flow rate of the water with the rotameter (R_w) and adjusting the drain valve (V14) to keep the level stable.
   **NOTE**: The range is sometimes very little- ⅛ turn or less. A student should be responsible for observing and controlling the water level with the drain valve (V14) all the time.
6. When the level is stable and students are familiar with controlling the water level by drain valve (V14), BA mixture can be introduced to the column.
   **NOTE**: Make sure the BA outlet valve (V11) on the top of the raffinate tank must be open to avoid BA overflow and spill on the floor.
7. Introduce BA into the column to the flow rate for Run 1 by rotameter (R_{BA}).
NOTE 1: Starting with a low BA flow rate to learn the interface control and then increasing the BA flow slowly.

NOTE 2: To control the level of the water, the drain valve (V14) must be opened more.

NOTE 3: The interface between the water and the BA will form and must be observed at a proper position. Adjustment of the drain valve should be the ONLY way to control the interface level.

WHAT TO DO IF THE INTERFACE GOES TOO HIGH AND YOU CAN’T CONTROL IT WITH THE DRAIN VALVE? SHUT OFF THE WATER INLET VALVE (V5) TO DROP THE INTERFACE LEVEL.

Start an Experimental Run
1. Adjust the BA flow rate (V) and water flow rate (L) to the desired values using the rotameter R_{BA} and R_{w}, respectively.
2. Control the interface level by adjusting the drain valve (V14) to maintain the level above the top of the rings and also below the raffinate extt pipe
   **NOTE:** No waste are allowed to exit with BA due to the re-usage of the butyl acetate. Interface level must be watched carefully and constantly.
3. Samples of the inlet BA (feed) and outlet BA (raffinate) should be taken by opening valves V9 and V12, respectively, every 10-15 minutes until the system reaches steady-state.
   **NOTE:** Steady state is defined as the point at which the measured flow of acetone entering the column is the same as the flow leaving, to within a tolerance of +/-5%.
4. Determine acetone concentration in each sample using the recommended Titration Method in the fume hood.
5. Once the titration is completed, perform an acetone mass balance to determine if the column is at steady state.
6. Calculate the absorption factor (A) by Eq. (3), number of transfer units (N_{OL}) by Eq. (4), height of transfer units (H_{OL}) by Eq. (5) and overall mass transfer coefficient (K_{xa}) by Eq. (6) to complete Table 1.
7. Use correlation method to find C_{1}, C_{2} and C_{3} in Eq. (7). (Refer Correlation for Overall Mass Transfer Coefficient in Theory section)

Predict the Acetone Concentration in Raffinate
1. Set a certain flow rate for water (L_{2}) and BA (V_{1}).
2. Calculate $K_{ix}$ from the Eq. (7), $H_{OL}$ from Eq. (5) and $N_{OL}$ from Eq. (4).

3. Thus, the predicted $y_R$ can be obtained from Eq. (4).

4. Follow the procedures in previous section, then, experimental $y_R$ can be found by titration after the system reaches steady-state.

5. Calculate the error between predicted $y_R$ and experimental $y_R$ by Eq. (9).

**Change Columns**

1. Shut off BA feed by closing BA rotameter ($R_{BA}$) and BA inlet valve (V7).

2. Close the drain valve (V14) to fill the column with water to push the BA at the top of the column into the raffinate tank on the 1st floor.

3. When the BA/water interface is about to the raffinate exit pipe, shut off the water inlet valve (V5) and close the water rotameter ($R_w$) immediately. It is better to lose some BA than contaminate it with water.

4. Open the drain valve (V14) as much as possible to drain out the extract into the waste drum.

5. Close the BA inlet valves (V8) and BA rotameter ($R_{BA}$).

6. Completely drain the column through the waste water/acetone exit stream into the waste drum outside.

7. Close the BA outlet valve (V10) and the extract outlet valve (V13).

8. Close the drain valve (V14).

9. Prepare another column according to the instructions for "preparing the column".

**Calibration of pH Meter**

1. Turn on the pH meter.

2. Check if there is liquid in the probe.

3. Put the probe into pH 4.0 standard buffer and press "Standard" to calibrate the pH meter.

4. Remove the probe from pH 4.0 standard buffer, clean the probe with DI water, dap the probe with Kimwipe.

5. Put the probe into pH 7.0 standard buffer and press "Standard" to calibrate the pH meter.

6. Remove the probe from pH 7.0 standard buffer, clean the probe with DI water, dap the probe with Kimwipe.

7. The pH meter is ready to use.
**Titration Method**

1. Pour 300 ml of hydroxylammonium chloride (HONH$_2$-HCl) solution into a beaker.  
   **NOTE:** This only needs to be done once for every 6 titrations.

2. Put a magnetic stir into the beaker, place onto a stirring plate, and turn on the stirring plate. Set the stirring speed such that only a slight vortex is produced at the liquid surface.

3. Washing the probe of pH meter by DI water, wipe the outside with a Kimwipe, and put it into the beaker containing hydroxylamine HCl solution.

4. Record the initial pH value.

5. Record the initial height of sodium hydroxide (NaOH) in the burette.

6. With a pipette, add 1 cm$^3$ of your sample into the beaker. The pipettes provided are single dose aliquots of the solution.  
   **NOTE:** Acetone reacts with hydroxylammonium chloride and releases HCl, thus the pH of the solution should decrease.

7. Titrate your sample with the 0.1 N NaOH solution provided, bringing the pH of the solution back to its initial pH.

8. Record the final NaOH level on the burette. Calculate the volume of NaOH needed to titrate the sample.

9. The moles of acetone in the solution should be equal to the mole of the NaOH been added. The chemistry behind this titration is explained in Theory, Titration.

10. Between titrations, rinse the pH meter with DI water, wipe with a Kimwipe, and place in the buffer solution.  
    **WARNING:** THE PH METER CAN BE DAMAGED IF IT IS LEFT IN OPEN AIR FOR EXTENDED PERIOD OF TIME.

11. After six titrations or if the beaker is full, empty the waste into the blue waste bottle located to the left of the fume hood.
    **WARNING:** USE A FUNNEL to transfer the waste from the beaker to the waste bottle. ALWAYS carry the funnel over the beaker when moving it from the fume hood to the waste container and back.

**Notations**

- $V_1$: inlet water mass flow rate (kg/s)  
- $L_2$: inlet acetone mass flow rate (kg/s)  
- $A$: absorption factor (-)  
- $y_R$: acetone weight fraction in the raffinate (-)  
- $y_F$: acetone weight fraction in the feed (-)
\[ x_S \] acetone weight fraction in the solvent (-)
\[ x_E \] acetone weight fraction in the extract (-)
\[ A_{cross} \] cross section area of packing tower \((m^2)\)
\[ m \] equilibrium constant for dilute solution (-)
\[ K \] distribution coefficient (-)
\[ h \] height of the packing bed \((m)\)
\[ N_{OL} \] number of transfer units (-)
\[ H_{OL} \] height of transfer units \((m)\)
\[ K_{x,a} \] overall mass transfer coefficient \((kg/s \cdot m^3)\)

**References**

1. Perry’s Chemical Engineers Handbook
