

melting point of fluorene? Report the original weight of both the impure fluorene and the weight of the crystallized fluorene. Calculate the percentage recovery and comment on several sources of loss.

3. The solubility of fluorene in each solvent used in Experiment 3B corresponds to one of the three curves shown in Figure 11.1 (p. 648). For each solvent, indicate which curve best describes the solubility of fluorene in that solvent.

### Experiment 3D

Record all melting points and state the identity of your unknown.

### Experiment 3E

For each compound assigned, state your predictions, along with an explanation. Then give the relevant information from *The Merck Index* that supports or contradicts your predictions. Try to explain any differences between your predictions and information found in *The Merck Index*.

## QUESTIONS

1. Consider a crystallization of sulfanilamide in which 10 mL of hot 95% ethyl alcohol is added to 0.10 g of impure sulfanilamide. After the solid has dissolved, the solution is cooled to room temperature and then placed in an ice-water bath. No crystals form, even after scratching with a glass rod. Explain why this crystallization failed. What would you have to do at this point to make the crystallization work? (You may need to refer to Figure 11.2 on p. 648.)
2. Benzyl alcohol (bp 205°C) was selected by a student to crystallize fluorenol (mp 153–154°C) because the solubility characteristics of this solvent are appropriate. However, this solvent is not a good choice. Explain.
3. A student performs a crystallization on an impure sample of biphenyl. The sample weighs 0.5 g and contains about 5% impurity. Based on his knowledge of solubility, the student decides to use benzene as the solvent. After crystallization, the crystals are dried and the final weight is found to be 0.02 g. Assume that all steps in the crystallization are performed correctly, there are no spills, and the student lost very little solid on any glassware or in any of the transfers. Why is the recovery so low?

## 4

## EXPERIMENT 4

# Extraction

### Extraction

#### Critical thinking application

Extraction is one of the most important techniques for isolating and purifying organic substances. In this method, a solution is mixed thoroughly with a second solvent that is **immiscible** with the first solvent. (Remember that immiscible liquids do not mix; they form two phases, or layers.) The solute is extracted from one solvent into the other because it is more soluble in the second solvent than in the first.

The theory of extraction is described in detail in Technique 12, Sections 12.1–12.2, pp. 669–671. You should read these sections before continuing this experiment. Because solubility is the underlying principle of extraction, you may also wish to reread the introduction to the experiment on solubility.

Extraction is not only a technique used by organic chemists but it is also used to produce common products with which you are familiar. For example, vanilla extract, the popular flavoring agent, was originally extracted from vanilla beans using alcohol as the organic solvent. Decaffeinated coffee is made from coffee beans that have been decaffeinated by an extraction technique (see essay on caffeine, p. 87). This process is similar to the procedure in Experiment 4A of this experiment, in which you will extract caffeine from an aqueous solution.

The purpose of this experiment is to introduce the microscale technique for performing extractions and allow you to practice this technique. This experiment also demonstrates how extraction is used in organic experiments.

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## REQUIRED READING

*New:*    Technique 12    Extraction  
           Essay            Caffeine (p. 87)

*Review:* Technique 10    Solubility

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## SPECIAL INSTRUCTIONS

Be careful when handling methylene chloride. It is a toxic solvent, and you should not breathe its fumes excessively or spill it on yourself.

In Experiment 4B, it is advisable to pool the data for the distribution coefficients and calculate class averages. This will compensate for differences in the values due to experimental error.

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## SUGGESTED WASTE DISPOSAL

You must dispose of all methylene chloride in a waste container marked for the disposal of halogenated organic wastes. Place all other organic wastes into the nonhalogenated organic waste container. The aqueous solutions obtained after the extraction steps must be disposed of in the container designated for aqueous waste.

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### 4A

### EXPERIMENT 4A

## *Extraction of Caffeine*

One of the most common extraction procedures involves using an organic solvent (nonpolar or slightly polar) to extract an organic compound from an aqueous solution. Because water is highly polar, the mixture will separate into two layers, or phases: an aqueous layer and an organic (nonpolar) layer.

In this experiment, you will extract caffeine from an aqueous solution using methylene chloride. You will perform the extraction step three times

using three separate portions of methylene chloride. Because methylene chloride is more dense than water, the organic layer (methylene chloride) will be on the bottom. After each extraction, you will remove the organic layer. The organic layers from all three extractions will be combined and dried over anhydrous sodium sulfate. After transferring the dried solution to a preweighed container, you will evaporate the methylene chloride and determine the weight of caffeine extracted from the aqueous solution. This extraction procedure succeeds because caffeine is much more soluble in methylene chloride than in water.

### *Pre-Lab Calculation*

In this experiment, 0.070 g of caffeine is dissolved in 4.0 mL of water. The caffeine is extracted from the aqueous solution three times with 2.0-mL portions of methylene chloride. Calculate the total amount of caffeine that can be extracted into the three portions of methylene chloride (see Technique 12, Section 12.2, p. 670). Caffeine has a distribution coefficient of 4.6, between methylene chloride and water.

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## PROCEDURE

### *Preparation*

Before beginning this experiment, check your screw-cap centrifuge tube for leaks.<sup>1</sup> Add exactly 0.070 g of caffeine to the centrifuge tube. Then add 4.0 mL of water to the tube. Cap the tube and shake it vigorously for several minutes until the caffeine dissolves completely. It may be necessary to heat the mixture slightly to dissolve all the caffeine.

### *Extraction*

Add 2.0 mL of methylene chloride to the tube. The two layers must be mixed thoroughly so that as much caffeine as possible is transferred from the aqueous layer to the methylene chloride layer. However, if the mixture is mixed too vigorously, it may form an emulsion. Emulsions look like a third frothy layer between the other two layers, and they can make it difficult for the layers to separate. The best way to prevent an emulsion is to shake gently at first and observe whether the layers separate. If they separate quickly, continue to shake, but now more vigorously. The correct way to shake is to invert the tube and right it in a rocking motion. A good rate of shaking is about one rock per second. When it is clear that an emulsion is not forming, you may shake it more vigorously, perhaps two to three times per second. (Note that it is usually not prudent to shake the heck out of it!) Shake the tube for about one minute.

After shaking, place the tube in a test tube rack or beaker and let it stand until the layers separate completely.<sup>2</sup> It may be necessary to tap the sides of

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<sup>1</sup> Place about 2 mL of water in the tube. Cap it and shake vigorously. If it leaks, try screwing the cap on more tightly or use a different cap. Sometimes you may need to replace the centrifuge tube itself. Discard the water in the tube.

<sup>2</sup> If an emulsion has formed, the two layers may not separate on standing. If they do not separate after about 1–2 minutes, it will be necessary to centrifuge the mixture to break the emulsion. Remember to balance the centrifuge by placing a tube of equal weight on the opposite side.

the tube to force all the methylene chloride layer to the bottom of the vial. Occasionally, a drop of water will get stuck in the very bottom part of the tube, below the methylene chloride layer. If this happens, depress the bulb slightly and try to draw the water drop into a Pasteur pipet. Transfer this drop to the upper layer.

Using a Pasteur pipet, you should now transfer the organic (bottom) layer into a test tube. Ideally, the goal is to remove all the organic layer without transferring any of the aqueous layer. However, this is difficult to do. Try to squeeze the bulb so that when it is released completely, you will draw up the amount of liquid that you desire. If you have to hold the bulb in a partially depressed position while making a transfer, it is likely that you will spill some liquid. It is also best to transfer the liquid in two steps. First, depress the bulb so that most (about 75%) of the bottom layer will be drawn into the pipet. Place the tip of the pipet squarely in the V at the bottom of the centrifuge tube and release the bulb slowly. When making the transfer, it is essential that the centrifuge tube and the test tube be held next to each other. A good technique for this is illustrated in Figure 12.6, p. 675. After transferring the first portion, depress the bulb partially, just enough to draw up the remaining liquid in the bottom layer, and place the tip of the pipet in the bottom of the tube. Draw the liquid into the pipet and transfer this liquid to the test tube.

Repeat this extraction two more times using 2 mL of fresh methylene chloride each time. Combine the organic layer from each of these extractions with the methylene chloride solution from the first extraction.

### *Drying the Organic Layers*

Dry the combined organic layers over granular anhydrous sodium sulfate, following the instructions given in Technique 12, Section 12.9, "Drying Procedure with Anhydrous Sodium Sulfate," p. 681. Read these instructions carefully and complete Steps 1–3 in the "Microscale Drying Procedure." Step 4 (p. 683) is described in the next section, "Evaporation of Solvent."

### *Evaporation of Solvent*

Transfer the dried methylene chloride solution with a clean, dry Pasteur pipet to a dry, preweighed 10-mL Erlenmeyer flask or test tube while leaving the drying agent behind.<sup>3</sup> (If you had to add more than 3–4 microspatulafuls of anhydrous sodium sulfate, rinse the sodium sulfate with about 0.5 mL of fresh methylene chloride. Stir this with a dry spatula and then transfer this solution to the same preweighed flask.) Evaporate the methylene chloride by heating the flask in a hot water bath at about 45°C. This should be done in a hood and can be accomplished more rapidly if a stream of dry air or nitrogen gas is directed at the surface of the liquid (see Technique 7, Section 7.10, p. 611). When the solvent is evaporated, remove the flask from the bath and dry the outside of the flask. When the flask has cooled to room temperature, weigh it to determine the amount of caffeine that was in the methylene chloride solution. Compare this weight with the amount of caffeine calculated in the Pre-Lab Calculation.

<sup>3</sup> It is easier to avoid transferring any drying agent if you use a filter-tip pipet (Section 8.6, p. 625).

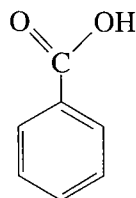
## 4B

## EXPERIMENT 4B

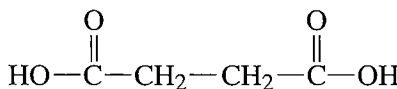
## Distribution of a Solute between Two Immiscible Solvents

In this experiment, you will investigate how several different organic solids distribute themselves between water and methylene chloride. A solid compound is mixed with the two solvents until equilibrium is reached. The organic layer is removed, dried over anhydrous sodium sulfate, and transferred to a tared container. After evaporating the methylene chloride, the weight of the organic solid that was in the organic layer is determined. By finding the difference, the amount of solute in the aqueous layer can also be determined. The distribution coefficient of the solid between the two layers can then be calculated and related to the polarity of the solid and the polarities of the two liquids.

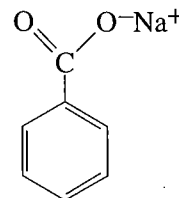
Three different compounds will be used: benzoic acid, succinic acid, and sodium benzoate. Their structures are given below. You should perform this experiment on one of the solids and share your data with two other students who worked with the other two solids. Alternatively, data from the entire class may be pooled and averaged.



Benzoic acid



Succinic acid



Sodium benzoate

### PROCEDURE

Place 0.050 g of one of the solids (benzoic acid, succinic acid, or sodium benzoate) into a 5-mL conical vial. Add 2.0 mL of methylene chloride and 2.0 mL of water to the vial. Cap the vial and shake it as described in Experiment 4A for about 1 minute. Check for undissolved solid. Continue shaking the vial until all the solid is dissolved. After the layers have separated, transfer the bottom organic layer to another vial or a small test tube. Using the same procedure just described in Experiment 4A (see the section on "Drying the Organic Layers"), dry this organic layer over granular anhydrous sodium sulfate.

Transfer the dried methylene chloride solution with a clean, dry Pasteur pipet to a dry, preweighed conical vial, leaving the drying agent behind. Evaporate the methylene chloride by heating the vial in a hot water bath while directing a stream of dry air or nitrogen gas at the surface of the liquid. When the solvent is evaporated, remove the vial from the bath and dry the outside of the vial. When the vial has cooled to room temperature, weigh the vial to determine the amount of solid solute that was in the methylene chloride layer. Determine by difference the amount of the solid that was dissolved in the aqueous layer. Calculate the distribution

coefficient for the solid between methylene chloride and water. Because the volume of methylene chloride and water was the same, the distribution coefficient can be calculated by dividing the weight of solute in methylene chloride by the weight of solute in water.

### *Optional Exercise*

Repeat the preceding procedure using 0.050 g of caffeine, 2.0 mL of methylene chloride, and 2.0 mL of water. Determine the distribution coefficient for caffeine between methylene chloride and water. Compare this to the literature value of 4.6.

## 4C EXPERIMENT 4C

# *How Do You Determine Which One Is the Organic Layer?*

A common problem that you might encounter during an extraction procedure is not knowing for sure which layer is organic and which is the aqueous one. Although the procedures in this textbook often indicate the expected relative positions of the two layers, not all procedures will give this information, and you should be prepared for surprises. Sometimes knowing the densities of the two solvents is not sufficient, because dissolved substances can significantly increase the density of a solution. It is very important to know the location of the two layers because usually one layer contains the desired product and the other layer is discarded. A mistake at this point in an experiment would be disastrous!

The purpose of this experiment is to give you some practice in determining which layer is aqueous and which layer is organic (see Technique 12, Section 12.8, p. 679). As described in Section 12.8, one effective technique is to add a few drops of water to each layer after the layers have been separated. If the layer is water, then the drops of added water will dissolve in the aqueous layer and increase its volume. If the added water forms droplets or a new layer, then it is the organic layer.

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## PROCEDURE

Obtain three test tubes, each containing two layers.<sup>4</sup> For each tube, you will be told the identity of the two layers, but you will not be told their relative positions. Determine experimentally which layer is organic and which layer is aqueous. Dispose of all these mixtures into the waste container designated for halogenated organic wastes. After determining the layers experimentally, look up the densities of the various liquids in a handbook to see if there is a correlation between the densities and your results.

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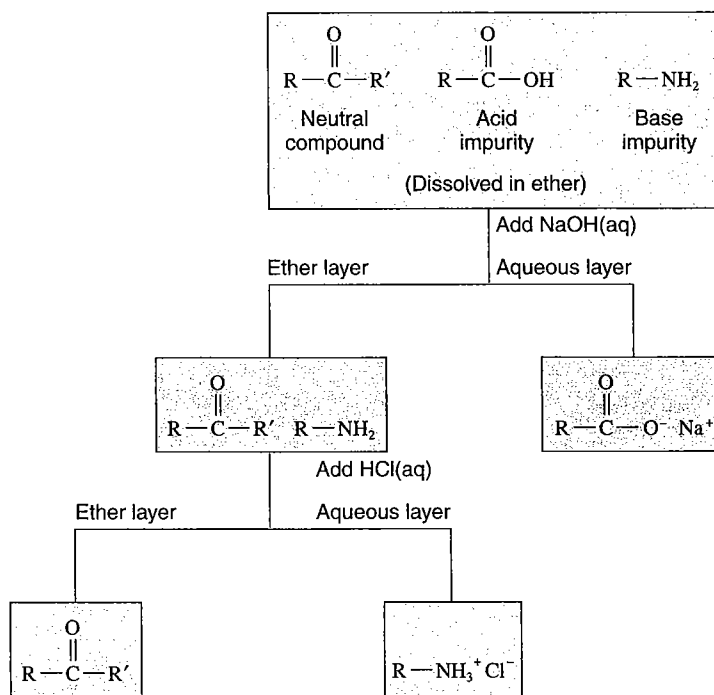
<sup>4</sup>The three mixtures will likely be (1) water and *n*-butyl chloride, (2) water and *n*-butyl bromide, and (3) *n*-butyl bromide and saturated aqueous sodium bromide.

## 4D EXPERIMENT 4D

## Use of Extraction to Isolate a Neutral Compound from a Mixture Containing an Acid or Base Impurity

In this experiment you will be given a solid sample containing an unknown neutral compound and an acid or base impurity. The goal is to remove the acid or base by extraction and isolate the neutral compound. By taking the melting point of the neutral compound, you will identify it from a list of possible compounds. There are many organic reactions in which the desired product, a neutral compound, is contaminated by an acid or base impurity. This experiment illustrates how extraction is used to isolate the product in this situation.

In Technique 10, "Solubility," you learned that organic acids and bases can become ions in acid-base reactions (see "Solutions in Which the Solute Ionizes and Dissociates," p. 642). Before reading on, review this material if necessary. Using this principle, it is possible to separate an acid or base impurity from a neutral compound. The following scheme, which shows how both an acid and a base impurity are removed from the desired product, illustrates how this is accomplished:



Flow chart showing how acid and base impurities are removed from the desired product.

The neutral compound can now be isolated by removing the water dissolved in the ether and evaporating the ether. Because ether dissolves a

relatively large quantity of water (1.5%), the water must be removed in two steps: In the first step, the ether solution is mixed with a saturated aqueous NaCl solution. Most of the water in the ether layer will be transferred to the aqueous layer in this step (see Technique 12, Section 12.9, p. 680). Finally, the remainder of the water is removed by drying the ether layer over anhydrous sodium sulfate. The neutral compound can then be isolated by evaporating the ether. In most organic experiments that use a separation scheme such as this, it would be necessary to perform a crystallization step to purify the neutral compound. However, in this experiment the neutral compound should be sufficiently pure at this point to identify it by melting point.

The organic solvent used in this experiment is ether. Recall that the full name for ether is diethyl ether. Because ether is less dense than water, this experiment will give you practice in performing extractions where the non-polar solvent is less dense than water.

The following procedure details the removal of an acid impurity from a neutral compound and isolating the neutral compound. It contains an additional step that is not normally part of this kind of separation scheme: The aqueous layers from each extraction are segregated and acidified with aqueous HCl. The purpose of this step is to verify that the acid impurity has been removed completely from the ether layer. In the Optional Exercise, the sample contains a neutral compound with a base impurity; however, a detailed procedure is not given. If you are assigned this exercise, you must create a procedure by using the principles discussed in this introduction and by studying the following procedure for isolating the neutral compound from an acid impurity.

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## PROCEDURE

**Isolating a Neutral Compound from a Mixture Containing an Acid Impurity.** Add 0.150 g of an unknown mixture<sup>5</sup> to a screw-cap centrifuge tube. Add 4.0 mL of ether to the tube and cap it. Shake the tube until all the solid dissolves completely.

Add 2.0 mL of 1.0 M NaOH to the tube and shake for 30 seconds. Let the layers separate. Remove the bottom (aqueous) layer, and place this in a test tube labeled "1st NaOH extract." Add another 2.0-mL portion of 1.0 M NaOH to the centrifuge tube and shake for 30 seconds. When the layers have separated, remove the aqueous layer and put this in a test tube labeled "2nd NaOH extract."

With stirring, add 6 M HCl dropwise to each of the two test tubes containing the NaOH extracts until the mixture is acidic. Test the mixture with litmus or pH paper to determine when it is acidic. Observe the amount of precipitate that forms. What is the precipitate? Does the amount of precipitate in each tube indicate that all the acid impurity has been removed from the ether layer containing the unknown neutral compound?

The drying procedure for an ether layer requires the following additional step compared to the procedure for drying a methylene chloride layer (see Technique 12, Section 12.9, "Saturated Salt Solution," p. 680). To the ether layer in the

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<sup>5</sup> The mixture contains 0.100 g of one of the neutral compounds given in the list on page 39 and 0.050 g of benzoic acid, the acid impurity.



centrifuge tube, add 2.0 mL of saturated aqueous sodium chloride. Shake for 30 seconds and let the layers separate. Remove and discard the aqueous layer. With a clean, dry Pasteur pipet, transfer the ether layer (without any water) to a clean, dry test tube. Now dry the ether layer over granular anhydrous sodium sulfate (see Technique 12, Section 12.9, "Drying Procedure with Anhydrous Sodium Sulfate," p. 681).

Transfer the dried ether solution with a clean, dry Pasteur pipet to a dry, preweighed test tube, leaving the drying agent behind. Evaporate the ether by heating the tube in a hot water bath. This should be done in a hood and can be accomplished more rapidly if a stream of dry air or nitrogen gas is directed at the surface of the liquid (see Technique 7, Section 7.10, p. 611). When the solvent has evaporated, remove the test tube from the bath and dry the outside of the tube. Once the tube has cooled to room temperature, weigh it to determine the amount of solid solute that was in the ether layer. Obtain the melting point of the solid and identify it from the following list:

	Melting Point
Fluorenone	82–85°C
Fluorene	116–117°C
1,2,4,5-Tetrachlorobenzene	139–142°C
Triphenylmethanol	162–164°C

**Optional Exercise: Isolating a Neutral Compound from a Mixture Containing a Base Impurity.** Obtain 0.150 g of an unknown mixture containing a neutral compound and a base impurity.<sup>6</sup> Develop a procedure for isolating the neutral compound, using the preceding procedure as a model. After isolating the neutral compound, obtain the melting point and identify it from the list of compounds given above.

**4E****EXPERIMENT 4E***Critical Thinking Application***PROCEDURE**

1. Add 4 mL of water and 2 mL of methylene chloride to a screw-capped centrifuge tube.
2. Add 4 drops of solution A to the centrifuge tube. Solution A is a dilute aqueous solution of sodium hydroxide containing an organic compound.<sup>7</sup> Shake the mixture for about 30 seconds, using a rapid rocking motion. Describe the color of each layer (see the following table).

<sup>6</sup> The mixture contains 0.100 g of one of the neutral compounds given in the list above and 0.050 g of ethyl 4-aminobenzoate, a base impurity.

<sup>7</sup> Solution A: Mix 25 mg of 2,6-dichloroindophenol (sodium salt) with 50 mL of water and 1 mL of 1 M NaOH. This solution should be prepared the same day it is used.

3. Add 2 drops of 1 M HCl. Let the solution sit for 1 minute and note the color change. Then shake for about 1 minute, using a rapid rocking motion. Describe the color of each layer.
4. Add 4 drops of 1 M NaOH and shake again for about 1 minute. Describe the color of each layer.

## Color

Step 2	Aqueous	
	Methylene chloride	
Step 3	Aqueous	
	Methylene chloride	
Step 4	Aqueous	
	Methylene chloride	

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**REPORT**
**Experiment 4A**

1. Show your calculations for the amount of caffeine that should be extracted by the three 2.0-mL portions of methylene chloride (see Pre-Lab Calculation).
2. Report the amount of caffeine isolated. Compare this weight with the amount of caffeine calculated in the Pre-Lab Calculation. Comment on the similarity or difference.

**Experiment 4B**

1. Report in table form the distribution coefficients for the three solids: benzoic acid, succinic acid, and sodium benzoate.
2. Is there a correlation between the values of the distribution coefficients and the polarities of the three compounds? Explain.
3. If you completed the Optional Exercise, compare the distribution coefficient you obtained for caffeine with the corresponding literature value. Comment on the similarity or difference.

**Experiment 4C**

1. For each of the three mixtures, report which layer was on the bottom and which one was on the top. Explain how you determined this for each mixture.
2. Record the densities for the liquids given in a handbook.
3. Was there a correlation between the densities and your results? Explain.

**Experiment 4D**

1. Answer the following questions about the first and second NaOH extracts.
  - a. Comment on the amount of precipitate for both extracts when HCl is added.
  - b. What is the precipitate formed when HCl is added?
  - c. Does the amount of precipitate in each tube indicate that all the acid impurity has been removed from the ether layer containing the unknown neutral compound?
2. Report the melting point and weight of the neutral compound you isolated.
3. Based on the melting point, what is the identity of this compound?
4. Calculate the percent recovery for the neutral compound. List possible sources of loss.

If you completed the Optional Exercise, complete Steps 1–4 for Experiment 4D.

**Experiment 4E**

Describe fully what occurred in Steps 2, 3, and 4. For each step, include (1) the nature (cation, anion, or neutral species) of the organic compound, (2) an explanation for all the color changes, and (3) an explanation for why each layer is colored as it is. Your explanation for (3) should be based on solubility principles and the polarities of the two solvents. (*Hint:* It may be helpful to review the sections in your general chemistry textbook that deal with acids, bases, and acid–base indicators.)

**REFERENCE**

Kelly, T. R. "A Simple, Colorful Demonstration of Solubility and Acid/Base Extraction." *Journal of Chemical Education*, 70 (1993): 848.

**QUESTION**

1. Caffeine has a distribution coefficient of 4.6 between methylene chloride and water. If 52 mg of caffeine are added to a conical vial containing 2 mL of water and 2 mL of methylene chloride, how much caffeine would be in each layer after the mixture had been mixed thoroughly?

**5****EXPERIMENT 5****Chromatography***Thin-layer chromatography**Column chromatography**Following a reaction with thin-layer chromatography*

Chromatography is perhaps the most important technique used by organic chemists to separate the components of a mixture. This technique involves the distribution of the different compounds or ions in the mixture between two phases, one of which is stationary and the other moving. Chromatography works on much the same principle as solvent extraction. In extraction, the components of a mixture are distributed between two solvents according to their relative solubilities in the two solvents. The separation process in chromatography depends on differences in how strongly the components of the mixture are adsorbed to the stationary phase and how soluble they are in the moving phase. These differences depend primarily on the relative polarities of the components in the mixture.

There are many types of chromatographic techniques, ranging from thin-layer chromatography, which is relatively simple and inexpensive, to high-performance liquid chromatography, which is very sophisticated and expensive. In this experiment, you will use two of the most widely used chromatographic techniques: thin-layer and column chromatography. The purpose of this experiment is to give you practice in performing these two techniques, to illustrate the principles of chromatographic separations, and to demonstrate how thin-layer and column chromatography are used in organic chemistry.