

**Michigan Technological University
Department of Chemical Engineering
CM 4110 Unit Operations Laboratory**

Liquid-Liquid Extraction Experimental Notes

Purpose

You will run the continuous, countercurrent, spray liquid-liquid extraction column (glass). It's inside diameter is 4", outside diameter is 4.5", and total height is 96". It has 17 nozzles that have an inside diameter of 1/16" that disperse the materials in the column. Water enters at the top of this column and settles out on the bottom. Oil enters from the bottom and settles on the top (explain why in your proposal). We want to run this column with the interface level high so the oil-acetic acid stream is completely dispersed, which will maximize mass transfer area. **Tell Tim Gasperich this before your run day so he can adjust this.** We also want to run this column at $\frac{Mass_water}{Mass_Oil}$ as low as possible (about 0.5 is as low as we can get with our equipment).

Background

We have Exxon's Isopar M in this column, so use the following equilibrium information for the Isopar M-acetic acid-water system at 80°F (determined by Julie King and Tim Gasperich on July 14, 2003 using a separatory funnel method). At equal amounts of water to oil (by mass):

$$K = 0.03317 = \frac{gmol_acetic_acid / liter_oil_phase}{gmol_acetic_acid / liter_water_phase}$$

$$K = 0.04239 = \frac{g_acetic_acid / g_oil_phase}{g_acetic_acid / g_water_phase}$$

At $\frac{Mass_water}{Mass_Oil} = 0.75$:

$$K = 0.005165 = \frac{gmol_acetic_acid / liter_oil_phase}{gmol_acetic_acid / liter_water_phase}$$

$$K = 0.006603 = \frac{g_acetic_acid / g_oil_phase}{g_acetic_acid / g_water_phase}$$

At $\frac{Mass_water}{Mass_Oil} = 0.50$:

$$K = 0.003378 = \frac{\text{gmol}_{\text{acetic acid}} / \text{liter}_{\text{oil phase}}}{\text{gmol}_{\text{acetic acid}} / \text{liter}_{\text{water phase}}}$$

$$K = 0.004318 = \frac{\text{g}_{\text{acetic acid}} / \text{g}_{\text{oil phase}}}{\text{g}_{\text{acetic acid}} / \text{g}_{\text{water phase}}}$$

Experiment Information

1. In this experiment, you start with 1 wt% acetic acid in oil (Isopar M) in the feed tank. The MSDS's for these materials is in the MSDS book in basement UO lab (right across from this experiment). You have to figure out how to get this feed to be 1 wt% acetic acid in oil. The acetic acid you add is glacial acetic acid (concentrated). The purpose of this experiment is to remove the acetic acid from the oil stream and put the acetic acid in the water stream. Remember, water and oil are immiscible.

2. We will run the experiment at the temp that the water supply is at (about 60 °F).

3. At the beginning of your experiment day (you should start promptly at 9 am or you may not finish in time), you will do the following:

a) Make the 0.02M NaOH solution (3 liters total) of distilled water and using a balance in B003A.

b) Then make the 0.02M KHP (Potassium Hydrogen Phthalate, $\text{KHC}_8\text{H}_4\text{O}_4$) solution (100 ml total) with distilled water and using a balance in B003A.

c) Then check the molarity of the NaOH solution you made using the 0.02 M KHP solution. KHP is much more stable than NaOH. NaOH tends to react with air and is not very pure as compared to KHP. See Chemistry, 6th ed. by R. Chang for methods to use. Use 3 drops of 0.1 % phenolphthalein solution as the indicator. Use the value that you calculate here for the molarity of the NaOH for all your calculations for this experiment. You will use this NaOH to titrate the acetic acid/water and acetic acid/oil streams to get concentrations of acetic acid. See step 6 for more information.

d) Turn the fan on for ventilation (switch on the wall).

e) Collect a sample from the oil feed tank and determine if any water is present in the feed tank. If so, drain off until all the water is removed from the feed tank. You can dispose of the water (on the bottom layer) using the drains in UO. You can put the oil/acetic acid phase back in the feed tank.

f) Collect a sample from the oil product tank and determine if any water is present in the product tank. If so, drain off until all the water is removed from the product tank. You can dispose of the water (on the bottom layer) using the drains in UO. You can put the oil/acetic acid phase back in the feed tank.

g) Pump the product tank to the feed tank so all the oil/acetic acid is now in the feed tank. How will you know when this is done? Think about it. Note that there is an oil tank level gauge present.

h) Mix up the material in the feed tank by pumping from the feed tank and recirculating back to the feed tank for 20 minutes. Then collect 60 ml feed sample of oil/acetic acid to determine the amount of acetic acid (titrate with the NaOH solution) in the oil initially and to get the density (use a 10 ml pycnometer) of this material. Two to three density samples and 3 titrations per sample are recommended.

i) After you know the initial concentration of the acetic acid in the oil, determine how much glacial (pure) acetic acid to add to the feed tank to make up a 1% solution. Use the SS funnel to add the glacial acetic acid to the feed tank. Read the glacial acetic acid MSDS to determine the PPE to wear. When you are done adding any additional acetic acid to the feed tank put the threaded plug back in this line.

j) Mix up the material in the feed tank by pumping from the feed tank to the pump and back to the feed tank for 20 minutes.

k) Start the cool water (at about 60 °F, pure water) going to the extraction column.

l) Set the water flow rate in at 0.5 gpm. Set the oil/acetic acid flow rate in at 0.7 gpm. How do you read a rotometer? Read the float at the widest point.

m) Wait for 10 min since you started this run. Assume we are close to equilibrium. Collect 60-100 ml of samples at three points (oil/acetic acid out; oil/acetic acid in; and, water/acetic acid out). Record the temperature of the water in and oil / acetic acid stream in when you collect the samples. Then use the NaOH to titrate these 3 streams to determine acetic acid concentration.

n) Wait 10 minutes and collect 60-100 ml of samples at three points (feed, product, and water outlet). Record the temperature of the water in and oil/acetic acid stream in when you collected the samples. Titrate these 3 streams to determine acetic acid concentration.

o) Once you determine you are at equilibrium, repeat step n) every 5 minutes until you collect at least 5 sets of samples. You are doing this to be sure you are at steady state.

p) Pump all the material from the product oil/acetic tank back into the feed oil/acetic acid tank. Recirculate the feed for about 20 minutes to mix the old product and feed and form a new feed solution at a lower acetic acid concentration. Measure the new feed concentration and repeat the experiment.

4. How to do titrations for the oil/acetic acid solutions:

To 10 ml (measure exactly) of oil/acetic acid, add 10 ml of 190 ethanol (in storage cabinet close to Solvent Recovery Unit) and then 3 drops of 0.1% phenolphthalein (stored in cabinet close to MSDS book) to the flask. Add a stir bar to the flask. Place flask on stir plate and put NaOH solution in the buret. Let the ethanol/oil/acetic acid mix for 2 minutes before titrating (need time to allow the acetic acid to go into the ethanol so it is

easily titrated). Then carefully add the NaOH (record how much added) to the flask. You are done when the solution in the beaker turns a light pink color for 15 seconds. You should add NaOH dropwise toward the endpoint of the titration. Phenolphthalein is the indicator used. It is colorless at low pH (acidic) and red (or even red-violet) at higher pH (basic). When you do the calculations to determine the concentration of acetic acid, it is per 10 ml of solution (not 20 ml- does not include the ethanol added).

5. How to do titrations for the water/acetic acid solutions:

To 10 ml (measure exactly) of water/acetic acid, add 3 drops of 0.1% phenolphthalein to the flask. Add a stir bar to the flask. Place flask on stir plate and put NaOH solution in the buret. Let the water/acetic acid mix for 1 minute before titrating (to be well mixed). Then carefully add the NaOH (record how much added) to the flask. You are done when the solution in the beaker turns a light pink color for 15 seconds. You should add NaOH dropwise toward the endpoint of the titration. Phenolphthalein is the indicator used. It is colorless at low pH (acidic) and red (or even red-violet) at higher pH (basic).

6. How to do the titration for the KHP/NaOH:

To 20 ml (measure exactly) of KHP solution, add 3 drops of 0.1% phenolphthalein to the flask. Add a stir bar to the flask. Place flask on stir plate and put NaOH solution in the buret. Let the KHP solution mix for 1 minute before titrating (to be well mixed). Then carefully add the NaOH (record how much added) to the flask. You are done when the solution in the beaker turns a light pink color for 15 seconds. You should add NaOH dropwise toward the endpoint of the titration. Phenolphthalein is the indicator used. It is colorless at low pH (acidic) and red (or even red-violet) at higher pH (basic).

7. To get these titrations done quicker, you could set up 2 titration stands (2 burets with 2 stir plates).

8. Discard the water based acids and bases (and with phenolphthalein) down the sink with the water running to dilute it. **Put the oil based solutions in a large labeled waste container (label it Isopar M, ethanol, acetic acid, water, phenolphthalein, NaOH). Talk to Tim Gasperich about this container on the run day. After you are done with this experiment, Tim will properly take care of this material.**