Liquid/Liquid Extraction

LIQUID/LIQUID EXTRACTION

Objectives

- To observe the distribution coefficient of acetic acid in the immiscible mixture of kerosene/tributyl-phosphate and water.
- To observe the variation of the mass transfer coefficient with respect to flow rates.
- To observe the variation of the mass transfer coefficient with respect to rotor speed.
- To observe the stage efficiency of a single stage centrifugal contactor and how to improve the process by connecting multiple contactors in a counter current extraction system.

Introduction

In the following experiments it is important to know a few key terms. There are two major fluids, aqueous phase (water) and organic phase (30% tributyl-phosphate (TBP) in odorless kerosene (OK)) that will be used. Acetic acid will be dissolved in the aqueous phase; this solution is referred to as the feed. The feed will be run through the column in a counter current mode with the organic phase where some or most of the acetic acid will be extracted into the organic phase. The organic phase with acetic acid is called the extract (because the organic phase is extracting the acetic acid from the aqueous phase). The water and remaining acetic acid in the outflow are now called the raffinate. The ratio of acetic acid in the extract phase to the acetic acid in the raffinate at equilibrium is called the distribution coefficient K.

$$K = \frac{\text{Concentration of solute in extract (Y)}}{\text{Concentration of solute in raffinate (X)}} \qquad (1)$$

At low concentrations K is independent of concentration and Y=KX

In a dynamic extraction system like the liquid-liquid extraction column a mass balance is effective in determining the mass transfer coefficient. For our mass balance, let:

V_a =Aqueous phase flow rate (L/s)
V_o = Organic phase flow rate (L/s)
X = Acetic acid concentration in the aqueous phase (heavy phase)
Y = Acetic acid concentration in the organic phase (light phase)
1 = subscript that indicates the inlet
2 = subscript that indicates the outlet

The acetic acid extracted from the aqueous phase (raffinate)= $V_a(X_1-X_2)$
The acetic acid extracted by the organic phase (extract)= $V_o(Y_2-0)$

Since the mass transferred from one phase equals the mass transferred into the other phase we can equate the above terms giving:

$$V_a(X_1 - X_2) = V_o(Y_2 - 0) \qquad (2)$$

Note that fresh organic phase should contain zero acetic acid. If the previous lab group did not properly clean the organic solution there may still be residues of acetic acid present, which will result in problems with mass balance. Make sure you properly clean the organic solution after each experiment to reduce

this problem. The acid content of the organic phase may be determined in order to verify the mass balance. However, the organic phase cannot be directly titrated. Instead, extract the acid by taking a small sample of organic phase (10 mL) and contact three times with an equal volume of pure water. Consolidate these three water samples (30mL total) and carry out an acid-base titration to find the amount of acetic acid. Washing three times should be enough given that the 2 phases are properly mixed for at least 5 minutes.

For liquid-liquid extraction processes it is often of interest to calculate the % extracted of the solute (in our case acetic acid. This gives the operator a measure of how well the process is running. Often the operator will plot curves of %extraction versus certain parameters that he or she can vary (such as flow rates, stirring speed, pH of the aqueous phase, temperature etc.). It is very easy to calculate the %extraction (%E), one way is to calculate if from the distribution ratio, D (3). D = Y/X at the operating conditions.

$$\%E = 100\frac{D}{(1+D)} \tag{3}$$

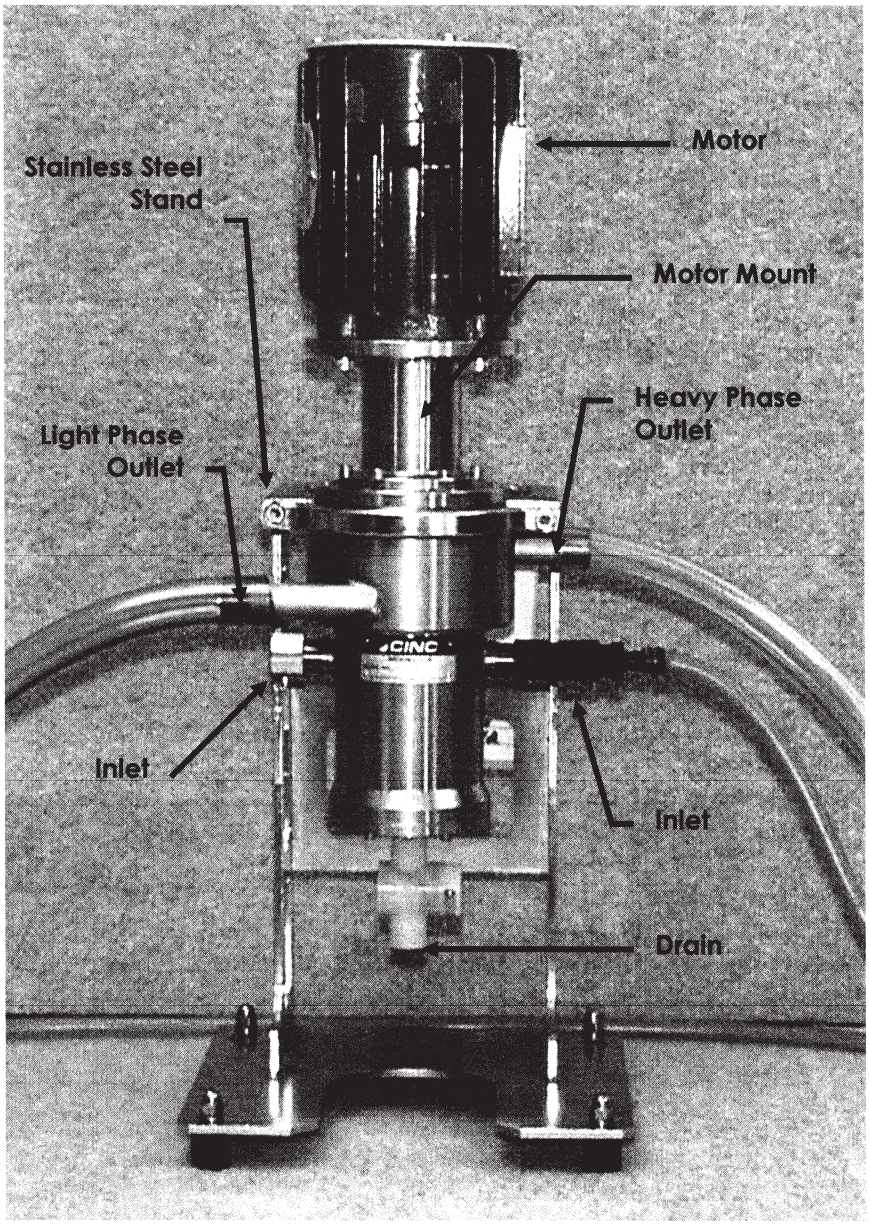
One important parameter to consider in using centrifugal contactors is the hold-up time and the mixing time. The total hold-up time can be found by taking the total volume of the mixing and separating compartments (hold-up volume) and divide it by the total flow rate of aqueous and organic phase (volume/unit time). The mixing time is of course the volume of the mixing compartment divided by the total flow rate. This gives the operator one more parameter to consider when preparing the process curves. Try to find data for the size of the mixing and settling compartments of the contactor so that you can calculate these parameters.

When you use one contactor you will obtain data related to a single stage. Since you have the possibility of connecting several stages in series you can enhance the overall extraction efficiency since each stage will result in a certain %E of the acetic acid. One of your tasks is to figure out how many stages you would need to connect to reach more than 95% of acetic acid recovery. Recovery means how much ends up in your product (extract) versus what was initially fed to the process.

NOTICE:

In preparation for this lab please review your lecture notes and textbook from your previous separations course (CBEMS 130). Many general separations theories are applicable to solvent extraction. It is important to understand that this experiment is a 2-phase multi-component system. To compare, distillation is a 2-phase process which often deals with only one or two components. Still, McCabe-Thiele diagrams for example are applicable to both types of processes.

Equipment



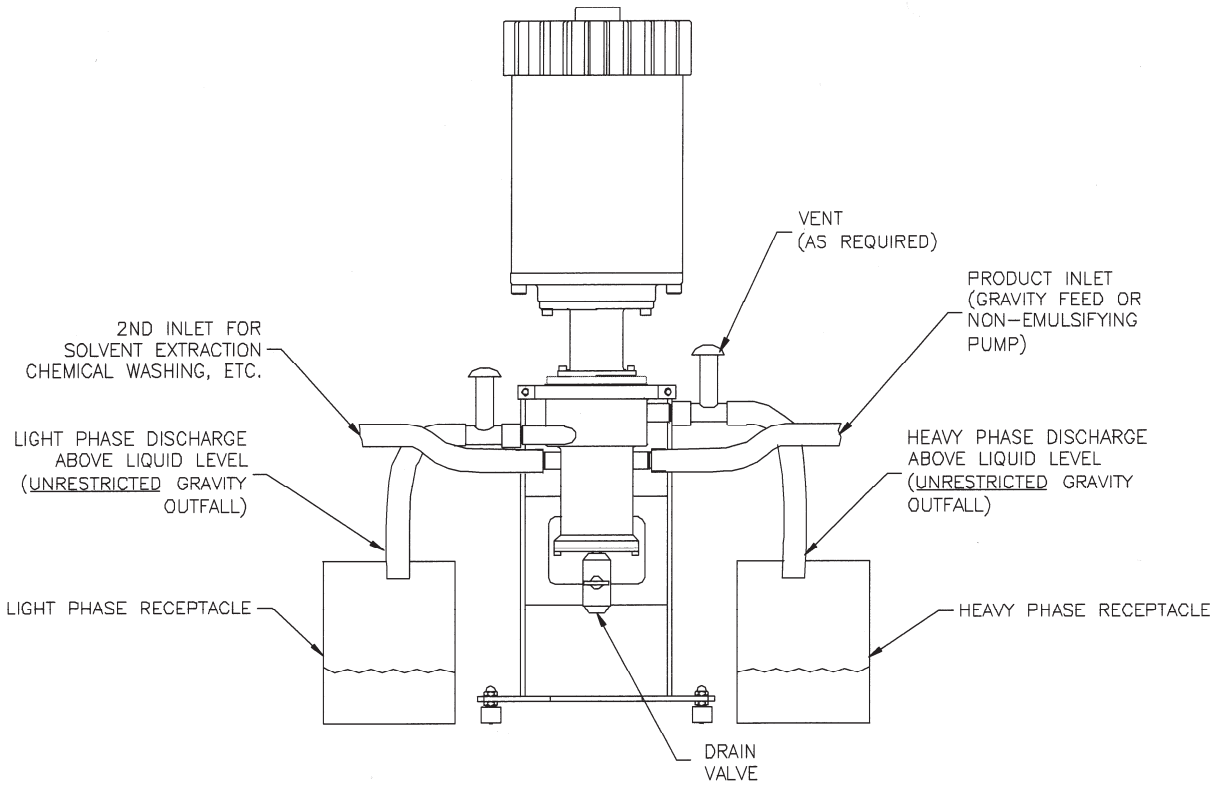
The CINC Model V-02 centrifugal contactor uses centrifugal force to separate two immiscible liquids of different densities. The unit shown above consists of an outer metal housing and stand with dual inlets and outlets (for heavy and light phase). The unit in the picture is connected with only one inlet for separation studies. All outer parts are stationary. The inner rotor is the only moving part and spins normally between 2000-6000 rpm. A motor is connected from the top to run the rotor. The motor is connected to a control box where the rotor speed can be set (as described below).

The motors for the contactors and pumps are controlled from the same central unit. Each digital operating device controls one pump (pump 1 to 4) or on rotor (unit 1 to 4). When the main power switch is turned on all the digital displays will be active.

To set the rotor speed (rpm) or pump speed (%) the following procedure can be done:

1. Press LO/RE (key 3), a green diode should light up indicating local control of the unit or pump.
2. Use the down arrow to cycle through the menus until Freq Ref (OPR) is blinking in the display. You should now see which rotor speed (or pump speed) that has been set.
3. Press ENTER (key 4)
4. You can now change the setting for the speed by using the F-keys and the up and down arrows. Once you have the correct setting press ENTER (key 4).
5. The words “Entry accepted” should appear to indicate that you have successfully changed the setting
6. Press ESC (key 1), this will take you back to the previous menu.
7. If you are ready to start the experiment press RUN (key 2)
8. Press STOP (key 5) if you want to stop the rotor or pump.

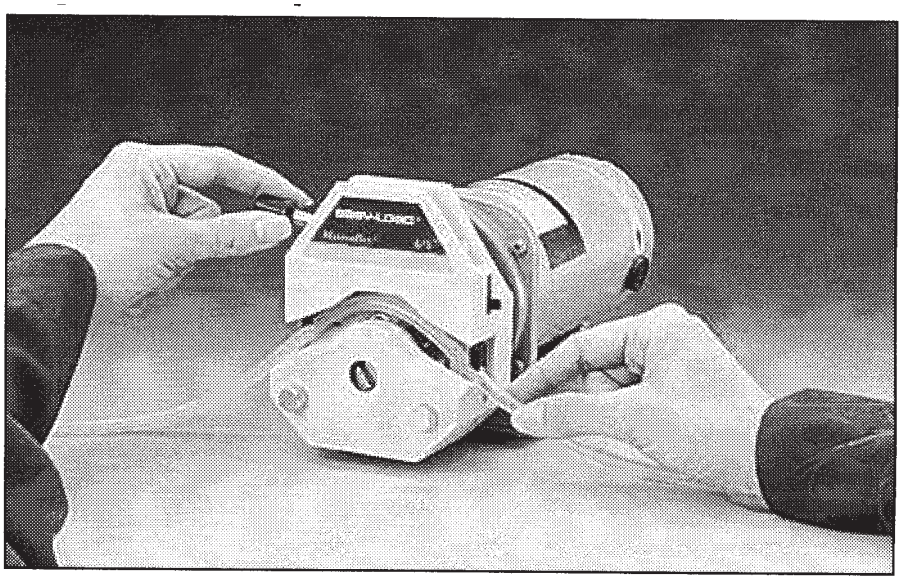
It is possible to change the setting while the motors are running by following steps 3 to 5. but consider residence time when taking sample. Make sure that you do not go outside the operating range of the contactors and that you do not change the flow rates of the pumps too drastically.



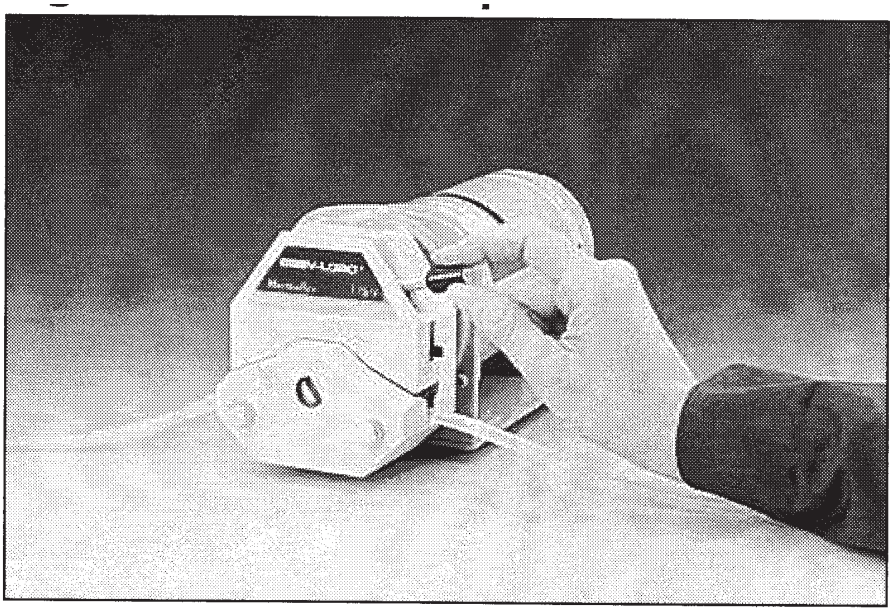
The CINC contactors can be used as single stages or multiple contactors can be connected in series for a separation cascade. Make sure that the liquid can flow freely from the outlets, pay attention to the liquid level in the tubes from the outlet to avoid flooding. Make sure that the vents are fully open to ensure proper operation.

The liquid can be routed back to the feed reservoir if you wish to re-circulate the solvent or aqueous feed. The exact process setup need to be determined together with a TA or instructor before pumps and contactors are started.

When you fill up the liquid reservoirs make sure you do not fill up more than 2/3 of full to avoid overflowing the containers in case of problems with phase separation. For example, if the phase separation is poor there may be an accumulation of organic solvent in the heavy outlet and the heavy phase receptacle may fill up quicker than expected. Always keep a close eye on the liquid levels in both inlets and outlets.



To load a tube in the pump make sure that the pump is turned off and move the lever to the left. Place the tube between the retainers. Make sure the tube is not twisted. Close the pump head by rotating the lever to the right.



Never leave the tubes in the pump heads for an extended period of time. When you are finished with the experiments open the pump head and remove the tubes. Leaving the tubes in the pump will flatten the tubes and reduce the life-time and function of the tubes.

Procedure

Preparation

- Prepare at least 500ml of 0.10 M NaOH as a standard for titrations. The starting material is solid, pure NaOH.

- 0.01 M HNO_3. The TA will have prepared 3.2 Molar HNO_3 as your starting material. (verify the exact concentration) for your to use. Handling strong nitric acid must be done in the fume hood, with gloves, goggles and a lab coat. Take utmost precautions to avoid getting acid on your skin and eyes. If you have any questions regarding chemical safety, do not hesitate to ask.

- 0.1M to 0.6 M Acetic Acid. The TA will have prepared ~5.8 Molar acetic acid as your starting material. Take the same precautions as with strong nitric acid when handling the strong acetic acid.

Experiment A – Determination of the Distribution Coefficient for Acetic acid Extraction

The goal of this particular experiment is to determine how much acetic acid transfers into the organic phase at equilibrium. It is assumed the 5 minutes of vigorous shaking is enough to reach equilibrium, is this assumption fair?

You will also determine if the extraction coefficient is independent of concentration of the solute (acetic acid).

1. Prepare 50ml of an aqueous solution that is 0.01 M in respect to HNO3 and 0.17M in respect to Acetic acid. This is now your aqueous feed.
2. Take a 5mL sample of the aqueous feed and keep for analysis, make sure you label this sample properly.
3. Take the remaining 45 ml aqueous feed and place it together with 45 ml of organic phase (TBP/OK) in a separating funnel.
4. Shake vigorously for a minimum of 5 minutes
5. Remove the bottom layer (the aqueous raffinate) into a beaker and drain the organic phase into a separate container.
6. Take a 5ml sample of the aqueous raffinate and keep for analysis, make sure you label this sample properly.
7. Titrate the aqueous phases with 0.1 M NaOH to determine the concentration of acetic acid in each phase. The aqueous phase without acetic acid should be your baseline (0M acetic acid). The feed should be the maximum concentration (X_1) and the raffinate the outlet concentration (X_2). Subtract the amount in the raffinate from the original amount in the feed to get the quantity of acetic acid that extracted into the organic phase.
8. Repeat the above procedure for at least four additional concentrations of acetic acid, using the same concentration of nitric acid. For example 0.5, 0.4 0.25 and 0.1 M acetic acid.
9. Also repeat the experiment with a solution that is 0M acetic acid, with the same concentration of nitric acid as before. Why is this particular data important?

Experiment B – The Effect of Flow Rate on the Mass Transfer Properties for Extraction of Acetic Acid

Before the experiment starts you need to calibrate the pump speed (%) to flow rates (ml/min). To do this simply run water through a tube from a reservoir and use a timer and measuring cylinder to find the flow rates. Take at least 5 data points to see produce a good calibration curve (% vs. ml/min).

The goal of this particular experiment is to vary the flow rates of the organic and aqueous phase to investigate how the stage efficiency changes with flow rates and the organic to aqueous flow ratio. What are the limits of flow rates before the extraction system fails (e.g. organic phase carries over to the aqueous phase or vice versa)?

1. For the aqueous feed reservoir prepare a single solution that is 0.01 M in respect to HNO_3 and 0.17M in respect to acetic acid. Estimate how much you will require for experiment B based on pump flow rates, residence mixing time, and estimated hold up. Verify the quantity you intend to make is reasonable with the TA.
2. In the organic phase reservoir pour in the 30% TBP in odorless kerosene.
3. Connect the tubes properly and make sure that there are no obstructions at the outlets and that the liquid can flow into a separate reservoir.
4. Set the rotor speeds to a suitable speed (between 2000 to 4000 RPM), do not turn on the rotors.
5. Set the speeds of the pumps to 20%, do not turn on any of the pumps.
6. Turn on the pump for the organic inlet and keep it running until you see the first indications that liquid is coming out from the outlets. The contactor is now primed with organic phase. Avoid getting significant amounts of organic phase in the aqueous outlet.
7. Turn on the rotor (unit) and turn on the pump for the aqueous feed.
8. Observe the system and make a note of how long it takes until you have clean phases in both outlets. Sometimes the aqueous outlet will be cloudy but to determine that there is no significant amounts of organic solvent in the aqueous outlet collect some liquid in a small beaker. If there is a layer forming on top of the aqueous phase the heavy outlet is not clean.
9. Once the system has come to steady state take samples of the aqueous outlet (raffinate) and of the feed.
10. Titrate the Raffinate and Feed samples (5mL each) with 0.1 M NaOH and 2-3 drops of phenolphthalein to determine the amount of acetic acid in each of the samples.
11. Increase each flow rate by 10% and repeat steps 9-10 after steady state has been reached.
12. Keep repeating the experiments and increase the flow rate to collect enough data to produce high quality graphs and trend lines to make proper assumptions on stage efficiency vs. flow rates. Changes can be implemented online, provided you follow the precautions listed in the contactor & pump instruction sections. How did you ensure the collected samples reflect the new process variable (e.g. flow rate), and doesn't show the old process values?

Experiment C – The Effect of rotor speed on the Mass Transfer Properties for Extraction of Acetic acid

The goal of this particular experiment is to vary the rotor speed of a contactor to investigate how the stage efficiency changes with the spinning speed. What is the lower limit or rotor speed at a certain flow rate before the extraction system fails (e.g. organic phase carries over to the aqueous phase or vice versa)?

Follow the procedure for part B, but instead vary rotor speed. Start the rotor speed at 3500 RPM and decrease by 500RPM increments. Set the speeds of the pumps to a suitable flow rate for these experiments (between 15% -50%) based on your part B results. Collect data for sufficient rotor speeds to produce high quality graphs and trend lines to make proper assumptions on stage efficiency vs. rotor speed. Also make a note of the lower limit of the rotor speed where significant carryover of one phase into the other appears.

Experiment D – Process efficiency using multiple contactors in series.

The goal of this experiment is to investigate how much the system improves by using more than one contactor, connected in a counter current flow system. Before you start your experiments make sure you connect all your tubes correctly and have the TA look at your experimental setup before starting the pumps. The more stages you connect the more solution you will need to prepare. **To save time, do not use more than 3 contactors**. From previous experiments you should be able to estimate how much fresh organic and aqueous feed you need.

1. In the feed reservoir, for the aqueous feed reservoir prepare a single solution that is 0.01M in respect to HNO_3 and 0.17M in respect to acetic acid.
2. In the organic phase reservoir pour in the 30% TBP in odorless kerosene.
3. Connect the tubes properly and make sure that there are no obstructions at the outlets and that the liquid can flow into a separate reservoir.
4. Set the rotor speeds to a suitable speed (between 2000 to 4000 RPM) do not turn on the rotor. Make sure all rotors spin with the same speed. (This is not strictly required but will simplify your calculations.)
5. Set the speeds of the pumps to a suitable flow rate (15% -50%), do not turn on any of the pumps.
6. Turn on the pump for the organic inlet and keep it running until you see the first indications that liquid is coming out from the outlet of the final contactor. All contactors are now primed with organic phase. Avoid getting significant amounts of organic phase in the final aqueous outlet. If necessary raise the outlet tube to create a small pressure gradient to avoid organic phase to escape that way.
7. Turn on the rotors (unit) and turn on the pump for the aqueous feed.
8. Observe the system and make a note of how long it takes until you have clear phases in both final outlets.
9. Add fresh organic phase and aqueous feed to the respective reservoirs if the liquid level runs low.
10. Once the system has come to steady state take samples of the aqueous outlet (raffinate) and of the feed.
11. Stop the pumps and stop the rotor motors.

12. Wait until the system has slowed down and then by using beakers drain each contactor from the bottom drain plug and collect all the liquid.
13. By using a separation funnel separate the aqueous and organic phase drained from each contactor and take a 5mL sample of each aqueous phase, make sure you remember which aqueous phase corresponds to which contactor.
14. Titrate the Raffinate, Feed and all the aqueous samples from the contactors as in earlier experiments
15. If you have time repeat the experiment with different operating conditions.

Clean up of the organic phase and the contactors:

The organic phase with extracted acetic acid needs to be cleaned for use by the next group. Use the large separation funnel and contact equal amounts of used organic phase with dilute NaOH (0.01 M, note the concentration difference) for ~5-10 minutes. Let the phases settle and remove the aqueous layer. Add DI water to the separation funnel to a volume equal to the organic phase and shake for 5 min, let the phases settle and drain the aqueous phase. Repeat the DI water wash 2 more times. Finally drain the washed organic phase in a bottle for storing. The organic phase used in each experiment can be cleaned after each experiment while waiting for the system to equilibrate.

Why does contacting the organic phase with NaOH bring acetic acid back into the aqueous phase?

By the end of the day flush the system with DI water by keeping the contactors on slow rotor speed and pump DI water through the system until pure water is all that exits in the contactors.

When leaving the contactors overnight open the drain valves and place beakers under each contactor.

Data Analysis

Experiment A

- Find the distribution coefficient K graphically.
- Comment on the dependence of K vs. acetic acid concentration.

Experiment B and C

- Verify the mass balance in equation (2)
- Plot graphs of distribution ratios versus flow rate and rotor speed and %E versus flow rate and rotor speed side by side or in a dual-axis chart.
- Comment on the D and %E as a function of flow rate and rotor speed.

Experiment D

- Verify the mass balance in equation (2)
- Comment on the %efficiency of single stage process vs. multi stage.
- How many stages would you need to reach 95% recovery?

From the distribution data you can calculate the theoretical number of stages needed. This can be done by either drawing a McCabe-Thiele diagram or by using the Kremser equation. Please note that if the equilibrium line and the operating line are both linear, a McCabe-Thiele diagram cannot be used. Use the calculations, or diagrams, to show how many theoretical stages would be required given a certain combination of flow rates.