CHEM 2219: Exp. #3 Solvent Extraction: Separation of a Binary Mixture

Objective: In this experiment you will learn how to separate a binary mixture by liquid/liquid extraction. Two solids – p-toluic acid and t-butyl phenol – have been dissolved in the solvent methyl tert-butyl ether (MTBE). The solids will be extracted from the solution by adding water and varying the pH of the solution. The products will be recovered using hydrochloric acid and isolated by vacuum filtration. The products will be characterized by their melting points. Percent recovery for each product will be determined.

* Solvent Extraction is also known as Liquid–liquid extraction (LLE) or partitioning. It is a method used to separate compounds based on their relative solubilities in two different immiscible liquids: usually the polar solvent water and a non-polar organic solvent. Immiscible means that the liquids do not mix and because of this form two distinct layers. The melting point (MP) is a physical property of a solid also used for the purpose of identification and purity determination.

Reading Assignment:

OCLT: pp. 203-246 (extraction); pp. 376-381 (extraction illustrations); 366 (vacuum filtration); and 309-315 (melting point).

Concepts:

Density, Emulsion, Extraction, Partition Coefficient (K), Percent Recovery, pH, Rocking, Salting Out, Venting

Chemicals:

hydrochloric acid, methyl tert butyl ether (MTBE), p-tert butyl phenol, p-toluic acid, sodium bicarbonate, sodium hydroxide and water

Safety Precautions:

Wear chemical splash-proof goggles and appropriate attire at all times.
Methyl tert butyl ether (MTBE) is a flammable liquid.
Hydrochloric acid is highly corrosive. Sodium hydroxide is extremely caustic.
If you spill an acid or a base on the counter or floor, call for a TA or an instructor to neutralize the spill.
If you spill an acid or a base on your skin, immediately walk to the nearest sink and wash thoroughly with cold water. Strong bases dissolve the fats in your skin to produce a soapy feeling. Keep rinsing with cold water until long after the "soapy" feeling is gone.
Do *not* attempt to neutralize a spill on your skin.

Materials:

balance, beakers (50 ml, 100 ml, 150 ml), copper pot, disposable pipet and bulb, filter flask, 3cm filter paper, glass stirring rod, graduated cylinder (10 ml, 100ml), 3cm Hirsch funnel, melting point apparatus, microspatula, ring clamp, ring stand, 125 ml separatory funnel with stopper, short stemmed funnel, vacuum tubing and weighing paper

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Extraction Procedure:

1. Acquire a 125 ml separatory funnel and stopper. Attach a ring clamp to a ring stand and place the separatory funnel in the ring as shown in Figure 1. (large empty flask may also be a beaker.

Note: Check to make sure the separatory funnel is not leaking. Close the stopcock by placing it in the horizontal position. Fill the separatory funnel with ~100 ml of water. Check that the tip does not drip. Place the stopper on the separatory funnel. Remove the funnel from the ring and invert it. If water leaks out, acquire a different stopper and check it. If not, place it back in the ring, remove the stopper and open the stopcock by turning it to the vertical position. Verify that the water flows out rather than dripping out slowly. If the water is dripping out, acquire a different separatory funnel and check it. If not, drain out all of the water.

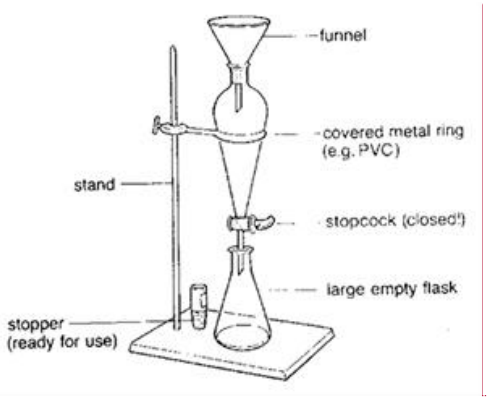

Figure 1: Separatory Funnel Set-up

2. Take a 50 ml beaker. Using the 100 ml graduated cylinders located on the benchtop, measure out ~25 ml of the stock solution of p-toluic acid and tert-butyl phenol in MTBE. Record the exact volume. Pour the solution into the 50 ml beaker.

3. Verify that the stopcock on the separatory funnel is closed. Place your short-stemmed glass funnel in the separatory funnel as shown in Fig. 1. Pour the stock solution into the separatory funnel.

Extraction of p-toluic acid:

4. Using a 10 ml graduated cylinder, acquire 10 ml of 0.5 M sodium bicarbonate ($NaHCO_3$) solution. Add the bicarbonate solution to the ether solution in the separatory funnel.

5. Remove the short-stemmed funnel and place the stopper on the separatory funnel.

6. Holding the stopper in place, carefully invert the separatory funnel as shown in Figure 2. Gently* mix the solution by rocking the separatory funnel back and forth.

***Note:** If the mixture is shaken violently, an emulsion might form. An emulsion is a suspension of droplets of one immiscible liquid in another. Formation of an emulsion is also dependent upon the relative densities of the liquid, their viscosities and surface tension. **This solution is unlikely to form an emulsion and may be shaken quite vigorously.** However, if an emulsion does occur, use a saturated $NaCl_{(aq)}$ solution to force the water to separate from the organic layer. Consult an instructor for the amount of NaCl soln needed.

Figure 2: Inverting a separatory funnel.

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7. To extract the p-toluic acid, invert the funnel and rock continuously for ~30 sec holding the stopper firmly. Stop frequently to vent the CO_2 gas and pressure. See Figure 3.

To vent the gas, hold the funnel in the inverted position with the end of the funnel facing away from you and your neighbors. Slowly open the stopcock. Leave the stopcock open until the hissing stops – indicating that the gas build-up has been relieved. Close the stopcock.

Continue mixing, gradually increasing the force of mixing until the mixture can be shaken quite vigorously with little to no gas being produced upon venting. Stop shaking after ~30 sec.

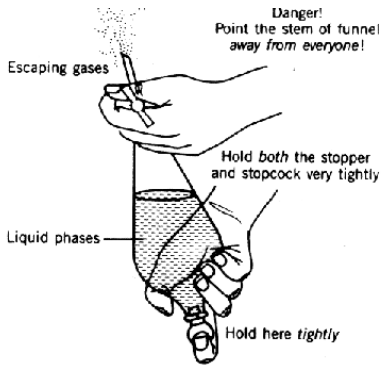

Figure 3: Venting a separatory funnel.

8. Place the separatory funnel in the ring clamp. Allow the layers to separate.

9. While the layers are separating, acquire a disposable pipet and bulb and ~ 1 ml of distilled water in a 10 ml graduated cylinder.

10. Once the layers have separated, remove the stopper from the funnel. Draw the water into the pipet. Lower the tip of the pipet until it is at the half-way point between the interface and the top of the upper layer. Add one or two drops of water from the pipet.* Carefully observe whether the water stays in the top layer or drops down to the lower layer. Record your results.

***Note:** If there is air in the tip of the pipet below the water, it will bubble up to the surface when added to the liquid. If in doubt, add a few more drops of water from the pipet and observe.

11. Acquire a clean 150 ml beaker and label it p-toluic acid. Place the beaker below the stopcock of the separatory funnel. Drain the lower layer* into the beaker making sure not to go past the interface of the two solvents.

***Note:** When draining liquid from the separatory funnel, always remove the stopper before opening the stopcock. If the stopper is not removed, a slight vacuum will be created and the lower layer will not drain from the funnel.

12. Using a 10 ml graduated cylinder, acquire a second 10 ml of 0.5 M sodium bicarbonate ($NaHCO_3$) solution. Add the bicarbonate solution to the separatory funnel.

13. As before, mix for ~30 seconds with frequent venting. Allow the two layers to form and drain the lower layer into the same 150 ml beaker.

14. Repeat with a third 10 ml portion of bicarbonate solution.

15. Using a 10 ml graduated cylinder, acquire 5 ml of distilled water. Add the distilled water to the separatory funnel. Mix for ~30 seconds with venting Drain the lower layer into the same 150 ml beaker.

16. Acquire a bottle of pH paper, a disposable pipet and bulb, and 7 ml of 3M HCl in a clean 10 ml graduated cylinder. Using the pipet, slowly* add the 3M HCl to the solution in the 150 ml beaker until a noticeable amount of precipitate forms and fizzing stops. This will require >5ml of 3M HCl.

***Caution:** 3M hydrochloric acid (HCl) is toxic and corrosive. Prevent contact with eyes, skin, and clothing. Avoid inhaling vapors or ingesting HCl. Adding HCl to $NaHCO_3$ produces CO_2 gas. If it is added too quickly it will cause a large amount of foaming resulting in loss of product and the potential of an unreacted HCl spill.

17. Once a precipitate has formed, test the pH of the solution. To test the pH, stir the solution with a glass stirring rod. Touch the stirring rod to the pH paper. Observe the color of the paper and compare it to the side of the bottle. The pH needs to be ≤ 3 in order to precipitate all of the p-toluic acid. If the pH is above this add more HCl and test again. Repeat until the pH ≤ 3.

18. Place the 150 beaker in an ice bath along with a 50 ml beaker with ~20 ml of distilled water for 5+ minutes.

19. Assemble a vacuum filtration apparatus (as shown in Fig. 4) using the 250 ml filter flask, the 3.0 cm Hirsch funnel and the 3.0 cm filter paper. (These items should in the common drawer.) Clamp the flask to a ringstand. Place the funnel on top of the flask. Make sure the seal is tight. Place the filter paper on the funnel. Seal the paper with a small amount of cold solvent. Make sure all of the holes in the funnel are covered by the filter paper and the edges are not curling up. Before connecting the hose to the flask, test the vacuum by attaching the hose to the vacuum and placing your thumb over the hole on the other end of the tube and turning the vacuum up until you can feel it. Once the vacuum is working, attach the hose to the flask. Seal the filter paper again using the cold distilled water.

20. Vacuum filter the solution to isolate the white crystalline product. (The filtrate should be colorless.) Rinse the crystals twice with 3-5 ml of cold distilled water. After the final rinsing, allow the crystals to dry over the vacuum for 10 minutes. Using a microspatula, scrape through the product being careful not to tear or lift the filter paper. Increasing the surface area of the product will allow it to dry faster. If the product "sticks" to the microspatula, allow it to continue to dry until the product is powdery or does not stick to the microspatula.

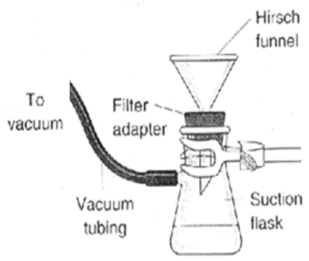

Figure 4: Vacuum filtration system.

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Extraction of p-tert-butyl phenol:

21. Repeat the extraction process (steps 4-15, skipping steps 9-10) used for p-toluic acid and noting the following:
    a. Substitute 10 ml of 0.5 M NaOH* for the 10 ml of 0.5 M $NaHCO_3$.
    b. Use a clean dry labeled 100 ml beaker.
    c. Once the extraction has been completed, take the 100 ml beaker to the hood and place it on a hot plate set at ~60 ºC to remove any trace amounts of MTBE.
    (*The solution will no longer smell like MTBE once it has all been removed.*)
    d. Allow the solution to cool to room temperature.
    e. Make sure there is still ice in the ice bath for step 23.

***Caution:** 0.5 M sodium hydroxide (NaOH) is toxic and corrosive. Prevent contact with eyes, skin, and clothing. Contact can cause pain, redness, burns, and blistering. If in doubt wash with copious amounts of water.

22. Acquire 10 ml of 3M HCl in a 10 ml graduated cylinder and repeat the precipitation process (steps 16-17) for the p-tert-butyl phenol. Repeat until the pH ≤ 3.

23. In the ice bath, chill the 100 ml beaker containing the p-tert-butyl phenol crystals and ~20 ml of distilled water in a 50 ml beaker for 5+ minutes.

Recovery of p-toluic acid:

24. Scrape the product off the filter paper onto a piece of tared weighing paper. Weigh the product. Record the exact mass to the nearest mg (0.001g).

Recovery of p-tert-butyl phenol:

25. Isolate the p-tert-butyl phenol crystals using the vacuum filtration set up in step 19, a clean 3.0 cm Hirsch funnel and a new piece of 3.0 cm filter paper. Seal the paper with the chilled distilled water.

26. Vacuum filter the solution to isolate the white crystalline product. (The filtrate should be colorless.) Rinse the crystals twice with 3-5 ml of cold distilled water. Allow the crystals to dry for 10-15 minutes over the vacuum. (*While the crystals are drying go to step 28.*)

27. Once the crystals are dry, scrape the product off the filter paper onto a piece of tared weighing paper. Weigh the product. Record the exact mass to the nearest mg (0.001g).

Characterization of the products:

28. Determine the melting point of the p-tert-butyl phenol. (If the determined MP range is >10 ºC, consult your instructor and redo the determination.) Record the name and number of the MP apparatus used. Consult handout for MP determination instructions.

29. Determine the melting point of the p-toluic acid. (If the determined MP range is >10 ºC, consult your instructor and redo the determination.) Record the name and number of the MP apparatus used. Consult handout for MP determination instructions.

Clean Up:

30. Dispose of filtrate and other chemicals in the general waste container. Clean and return all glassware and equipment to their original locations.

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Post Lab Calculations:

1. Determine the initial mass of each compound based on the ratio of x g / 25ml vs. the stock solution values listed in the Extraction PowerPoint. Show calculations in your lab notebook.

2. Determine %Recovery of each compound based on **%R = (final mass / initial mass) x 100.** Show calculations in your lab notebook.

3. Determine % Error for the melting point of each product. Show calculations in your lab notebook.

4. Tabulate your results in your lab book.

Post Lab Questions (*Record your answers in your lab notebook*):

1. What would you recover if during the extraction of p-toluic acid, you mistake the ether layer for the water layer?

2. What product(s) would you get if instead of doing a vacuum filtration, you evaporated off the water from the NaOH layer prior to adjusting the pH to 3 or less?

3. How would the extraction be affected if you used dichloromethane which has a density of 1.33 g/cm^3 instead of the MTBE (d = 0.704 g/cm^3)?

4. In your conclusion, discuss the success of the reaction based on the results of the melting point and the %Recovery. Also discuss any problems that arose during the experiment and your recommendation for how to avoid those problems if you were to redo the experiment.

References:

Bone, Terry. "Liquid-Liquid Extraction" PowerPoint. Missouri S & T. November 2018. PPT includes Figure 2 & 3.

Figure 1 available 11/4/2018 at: http://umich.edu/~chemh215/W13HTML/SSG5/ssg5.6/Sepfunnel.html

Manion, Jerry. "TECH 705: Separating Acids and Neutral Compounds by Solvent Extraction." Chemical Education Resources, Inc. Pennsylvania: 1997.